Structure of alumina glass

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The fabrication of novel oxide glass is a challenging topic in glass science. Alumina (Al2O3) glass cannot be fabricated by a conventional melt–quenching method, since Al2O3 is not a glass former. We found that amorphous Al2O3 synthesized by the electrochemical anodization of aluminum metal shows a glass transition. The neutron diffraction pattern of the glass exhibits an extremely sharp diffraction peak owing to the significantly dense packing of oxygen atoms. Structural modeling based on X-ray/neutron diffraction and NMR data suggests that the average Al–O coordination number is 4.66 and confirms the formation of OAl3 triclusters associated with the large contribution of edge-sharing Al–O polyhedra. The formation of edge-sharing AlO2 and AlO6 polyhedra is completely outside of the corner-sharing tetrahedra motif in Zachariasen’s conventional glass formation concept. We show that the electrochemical anodization method leads to a new path for fabricating novel single-component oxide glasses.

Oxide glasses, e.g., window glass, fiber glass, optical glass, and the cover glass of a smart phone are indispensable materials in our daily life. However, the fabrication of a novel single-component oxide glass is challenging particularly when a conventional melt–quenching method is used because the glass forming ability is governed by the viscosity of a high-temperature melt. Indeed, Angell proposed the concept of “fragility” to understand the relationship between the viscosity and the glass forming ability1. The basic idea behind the formation of covalent glass is the corner-sharing tetrahedral motif proposed by Zachariasen in 19322. Sun classified single-component oxides into glass formers, glass modifiers, and intermediates3. SiO2, B2O3, P2O5, and As2O3 are typical glass formers, in which the cation–oxygen coordination number is 3 or 4 and the glass network is formed by corner-sharing oxygen atoms. Alkali and alkali earth oxides are typical glass modifiers; they cannot form glass, but they can modify the network formed by a network former by breaking cation–oxygen bonds in the network and/or occupy voids4,5. Alumina (Al2O3) can be considered as an intermediate, because it can be both a glass former and a glass modifier in binary oxide glasses, although Al2O3 cannot solely form glass.

Al2O3 has many applications, e.g., in cements, substrates of electronic materials, and high-temperature ceramics. As mentioned above, it is impossible to prepare Al2O3 glass by the melt–quenching method; hence, sol–gel methods were used to prepare amorphous samples for studying optical properties6,7 and behaviors at high temperatures8. Another approach is the fabrication of thin films, such as the highly ductile amorphous Al2O3 thin films that have recently been reported9. However, the structure of amorphous Al2O3 is still largely unknown owing to a very limited number of structural studies. Lamparter and Kniep reported the formation of AlO4 tetrahedra with corner-sharing oxygen atoms as confirmed by neutron and X-ray diffraction measurements with the aid of the reverse Monte Carlo (RMC)10 modeling technique11. Hashimoto et al. reported the average Al–O coordination number of 4.7 determined by 27Al nuclear magnetic resonance (NMR) spectroscopic measurements12, whereas Lee and Ryu confirmed the formation of OAl3 triclusters by 27Al NMR measurements13. Shi et al. have recently reported the comparison between amorphous Al2O3 and liquid Al2O3, and they concluded on the basis of molecular dynamics (MD) and empirical potential structure refinement (EPSR)14 simulations based on diffraction data15 that the Al–O coordination number is increased in amorphous Al2O3.

In this study, we have found that amorphous Al2O3 synthesized by the anodization of aluminum metal shows a glass transition by differential thermal analysis (DTA). We have performed 27Al solid-state NMR and
high-energy X-ray and neutron diffraction measurements. Moreover, we constructed a structural model for the glass by a combined MD–RMC modeling technique to understand the structure of single-component intermediate oxide glass, because it is expected that the glass structure is inconsistent with Zachariasen’s rules.

Methods

Preparation of alumina glass. The Al2O3 sample was prepared according to our previous report12. High-purity (99.99%) aluminium sheets were immersed in 1.25 mol dm−3 NaOH for 20 s at 60 °C, washed with tap water, immersed in 3.9 mol dm−3 HNO3 for 60 s, and finally washed with deionized water to remove surface native oxides and contaminants. Constant-voltage anodization was performed for 80 V in 0.3 mol dm−3 H2CrO4 electrolyte for 2 h at 40 °C. After anodization, the sample was carefully washed with deionized water, dried at room temperature, and crushed into powder by an agate mortar. To remove physisorbed water, the powder sample was heat-treated at 300 °C for 4 h at a heating rate of 5 °C min−1 and were subsequently cooled in the furnace, as previously reported.

Density measurement. The density measurement was performed on a helium pycnometer (AccuPyc 1340TC, Shimadzu-Micromeritics). Before the measurement, the sample was dried for 24 h at room temperature in vacuum.

DTA measurement. The differential thermal analysis (DTA) experiment was performed on a Rigaku Thermo plus EVO apparatus. The sample was dried at a heating rate of 10 °C min−1 to 300 °C for 4 h and cooled in the furnace. After reaching 50 °C, the sample was heat-treated at a heating rate of 10 °C min−1 to 1350 °C.

NMR measurements. The 27Al magic angle spinning (MAS) nuclear magnetic resonance (NMR) experiment was performed on a JEOL JNM-ECA800 (18.79 T) spectrometer at a 27Al Larmor frequency of 208.58 MHz. The sample was packed in zirconia rotors and spun at 20 kHz using a 3.2 mm HXMAS probe. The 27Al chemical shift δiso, in parts per million (ppm) was referenced to an external 1 mol dm−3 AlCl3 solution (−0.1 ppm). The 27Al single-pulse MAS spectrum was obtained using 6/π pulses (0.67 us) with a recycle delay of 1 s and 512 scans. The spectrum was decomposed into three components, and fitting parameters, namely, the average isotropic chemical shift (δiso), the width of the Gaussian distribution of δiso (ΔCS), and the average quadrupolar coupling constant (CQ), were determined using the ‘Dmfit’ program16 applying a simple Czjzek model. The errors of fitting values for δiso and other parameters were <0.04% and <0.3%, respectively. The average NAl–O, was determined using the following equation: \[ N_{Al–O} = \sum_i N_{Al} \delta_i \] where N and δ represent the number of oxygen atoms around a given aluminium atom and the relative ratio of the corresponding peak area, respectively.

Diffraction measurements. The high-energy X-ray diffraction experiment was performed at the BL04B2 beamline at the SPring-8 synchrotron radiation facility, using a two-axis diffractometer dedicated to the study of disordered materials17. The energy of the incident X-rays was 61.4 keV. The raw data were corrected for polarization, absorption, and the background, and the contribution of Compton scattering was subtracted using standard data analysis software17. The neutron diffraction measurement was conducted on a high intensity total diffraclometer, NOVA18, installed at BL21 of the Materials and Life Science Experimental Facility at the J-PARC spallation neutron source. The wavelength range of the incident neutron beam was 0.12 Å < λ < 8.3 Å. The Å sample was transferred into vanadium-nickel null alloy cell 6 mm in diameter. The observed scattering intensity for the sample was corrected for instrumental background, attenuation of the sample and cell, and then normalized by the incident beam profile. All corrected data were normalized to give a Faber–Ziman19 total structure factor S(Q). A Lorch20 modification function was used in Fourier transform.

Structure modelling. We combined MD simulation with NVT ensemble–reverse Monte Carlo (RMC) modelling for structure modelling. The MD simulation was performed using the LAMMPS package21 and RMC modellings were performed using the RMC ++code22.

In the case of l-Al2O3, we used the Born–Mayer-type pair potential in the MD simulation given as

\[
\phi(r_{ij}) = e^3 \frac{q_i q_j}{r_{ij}} + B_i \exp\left(-\frac{r_{ij}}{R_{ij}}\right).
\]  

(1)

Here, e is the elementary charge and Bi and Ri are the parameters accounting for the repulsion of ionic cells. qAl = +3 and qO = −2 are the charges of Al3+ and O2−, respectively. The Bi and Ri values of 2.3708 × 10−16 J (Al–O), 2.4031 × 10−16 J (O–O) and zero (Al–Al) and the Ri values of 0.29 Å (Al–O and O–O) and zero (Al–Al) are found in Ref.23. A random configuration composed of 10,000 atoms was prepared with respect to the experimental density (0.08630 Å−3). This configuration was heated to 5000 K and treated above 50,000 steps. Subsequently, the configuration was cooled to 2400 K at a cooling rate of 1.3 K/ps. Eventually, the system was equilibrated at 2400 K for 100,000 steps. The long-range Coulomb interactions were calculated using Ewald summation and the simulation used periodic boundary conditions. A time step of 1 fs was used in the Verlet algorithm.

For g-Al2O3, the starting configuration, which contain 10,000 particles (Al, 4000: O, 6000) for g-Al2O3, was created using hard-sphere Monte Carlo (HSMC) simulation. The atomic number density is 0.09007 Å−3. The r-spacing for the calculations of the partial pair-distribution functions was set to 0.075 Å. Two kinds of
constraints were applied: the closest atom–atom approach and the coordination number. The first one can avoid unreasonable spikes in the partial pair-distribution functions. The second forces aluminium atoms to coordinate to averaged 4.6 oxygen atoms within a cut off distance of 2.50 Å. After the HSMC simulation, RMC simulation was conducted to reproduce the X-ray S(Q) and neutron S(Q) data. Following the RMC simulations, the atomic configuration was optimized by MD simulation. The MD simulation was performed using pairwise additive interatomic terms of the form

\[ V(r_{ij}) = e^{-q_i q_j r_{ij}} \frac{C_i C_j}{r_{ij}^{q_i + q_j}} + D(B_i + B_j) \exp \left( \frac{A_i A_j - r_{ij}}{B_i + B_j} \right), \]

where the terms represent Coulomb, van der Waals, and repulsion energy, respectively. Here, \( r_{ij} \) is the interatomic distance between atoms \( i \) and \( j \), \( D \) is a standard force constant 4184 JÅ−1 mol−1, \( q_i \) is the effective charge on atom \( i \) (\( q_i = 1.17 \)), \( q_o = 0.78 \). The repulsive radius \( A_i \) values are 0.7852 Å (Al), 1.8215 Å (O); the softness parameter \( B_i \) values are 0.034 Å (Al), 0.138 Å (O); and the van der Waals coefficient \( C_i \) values are 36.82 Å^6/kJ mol^{-1} (Al), 90.61 Å^6/kJ mol^{-1} (O). The parameters \( A, B, C \) can be found in Ref.\(^{24} \). The optimization of the atomic configuration was performed by minimizing the energy using the conjugate gradient method. We confirmed that these parameters are in better agreement with diffraction data; in particular, a very sharp principal peak (PP) in \( S^2(Q) \) for the glass was very well reproduced, while the parameters reported in Ref.\(^{25} \) underestimated the PP.

After the MD simulations, both configurations were refined by additional RMC simulations while constraining the \( \text{Al}–\text{O} \) coordination number, and the partial pair-distribution functions \( g_{ij}(r) \), within the first coordination shell to avoid unfavorable artifacts.

As a reference, we constructed three-dimensional structure model of g-SiO\(_2\) by combined MD–RMC simulation. The MD simulation of SiO\(_2\) glass was performed employing Born–Mayer type pair potentials, where the values \( q_o \) and \( q_o \) are + 2.4 and − 1.2; the \( B_i \) values were 21.39 × 10^{-16} J (Si–O), 0.6246 × 10^{-16} (O–O) or zero (Si–Si); the \( A_i \) values were 0.174 Å (Si–O), 0.562 Å (O–O) or zero (Si–Si)\(^{25} \). As the initial atomic configuration, 9000 atoms (Si, 3000: O, 6000) were randomly distributed in a cubic cell with respect to the experimental number density (0.06615 Å^−3). The simulation temperature was maintained at 4000 K for 20,000 time steps, then the temperature was reduced to 300 K over 200,000 time steps. Finally, the system was equilibrated at 300 K for 50,000 time steps. After the MD simulation, the obtained atomic configuration was refined by additional RMC simulation. In the RMC refinement, the MD results for the Si–O coordination number and the bond angle distribution for O–Si–O, and the partial pair-distribution functions were used as constraints. The cut off distance for the constraints for coordination of silicon and O–Si–O bond angle distribution was set to 1.90 Å.

Topological analyses. The bond angle distribution \( B(\theta) \) was calculated as the number of bonds between \( \theta \) and \( \theta + \Delta \theta \), which is dependent on the solid angle \( \Delta \Omega \sin \theta \) subtended at that value of \( \theta \). Thus, each bond angle distribution was plotted as \( B(\theta)/\sin \theta \) to compensate for the effect of \( \Delta \Omega \). The primitive\(^{26,27} \) (Al–O) ring size distributions for the g- and I-Al\(_2\)O\(_3\) were calculated using the R.I.N.G.S. code\(^ {28,29} \). The void analysis was conducted employing the pyMolDyn code\(^ {30} \) with a cutoff distance of \( r_c = 2.50 \) Å.

Results and discussion

Figure 1a shows a DTA curve for an Al\(_2\)O\(_3\) sample. Sharp intense and broad weak exothermic peaks at ~ 830 and ~ 1150 °C, respectively, are observed. The former peak is assigned to the solidification of \( \gamma \)-alumina from the amorphous phase and the latter peak is assigned to the phase transition from \( \gamma \)- to \( \alpha \)-alumina\(^ {21} \). Note that the slight baseline shift to the endothermic direction is observed in the low temperature region around 500 °C (inset of Fig. 1a), owing to glass transition, showing that the sample is Al\(_2\)O\(_3\) glass (\( \gamma \)-Al\(_2\)O\(_3\) ). The starting point of the shift, i.e., the glass transition temperature, is determined to be ~ 470 °C. In general, common glass-forming oxides have a ratio of glass transition temperature to melting point \((T_g/T_m)\) of ~ 0.67\(^ {32} \). On the other hand, the present g-Al\(_2\)O\(_3\) shows a \( T_g/T_m \) of ~ 0.32 (743 K/2345 K), which is extremely lower than that of general glass-forming oxides. The extraordinarily wide gap between \( T_g \) and \( T_m \) shows the low glass forming ability of alumina to maintain the deeply supercooling state without the formation of crystal nucleus from the \( T_m = 2072 \) °C to \( T_g = 470 \) °C for realizing the glassy state.

Figure 1b shows a typical\(^ {27} \) Al single-pulse MAS NMR spectrum normalized by the total peak area. This spectrum consists of three broad peaks located around ~ 64, ~ 36, and ~ 7 ppm, which are assigned to four- (AlO\(_4\)), five- (AlO\(_5\)), and six-fold (AlO\(_6\)) oxygen-coordinated polyhedra, respectively\(^ {22} \). This spectrum is decomposed into the three components and the fitting result (dotted curve) is in good agreement with the measured data (solid curve). The fractions of AlO\(_4\), AlO\(_5\), and AlO\(_6\) are 37.5, 52.1, and 10.3%, respectively, and the average coordination number is determined to be 4.73. The values obtained here are slightly different from those of our previous report\(^ {33} \); this variation depends on the resolution of the NMR equipment used. More precise values are obtained in the current study owing to the higher-resolution spectra obtained under higher magnetic fields. This precise local structural information is used as a constraint for the MD–RMC modeling as follows.

The mass density of g-Al\(_2\)O\(_3\) is 3.05 g cm\(^{-3}\), which corresponds to the atomic number density of 0.0901 Å\(^{-3}\). This value is smaller than 4.00 g cm\(^{-3}\) of \( \alpha \)-Al\(_2\)O\(_3\) and slightly larger than 2.92 g cm\(^{-3}\) of \( \gamma \)-Al\(_2\)O\(_3\). This trend is very different from SiO\(_2\), in which the density of glass (2.20 g cm\(^{-3}\)) is comparable to those of \( \alpha \)-cristobalite (2.30 g cm\(^{-3}\)) and \( \beta \)-cristobalite (2.20 g cm\(^{-3}\)), implying that a large density difference between the glass and crystal in Al\(_2\)O\(_3\) indicates a low glass forming ability in single-component oxide glasses.
Figure 2 shows neutron and X-ray total structure factors, $S_{\text{N,X}}(Q)$, for $g$-$\text{Al}_2\text{O}_3$, together with the results of the MD–RMC simulations. For comparison, the results of silica glass ($g$-$\text{SiO}_2$) and liquid alumina ($l$-$\text{Al}_2\text{O}_3$) at 2400 K are also shown. All the experimental $S_{\text{N,X}}(Q)$ data are well reproduced by the MD–RMC simulations. The first sharp diffraction peak (FSDP) from pseudo (quasi) Bragg planes (successive small cages) created along a void, is observed at $Q = 1.52$ Å$^{-1}$ for $g$-$\text{SiO}_2$, a typical glass forming oxide, whereas the FSDP observed at $Q \sim 2$ Å$^{-1}$ is not prominent in $g$-$\text{Al}_2\text{O}_3$, suggesting the formation of a densely packed structure with a small void volume. In addition, $g$-$\text{Al}_2\text{O}_3$ shows an extraordinarily sharp PP in the neutron $S(Q)$, nearly twice sharper than those of $l$-$\text{Al}_2\text{O}_3$ and $g$-$\text{SiO}_2$, suggesting the extremely high packing fraction of oxygen atoms manifested by the high density of $g$-$\text{Al}_2\text{O}_3$. A similar behavior is found in the neutron diffraction data of $g$-$\text{SiO}_2$ under a high pressure.

Figure 1. (a) DTA curve recorded at a heating rate of 10 °C min$^{-1}$ for $g$-$\text{Al}_2\text{O}_3$. (b) $^{27}$Al solid state NMR spectrum for $g$-$\text{Al}_2\text{O}_3$.
the overall profiles of $S^{g}(Q)$ for $l$-$Al_{2}O_{3}$ are broader than those for $g$-$Al_{2}O_{3}$, but the $S^{l}(Q)$ data of both $l$-$Al_{2}O_{3}$ and $g$-$Al_{2}O_{3}$ are more identical, suggesting that O–O correlations are different between $g$-$Al_{2}O_{3}$ and $l$-$Al_{2}O_{3}$.

The neutron and X-ray total correlation functions, $T^{g}(r)$, for $g$-$Al_{2}O_{3}$, $l$-$Al_{2}O_{3}$, and $g$-$SiO_{2}$ are shown in Fig. 3. The first peak observed at 1.81 Å in $T^{g}(r)$ for $g$-$Al_{2}O_{3}$ is assigned to the Al–O correlations. The second peak observed around 2.8 Å in $T^{g}(r)$ and that around 3.2 Å in $T^{l}(r)$ are assigned to the O–O and Al–Al correlations, respectively. Longer Al–O distances relative to $g$-$SiO_{2}$ and the asymmetric Al–O correlation peak with a tail of ~2.4 Å indicate the formation of distorted AlO$_{n}$ polyhedra with a coordination number higher than 4. The average Al–O coordination number calculated using the area of the first correlation peak of $T^{g}(r)$ is 4.6 ± 0.2, which is in agreement with the NMR result of 4.73 (37.5% of AlO$_{4}$; 52.1% of AlO$_{5}$; and 10.3% of AlO$_{6}$) and larger than 4.4 in $l$-$Al_{2}O_{3}$. Such a larger coordination number, which is often observed in nonglass-forming high-temperature oxide melts$^{37,41}$, cannot be observed in the typical glass-forming oxides. The overall profile for $g$-$Al_{2}O_{3}$ is similar to that for $l$-$Al_{2}O_{3}$, but the Al–O and O–O correlation peaks for $g$-$Al_{2}O_{3}$ are sharper than those for $l$-$Al_{2}O_{3}$, as apparently observed in $T^{g}(r)$. This behavior suggests that the packing of oxygen atoms in glass could differ from that in high-temperature liquid.

Figure 4a shows the partial structure factors, $S_{ij}(Q)$, derived from the MD–RMC models for $g$-$Al_{2}O_{3}$ and $l$-$Al_{2}O_{3}$ together with those for $g$-$SiO_{2}$. All the $S_{ij}(Q)$ give a positive peak at the FSDP position in $g$-$SiO_{2}$, but there is no positive peak at the expected FSDP position in $g$-$Al_{2}O_{3}$. It is confirmed that the PP comprises the sum of positive correlations of A–A and X–X and negative correlations of A–X. As can be seen in Fig. 2b the PP is absent because the positive correlations of A–A and X–X are completely canceled by the A–X correlations in the $S^{g}(Q)$ of $g$-$SiO_{2}$ and $g$-$Al_{2}O_{3}$. On the other hand, the contribution of the X–X correlations at PP position is largely enhanced in the $S^{l}(Q)$ (see Fig. 2a) due to large weighting factors of O–O correlations for neutrons. The positive O–O PP for $g$-$Al_{2}O_{3}$ is sharper than that for $l$-$Al_{2}O_{3}$, resulting in the exceptionally sharp PP observed in the $S^{l}(Q)$ for $g$-$Al_{2}O_{3}$. Both the absence of the FSDP as mentioned above and the sharp PP in the $S^{l}(Q)$ mainly originated from the O–O correlations allow us to expect the formation of the dense oxygen packing in $g$-$Al_{2}O_{3}$. The partial pair distribution functions, $g_{i}(r)$, derived from the MD–RMC models for $g$-$Al_{2}O_{3}$ and $l$-$Al_{2}O_{3}$ together with those for $g$-$SiO_{2}$ are shown in Fig. 4b. $g$-$SiO_{2}$ shows very prominent sharp Si–Si, Si–O, and O–O correlation peaks, whereas Al–Al, Al–O, and O–O correlation peaks are broader for $g$-$Al_{2}O_{3}$. Note that both the Al–O and O–O correlation peaks for $l$-$Al_{2}O_{3}$ are broader than those for $g$-$Al_{2}O_{3}$, whereas the Al–Al peak in the former is identical to the latter. This trend is consistent with the finding that the difference in $S^{g}(Q)$ between $l$-$Al_{2}O_{3}$ and $g$-$Al_{2}O_{3}$ is very small.

Table 1 shows coordination number distributions and polyhedral connections in $g$-$Al_{2}O_{3}$, $l$-$Al_{2}O_{3}$, and $g$-$SiO_{2}$. For a typical glass-forming oxide, $g$-$SiO_{2}$, the number of oxygen atoms around a Si atom ($N_{s_{i}O}$) is 4, the number of Si atoms around an oxygen atom ($N_{O_{i}Si}$) is 2, and the SiO$_{4}$ polyhedra are connected via 100% corner-sharing, which is definitely in accordance with Zachariasen’s conventional glass formation concept. On the other hand, for $g$-$Al_{2}O_{3}$, more than 50% of the cations have $N_{s_{i}O} ≥ 5$ and most of the oxygen atoms are connected with three Al atoms, showing the formation of OAl$_{l}$ triclusters and a significant number of OAl$_{4}$ tetracusters. In addition, a significant fraction of edge-sharing AlO$_{n}$ polyhedral units are observed in $g$-$Al_{2}O_{3}$. These features are completely inconsistent with Zachariasen’s rules. The fractions of AlO$_{3}$ and AlO$_{4}$ units, OAl$_{l}$ triclusters and OAl$_{4}$ tetracusters, and edge-sharing AlO$_{n}$ polyhedra are all characteristic features of a non-glass-forming behavior.

Figure 3. (a) Neutron total correlation functions, $T^{g}(r)$, for $g$-$Al_{2}O_{3}$, $l$-$Al_{2}O_{3}$, and $g$-$SiO_{2}$. (b) X-ray total correlation functions, $T^{g}(r)$, $g$-$Al_{2}O_{3}$, $l$-$Al_{2}O_{3}$, and $g$-$SiO_{2}$. Upper and lower panel data were obtained by Fourier transform with $Q_{max} = 25$ and 18 Å$^{-1}$, respectively. Note that the Al–Al correlation peak is not legibly marked owing to its small weighting factor for neutrons.
To understand the characteristic real space atomic arrangement of intermediate oxide glass, we analyzed the bond angle distribution. Figure S5 shows the bond angle distributions of \( g\)-\( \text{Al}_2\text{O}_3 \) and \( l\)-\( \text{Al}_2\text{O}_3 \) together with those of \( g\)-\( \text{SiO}_2 \). The \( O\)--\( Si\)--\( O\) distribution has a well-defined peak at 109° attributable to the formation of regular \( \text{Si}_4\text{O}_4\) tetrahedra. The \( Si\)--\( Si\)--\( Si\) distribution has a broad peak at around 109°, suggesting the formation of \( \text{Si}_4\text{O}_4\) hyper-tetrahedra. The \( Si\)--\( O\)--\( Si\) distribution shows a peak at 156° attributable to the formation of the corner-sharing network. On the other hand, the bond angle distributions of \( g\)- and \( l\)-\( \text{Al}_2\text{O}_3 \) show completely different behaviors. The \( O\)--\( Al\)--\( O\) distributions of \( g\)-\( \text{Al}_2\text{O}_3 \) and \( l\)-\( \text{Al}_2\text{O}_3 \) have a peak at 95° and 180°, respectively, suggesting that \( \text{Al}_2\text{O}_3 \) polyhedra are octahedral and are rather similar to those in non-glass-forming liquids, \( O\)--\( Zr\)--\( O\) in \( \text{Zr}_2\text{O}_7\) and \( O\)--\( Er\)--\( O\) in \( \text{Er}_2\text{O}_3\). The \( Al\)--\( O\)--\( Al\) distributions have two peaks at 97° (edge-sharing) and 120° (OAl3 tricluster) of \( \text{Al}_2\text{O}_3 \), which become a broad single peak in \( g\)-\( \text{Al}_2\text{O}_3 \) owing to highly densely packed structure. Both the \( O\)--\( Al\)--\( O\) and \( Al\)--\( O\)--\( Al\) distributions of \( g\)-\( \text{Al}_2\text{O}_3 \) are slightly different from the results recently reported by Shi et al., because they do not have neutron diffraction data. The most striking difference between \( g\)-\( \text{SiO}_2 \) and \( g\)-\( /l\)-\( \text{Al}_2\text{O}_3 \) is the \( A\)--\( A\)--\( A\) distribution. The \( Si\)--\( Si\)--\( Si\) distribution suggests the formation of \( \text{Si}_4\text{O}_4\) hyper-tetrahedra probably associated with the prominent FSDP, but the \( Al\)--\( Al\)--\( Al\) distribution shows two peaks at 60° and 115°, suggesting that \( \text{Al}_2\text{O}_3 \) polyhedra are octahedral and are rather similar to those in non-glass-forming liquids, \( O\)--\( Zr\)--\( O\) in \( \text{Zr}_2\text{O}_7\) and \( O\)--\( Er\)--\( O\) in \( \text{Er}_2\text{O}_3\). The \( Al\)--\( O\)--\( Al\) distributions have two peaks at 97° (edge-sharing) and 120° (OAl3 tricluster) of \( \text{Al}_2\text{O}_3 \), which become a broad single peak in \( g\)-\( \text{Al}_2\text{O}_3 \) owing to highly densely packed structure. Both the \( O\)--\( Al\)--\( O\) and \( Al\)--\( O\)--\( Al\) distributions of \( g\)-\( \text{Al}_2\text{O}_3 \) are slightly different from the results recently reported by Shi et al., because they do not have neutron diffraction data. The most striking difference between \( g\)-\( \text{SiO}_2 \) and \( g\)-\( /l\)-\( \text{Al}_2\text{O}_3 \) is the \( A\)--\( A\)--\( A\) distribution. The \( Si\)--\( Si\)--\( Si\) distribution suggests the formation of \( \text{Si}_4\text{O}_4\) hyper-tetrahedra probably associated with the prominent FSDP, but the \( Al\)--\( Al\)--\( Al\) distribution shows two peaks at 60° and 115°, suggesting that the \( Al\) distribution of \( Al\) atoms is due to a typical dense random packing, which cannot give rise to an FSDP in the diffraction data. The \( O\)--\( O\)--\( O\) distributions of \( g\)-\( \text{Al}_2\text{O}_3 \) and \( l\)-\( \text{Al}_2\text{O}_3 \) are also very different from that of \( g\)-\( \text{SiO}_2 \), and suggest that the distributions of oxygen atoms are dense also due to the random packing. Moreover, it is suggested that the oxygen packing fraction of \( g\)-\( \text{Al}_2\text{O}_3 \) increases owing to the higher mass density in the glass in comparison with the liquid (see Table S1). Indeed, the distribution peak of \( g\)-\( \text{Al}_2\text{O}_3 \) is sharper than that of \( l\)-\( \text{Al}_2\text{O}_3 \). Both the \( O\)--\( O\)--\( Al\) and \( O\)--\( Al\)--\( O\) distributions of \( g\)-\( \text{Al}_2\text{O}_3 \) and \( l\)-\( \text{Al}_2\text{O}_3 \) are also different from the \( O\)--\( O\)--\( Si\) and \( O\)--\( S\)--\( Si\) distributions in \( g\)-\( \text{SiO}_2 \).

To understand the topology of \( g\)-\( \text{Al}_2\text{O}_3 \) and \( l\)-\( \text{Al}_2\text{O}_3 \), we calculated the primitive ring size distribution and compared it with the \( g\)-\( \text{SiO}_2 \) data in Fig. 5b. \( g\)-\( \text{SiO}_2 \) shows a broad ring size distribution from threefold to ninefold rings, which is topologically disordered according to Gupta and Cooper. Both \( g\)-\( \text{Al}_2\text{O}_3 \) and \( l\)-\( \text{Al}_2\text{O}_3 \) show broad ring size distributions that are nearly identical, but they have large fractions of small rings, e.g., twofold rings (edge-sharing) and threefold rings, which is a signature of the low glass forming ability of \( \text{Al}_2\text{O}_3 \).

We show the atomic configuration of the glass obtained from the MD–RMC model in Fig. 6a to understand the structure of \( g\)-\( \text{Al}_2\text{O}_3 \). It is easily recognized that the assembly of two-membered rings (edge-sharing polyhedra) forms a lattice-like structure (black dotted line). The \( O\)--\( O\) atomic distance, which is the diagonal of one square, is ~2.3–2.7 Å, which is nearly consistent with the periodicity of ~2.3 Å estimated from the peak position.

![](https://www.nature.com/scientificreports/)
of the PP observed in the $S^Q$ for $g$-$Al_2O_3$. Therefore, we conclude that, in addition to the large fraction of corner-sharing $OAl_3$ triclusters associated with the formation of octahedral $AlO_n$ polyhedra, the larger fraction of edge-sharing $AlO_n$ polyhedra for $g$-$Al_2O_3$ (19.3%) than for $l$-$Al_2O_3$ (17.6%) must be the origin of the exceptionally sharp PP observed in the $S^Q$ for $g$-$Al_2O_3$. We show the $OAl_3$ triclusters (red) and $OAl_4$ tetraclusters (yellow) in Fig. 6b. Such a cluster network can be found in $g$-$SiO_2$ at a high pressure of 200 GPa$^{45}$, but it is possible to fabricate such a glass structure at ambient pressure through the electrochemical anodization process under high electric field$^{46,47}$. The voids (highlighted in green) of $g$-$SiO_2$ according to our previous study is 32%$^5$, whereas those in $g$-$Al_2O_3$ and $l$-$Al_2O_3$ is only 4.5% and 5.5%, respectively, indicating that a highly densely packed structure is formed in them. The dense-random-packing-like bond angle distribution (see Fig. 5a) with significantly octahedral $AlO_n$ polyhedra is very different from that

![Figure 5](image-url)

**Figure 5.** (a) Bond angle distributions for $g$-$Al_2O_3$, $l$-$Al_2O_3$, and $g$-$SiO_2$. (b) Primitive ring size distributions for $g$-$Al_2O_3$, $l$-$Al_2O_3$, and $g$-$SiO_2$. $A$ = Si or Al and $X$ = O.

![Figure 6](image-url)

**Figure 6.** (a) Atomic configuration of $g$-$Al_2O_3$ (stick bonds schematic). (b) Atomic configuration of $g$-$Al_2O_3$ (schematic of the $OAl_3$ triclusters (red) and $OAl_4$ tetraclusters (yellow)). (c) Atomic configuration of $g$-$Al_2O_3$ with voids. Pink and red circles represent Al and O atoms, respectively, and green regions show the voids.
of conventional oxide glass but rather similar to that of metallic glass in whichicosahedra is highly distorted owing to geometric frustration.48

The electrochemically prepared g-Al2O3, has many features that are completely outside of Zachariasen’s rules. Regardless of the dense oxygen packing structure with a large fraction of edge-sharing polyhedral motifs, g-Al2O3 can stably exist as glass. The electrochemical anodization chemistry can be regarded as a powerful tool for our questing for novel intermediate oxide glasses with an extremely dense structure, and the comprehensive understanding of the atomic structure of the glasses will give new insights into the fabrication of novel glass materials.

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Author contributions

S.K. and H.H. formulated the research project. H.H. prepared the materials. H.H. and K.Y. performed NMR measurements. H.H. and H.S. performed thermal analysis. Y.O. preformed neutron diffraction measurements and analyzed the measured data. S.K. and K.O. performed high-energy X-ray diffraction measurements and analyzed the measured data. Y.O. S.T., and S.K. performed MD–RMC modelling. Y.O., S.K., and M.M. analyzed the structural model. H.H., Y.O., and S.K. wrote the paper with the input of all the authors.

Competing interests

The authors declare no competing interests.

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