

Atomic and Electronic Structure in MgO–SiO₂

Yuta Shuseki, Shinji Kohara,* Tomoaki Kaneko, Keitaro Sodeyama, Yohei Onodera, Chihiro Koyama, Atsunobu Masuno, Shunta Sasaki, Shohei Hatano, Motoki Shiga, Ippei Obayashi, Yasuaki Hiraoka, Junpei T. Okada, Akitoshi Mizuno, Yuki Watanabe, Yui Nakata, Koji Ohara, Motohiko Murakami, Matthew G. Tucker, Marshall T. McDonnell, Hirohisa Oda, and Takehiko Ishikawa



Cite This: *J. Phys. Chem. A* 2024, 128, 716–726



Read Online

ACCESS |



Metrics & More

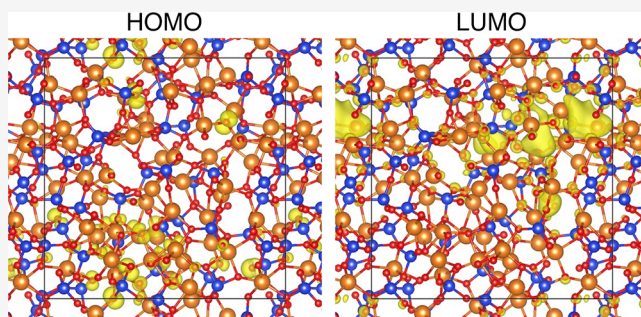


Article Recommendations



Supporting Information

ABSTRACT: Understanding disordered structure is difficult due to insufficient information in experimental data. Here, we overcome this issue by using a combination of diffraction and simulation to investigate oxygen packing and network topology in glassy (*g*-) and liquid (*l*-) MgO–SiO₂ based on a comparison with the crystalline topology. We find that packing of oxygen atoms in Mg₂SiO₄ is larger than that in MgSiO₃, and that of the glasses is larger than that of the liquids. Moreover, topological analysis suggests that topological similarity between crystalline (*c*-) and *g*- (*l*-) Mg₂SiO₄ is the signature of low glass-forming ability (GFA), and high GFA *g*- (*l*-) MgSiO₃ shows a unique glass topology, which is different from *c*-MgSiO₃. We also find that the lowest unoccupied molecular orbital (LUMO) is a free electron-like state at a void site of magnesium atom arising from decreased oxygen coordination, which is far away from crystalline oxides in which LUMO is occupied by oxygen's 3s orbital state in *g*- and *l*-MgO–SiO₂, suggesting that electronic structure does not play an important role to determine GFA. We finally concluded the GFA of MgO–SiO₂ binary is dominated by the atomic structure in terms of network topology.



INTRODUCTION

The MgO–SiO₂ system is very important in both glass science and geoscience¹ since glassy (*g*-)MgO–SiO₂ is a typical binary silicate glass system and crystalline (*c*-)MgSiO₃ (enstatite) and *c*-Mg₂SiO₄ (forsterite) are Mg-end members of main components of the Earth's mantle. Liquid (*l*-)Mg₂SiO₄ can be classified as a fragile liquid, while *l*-MgSiO₃ is a stronger liquid according to Angell.² Particularly, viscosity under high pressure and high temperature is an important thermophysical property to understand magma ocean solidification.³ The structures of *g*-MgSiO₃ (high glass-forming ability (GFA)) and *g*-Mg₂SiO₄ (low GFA) have been widely studied because the use of the levitation technique⁴ made it possible to synthesize a bulk *g*-Mg₂SiO₄.⁵ Numerous studies using X-ray^{6–9} and neutron^{7–9} diffraction, NMR,^{5,10–13} Raman spectroscopy,¹⁴ and reverse Monte Carlo (RMC)¹⁵–density functional (DF) theory simulation have been reported.⁹ The structure of liquid (*l*-)MgSiO₃ has been studied by X-ray diffraction^{16,17} and DF–molecular dynamics (MD) simulation.⁹ In the case of *l*-Mg₂SiO₄, available data are very limited due to a high melting point (1850 °C); only synchrotron X-ray diffraction data¹⁷ are available, while DF–MD simulation data are reported.⁹ The previous diffraction studies report that SiO₄ tetrahedra are stable, and the Mg–O coordination number (CN) is around 5 in *l*- and *g*-MgO–SiO₂, although there are some discrepancies

in Mg–O CN's in the previous reports. NMR spectroscopy confirmed that the Q² species (SiO₄ chain) are dominant in *g*- and *l*-MgSiO₃, while Si₂O₇^{6–} dimers and isolated SiO₄^{4–} are dominant in *g*- and *l*-Mg₂SiO₄.

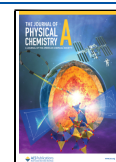
In this article, we performed high-energy X-ray diffraction and neutron diffraction measurements on *l*-MgSiO₃ and *l*-Mg₂SiO₄ to obtain more detailed structural information about the liquids. To obtain atomic configurations with detailed electronic structures of *g*- and *l*-MgO–SiO₂, advanced DF–MD simulations for *g*- and *l*-MgO–SiO₂ were conducted to understand the electronic structure in MgO–SiO₂. We measured the density of *l*-Mg₂SiO₄ by using an electrostatic levitation furnace (ELF) under microgravity at the International Space Station (ISS). Moreover, we performed several topological analyses (ring, polyhedral connection analysis, and persistent homology) on crystalline (*c*-), *g*-, and *l*-MgO–SiO₂ to extract topological similarity among the crystal, glass, and

Received: August 17, 2023

Revised: December 21, 2023

Accepted: December 26, 2023

Published: January 18, 2024



liquid to understand the relationship between the topology and GFA.

EXPERIMENTAL AND SIMULATION PROCEDURES

Stoichiometric mixtures of MgO and SiO₂ were annealed in air in 12 h to obtain polycrystalline MgSiO₃ and Mg₂SiO₄ for levitation experiments. Spherical samples with a diameter of 2–3 mm were prepared by melting the *c*-MgSiO₃ and *c*-Mg₂SiO₄ using a CO₂ laser heating on an aerodynamic levitator. Samples of *g*-MgSiO₃ were obtained during cooling, while 2–3 mm Mg₂SiO₄ was too large to be vitrified because of its low GFA.

The density of *l*-MgO–SiO₂ was measured with an ELF at the ISS. The following obstacles exist when measuring oxide materials using an ELF on the ground: (1) A large voltage is required to overcome the gravity, but this voltage is discharged. (2) A vacuum is required to avoid discharge, but in that case, the oxides will volatilize. On the other hand, the above two problems can be avoided in space; this is why the measurements must be performed on the ISS. A sample was 2 mm in diameter. It was charged by friction or contact with other materials in ISS–ELF¹⁸ and then levitated to the center between six electrodes that applied Coulomb force. The sample position was stabilized by tuning voltages between electrodes at 1000 Hz and monitoring the image of the sample backlit with 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 recalcence and the reference value of the melting point (MgSiO₃: 1650 °C and Mg₂SiO₄: 1850 °C¹⁹). After melting, the nonspherical sample became spherical upon cooling after shutting off the lasers. During cooling, the sample image was observed by ultraviolet back light and a CCD camera. The pixel size was calibrated against an image of 2.0 mm stainless steel spheres, which was recorded under the same conditions as the sample. The sample volume was calculated from its diameter obtained from the image. The density was calculated from the volume and weight measured by UMX2 (Mettler TOLEDO) after the sample was returned to the earth.

The X-ray diffraction measurements of *l*-MgSiO₃ and *l*-Mg₂SiO₄ were performed at the BL04B2 beamline²⁰ of SPring-8 using an aerodynamic levitator.²¹ The energy of the incident X-rays was 61.4 keV. The 2 mm sample was levitated in dry air and heated by a 200 W CO₂ laser. The temperature of the sample specimen was monitored by a two-color pyrometer (0.9 and 1.05 μm). The instrument background was successfully reduced by shielding the detectors 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 procedures.²²

The neutron diffraction measurements were conducted on the Nanoscale-Ordered Materials Diffractometer (NOMAD) diffractometer²³ at SNS of Oak Ridge National Laboratory using an aerodynamic levitator. The 3 mm sample was levitated in dry argon and heated by a 400 W CO₂ laser. The temperature of the sample specimen was monitored by a two-color pyrometer. The measured scattering intensities for the samples were corrected for instrument background, absorption of the samples, and multiple and incoherent scattering and then normalized by the incident beam profile.

The fully corrected data sets were normalized to give the Faber–Ziman²⁴ total structure factor $S(Q)$, and the total correlation function $T(r)$ was obtained by a Fourier transform of $S(Q)$.

The initial configurations for *l*-MgO–SiO₂ were generated by RMC modeling started with a random configuration using both X-ray and neutron diffraction data. The RMC++²⁵ code was used. The number of particles in the unit cells was 510 and 511 for MgSiO₃ and Mg₂SiO₄, respectively. DF–MD calculations were performed using the CP2K code,²⁶ which is a software package for DF–MD calculations using the hybrid Gaussian (MOLOPT-DZVP-SR) and plane wave basis set. The generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof²⁷ was adopted for the exchange–correlation energy functional. The norm-conserving pseudo-potentials of Goedecker, Teter, and Hutter²⁸ were adopted. The cutoff energy of the plane wave was set to 400 Ry. NVT simulations were carried out using the Nose–Hoover chain method with three thermostats. We performed MD simulations for 20 ps with the time step of 1 fs at 293 K for glass and at 2073 K for liquid.

For the electronic structure calculations, we used the structures of DF–MD at 10 ps for glasses and 10 and 20 ps for liquids. We employed the PHASE/0 code,²⁹ which is DF calculations using a plain wave basis set. The norm-conserving pseudo potentials³⁰ were used for Mg and Si atoms, while ultrasoft pseudo potential³¹ was used for O atoms. The PBE0 hybrid functional³² with fraction $\alpha = 0.3$ was used for much more reliable estimation of band gap, where Γ is the fraction of the exact exchange term in the functional. The k -sampling was $2 \times 2 \times 2$ for the Γ point centered mesh with tetrahedron method. The cutoff energies of plane wave basis set and charge density were 25 and 225 Ry, respectively. For the evaluation of the exact exchange term, only the gamma point was sampled, and the real-space method was used for the deficit charge term.

King ring size distributions were calculated by using R. I. N. G. S. code.³³ The homology of atomic configurations for *c*-, *g*-, and *l*-MgO–SiO₂ was investigated using the PD₁, which is comprised of two-dimensional histograms showing a persistent homology. Figure 1 shows the methodology of PD₁.³⁴ D₁ of a

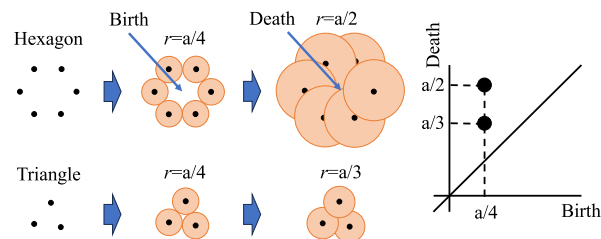


Figure 1. Methodology of the persistent diagram.

set of atoms given by the following thickening process of spheres: (i) place a sphere with a radius r at the center of each atom, (ii) increase the radii of the spheres from 0 to a sufficiently large value, and (iii) encode the pair of birth and death radii (b_i, d_i) for each ring c_i , consisting of a set of spheres. The PD₁ 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 detected as the radius of spheres at which 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

exhibits information about the size of the ring. The PD₁ provides statistical information on the shapes of all rings and thereby provides insight into intermediate-range ordering in a disordered structure. The rings detected by this process are recorded for the computation of the PD₁s; hence, their geometric shapes can be identified for further analyses. The PD₁s were calculated using the HomCloud package.³⁵

RESULTS AND DISCUSSION

Density Data. Table 1 summarizes the published density data for MgO–SiO₂. Note that density data for *l*-Mg₂SiO₄ is

Table 1. Density (g cm^{−3}) Data for MgO–SiO₂

	MgSiO ₃	Mg ₂ SiO ₄
crystal	3.210 ³⁶	3.220 ³⁷
glass	2.740 ^{7,9}	2.930 ⁹
liquid	2.511 ³⁸	2.677 ⁹

estimated in the supplemental data of ref 9. Density of *l*-Mg₂SiO₄ as a function of the temperature measured at the ISS

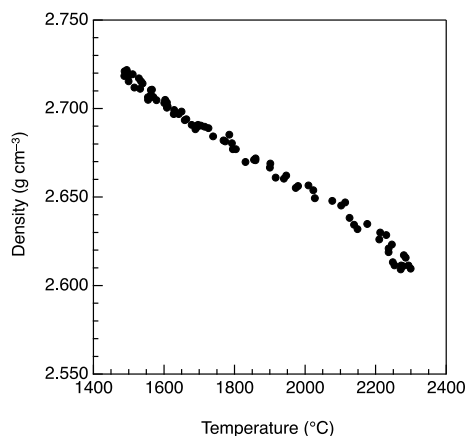


Figure 2. Measured density of *l*-Mg₂SiO₄ as a function of temperature. Error bar was estimated to be 3%.

using ELF is depicted in Figure 2. The density showed a linear temperature dependence, which can be fitted to

$$\rho(T) = (2911 \pm 7) - (0.13 \pm 0.003)T \text{ (kg m}^{-3}\text{)} \quad (1495 - 2270 \text{ }^{\circ}\text{C}) \quad (1)$$

with 99% confidence interval. The density is 2.678 g cm^{−3} at 1800 °C, very close to the estimated value of 2.677 g cm^{−3} given in Table 1. Experimental density data of *l*-xMgO–(100 − x)SiO₂ (x = 30, 40, 50, 60, 66.7, 70) were also obtained (Figure S1). Both the densities for *g*- and *l*-Mg₂SiO₄ are higher than those of *g*- and *l*-MgSiO₃, respectively. However, the density for *c*-Mg₂SiO₄ is comparable to that of *c*-MgSiO₃ despite the increase in MgO content. The densities of the liquids are lower than those for the glasses, which is a common trend in oxide materials. It is worth mentioning that the density difference between *c*-MgSiO₃ and *g*-MgSiO₃ is much larger than that between *c*-Mg₂SiO₄ and *g*-Mg₂SiO₄.

Diffraction Data. Figure 3 shows X-ray and neutron total structure factors, *S*(*Q*), for *g*- and *l*-MgSiO₃ (a) and Mg₂SiO₄ (b), respectively. And also, Figure S2 shows X-ray total structure factors, *S*(*Q*), for *l*-xMgO–(100 − x)SiO₂ were

corrected using density data from Figure S1. The liquid data show broader features in comparison with the glass data due to the high temperature in Figure 3. A first sharp diffraction peak (FSDP)³⁹ is observed at *Q* ~ 2 and 2.2 Å^{−1} in the X-ray and neutron *S*(*Q*) for MgSiO₃ and Mg₂SiO₄, respectively. An FSDP is considered the symbol of intermediate-range order which is composed of corner-sharing of SiO₄ tetrahedra across the void. A principal peak (PP)⁴⁰ is observed at *Q* ~ 2.8 Å^{−1} in only the neutron *S*(*Q*) because the PP reflects the packing fraction of oxygen atoms,⁴¹ which neutrons are more sensitive to. The position of the FSDP in *g*-MgSiO₃ is higher in *Q* than that of *g*-SiO₂⁹ and that in *g*-Mg₂SiO₄ is higher in *Q* than that of *g*-MgSiO₃ because the network comprised by the corner-sharing of SiO₄ tetrahedra is broken down into MgSiO₃ and Mg₂SiO₄ by the addition of MgO associated with the reduction of the cavity volume.⁹ On the other hand, the position of the PP in the neutron *S*(*Q*) is almost identical, but the peak heights for glasses are greater than those for liquids. This trend is consistent with density data because the PP reflects the packing fraction of the oxygen atoms as mentioned earlier.

The total correlation functions, *T*(*r*), for MgO–SiO₂ glasses and liquids are shown in Figure 3. The real-space resolution in the glass data is better than that in the liquid data because we have measured the glass data with a wider *Q* range. In addition, the liquid structure is inherently more disordered than the glass structure, making peak assignment more difficult in the liquid data, as shown in Figure 3d. As can be seen in Figure 3c, we observe well-defined Si–O, Mg–O, and O–O peaks at approximately 1.63, 2.02, and 2.71 Å, respectively, but both the Mg–O and the O–O atomic distances in *g*-Mg₂SiO₄ are slightly longer than those in *g*-MgSiO₃. We evaluated CNs using experimental and simulation data (Figure S3 and Tables S1 and S2), and it shows that the Si–O and Mg–O CNs are approximately 4 and 5 in both MgSiO₃ and Mg₂SiO₄, although the Mg–O CNs in the glasses are slightly larger than those in the liquids, and those in Mg₂SiO₄ are larger than those in MgSiO₃. These behaviors are in line with the behaviors of the PP in the neutron *S*(*Q*) and density data because the glasses are much denser than the liquids, and *g*- and *l*-Mg₂SiO₄ are denser than *g*- and *l*-MgSiO₃. The average CN_{Mg–O} of DF–MD model of *g*-MgSiO₃ shows 5.0 and the distribution of the value CN_{Mg–O} gives ^[4]Mg (21.6%), ^[5]Mg (55.9%), and ^[6]Mg (22.5%) using the cutoff distance 2.60 Å. The previous results obtained by neutron diffraction, RMC, and empirical potential structure refinement (EPSR) show CN_{Mg–O} around 4.50,⁴² 4.50,⁴³ and 4.48,⁴⁴ respectively. Our DF–MD model has higher CN_{Mg–O} than those because a lot of ^[5]Mg exist. On the other hand, ^[4]Mg is predominant in other previous models; it might be our model slightly overestimates the Mg–O coordination.

Partial Structure and Short-Range Structure Derived from DF–MD Simulation. X-ray and neutron total structure factors, *S*(*Q*), for *g*-MgO–SiO₂ and *l*-MgO–SiO₂ derived from DF–MD simulations are shown in Figure 4. Figure 5a shows the partial structure factors, *S_{ij}*(*Q*), for MgO–SiO₂. The *S_{ij}*(*Q*) except *S_{Si–Mg}*(*Q*) exhibits a negative peak at the FSDP position. Similar behavior is found in 22.7R₂O–77.3SiO₂ glasses (R=Na and/or K).⁴⁵ The cation–oxygen *S_{ij}*(*Q*) (*S_{Si–O}*(*Q*) and *S_{Mg–O}*(*Q*)) exhibit a positive peak at the PP position, while the cation–cation *S_{ij}*(*Q*) (*S_{Si–Si}*(*Q*), *S_{Si–Mg}*(*Q*), and *S_{Mg–Mg}*(*Q*)) and O–O(*Q*) exhibit a positive peak. The alkali–oxygen *S_{ij}*(*Q*) in 22.7R₂O–77.3SiO₂ glasses do not exhibit such a negative peak at the PP position because alkali

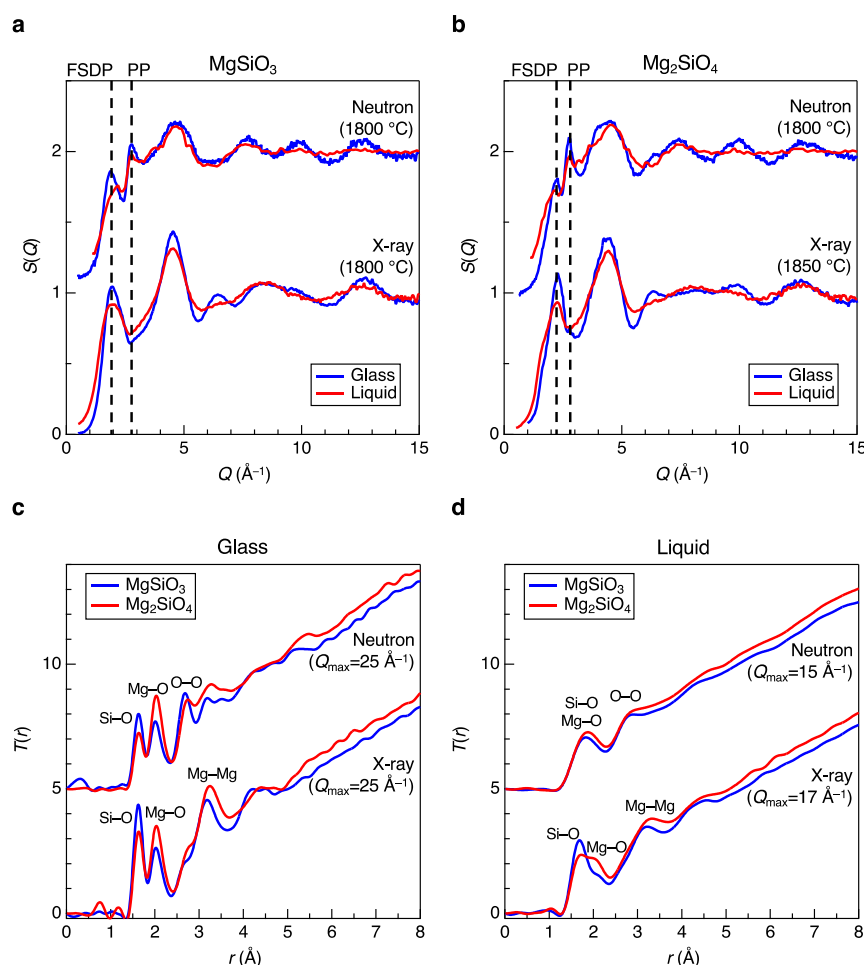


Figure 3. Diffraction data for MgO–SiO₂ glasses and liquids. (a) Neutron (upper) and X-ray (lower) structure factors, $S(Q)$ for g -^{7,9} and l -MgSiO₃. (b) Neutron (upper) and X-ray (lower) structure factors, $S(Q)$ for g -^{7,9} and l -Mg₂SiO₄. (c) Neutron (upper) and X-ray (lower) total correlation functions, $T(r)$ for g -^{7,9} MgSiO₃ (blue line) and Mg₂SiO₄ (red line). (d) Neutron (upper) and X-ray (lower) total correlation functions, $T(r)$ for l -MgSiO₃ (blue line) and Mg₂SiO₄ (red line). Dashed lines are guides for the eyes.

and magnesium have different valences, which results in different oxygen coordination numbers. Indeed, oxygen coordination numbers are mostly smaller than 5 in 22.7R₂O–77.3SiO₂ glasses. The partial pair distribution functions, $g_{ij}(r)$, for MgO–SiO₂ derived from the DF–MD simulations are shown in Figure 5b. The first correlation peaks for the glasses are sharper than those of the liquids. The first correlation peaks of $g_{\text{Si–Si}}(r)$ in MgSiO₃ are sharper than those in Mg₂SiO₄ and the first correlation peaks of $g_{\text{Mg–Mg}}(r)$ in Mg₂SiO₄ are sharper than those in MgSiO₃, which reflect the composition difference between MgSiO₃ (MgO–SiO₂) and Mg₂SiO₄ (2MgO–SiO₂).

It is confirmed that both the Si–O and Mg–O CNs derived from the DF–MD simulations are comparable to the experimental data. These behaviors suggest that there is no considerable structural difference in cation–oxygen coordination between MgSiO₃ and Mg₂SiO₄ and between liquids and glasses. On the other hand, $g_{\text{O–O}}(r)$ shows significant differences between them, although the difference in oxygen atomic fractions between MgSiO₃ (atomic fraction is 0.6) and Mg₂SiO₄ (atomic fraction is 0.57) is subtle. The O–O CNs for g -MgSiO₃, g -Mg₂SiO₄, l -MgSiO₃, and l -Mg₂SiO₄ are found to be 12.17, 12.70, 11.24, and 11.80, respectively. The difference between MgSiO₃ and Mg₂SiO₄ and between liquids and glasses is large, which agrees well with the behavior of the PP in

neutron $S(Q)$. These results suggest that differences in packing fraction of oxygen atoms⁴⁶ are an important parameter to understand the glass structure.

Three Body Correlations. Figure 6a shows the bond angle distributions (BAD) for Mg–SiO₂ glasses and liquids. It is worth mentioning that l -MgSiO₃, l -Mg₂SiO₄, and g -Mg₂SiO₄ data are very similar, and only g -MgSiO₃ exhibits a difference in fine structure in the Mg–O–Si and Mg–O–Mg BADs.

Especially, the Mg–O–Mg BAD exhibit that the MgO_x polyhedra of g -MgSiO₃ have a unique connectivity because c -MgSiO₃ shows only a single broad peak at $\sim 97^\circ$ (no peak at $\sim 120^\circ$). The O–Mg–O BADs of g -MgSiO₃ and g -Mg₂SiO₄ have two distinct peaks at ~ 90 and $\sim 180^\circ$, which are very different from a single well-defined peak for O–Si–O (109°), suggesting that MgO_x polyhedra are octahedral, although the Mg–O CN is 5. The O–Mg–O BADs are rather similar to O–Er–O of l -Er₂O₃ (Er–O CN is 6.1)⁴⁷ and O–Al–O of g -Al₂O₃ (Al–O CN is 4.7). Note that the Er₂O₃ is a nonglass-forming liquid and Al₂O₃ glass can be obtained only by electrochemical method⁴⁸ since Al₂O₃ is classified into intermediate (nonglass former).⁴⁹

Topological Analysis. From previous research,⁹ the addition of MgO decreases SiO₄ tetrahedra rings because MgO worked as intermediate oxide. Especially, g -Mg₂SiO₄ has no SiO₄ tetrahedra rings, and SiO₄ monomer and Si₂O₇ dimer

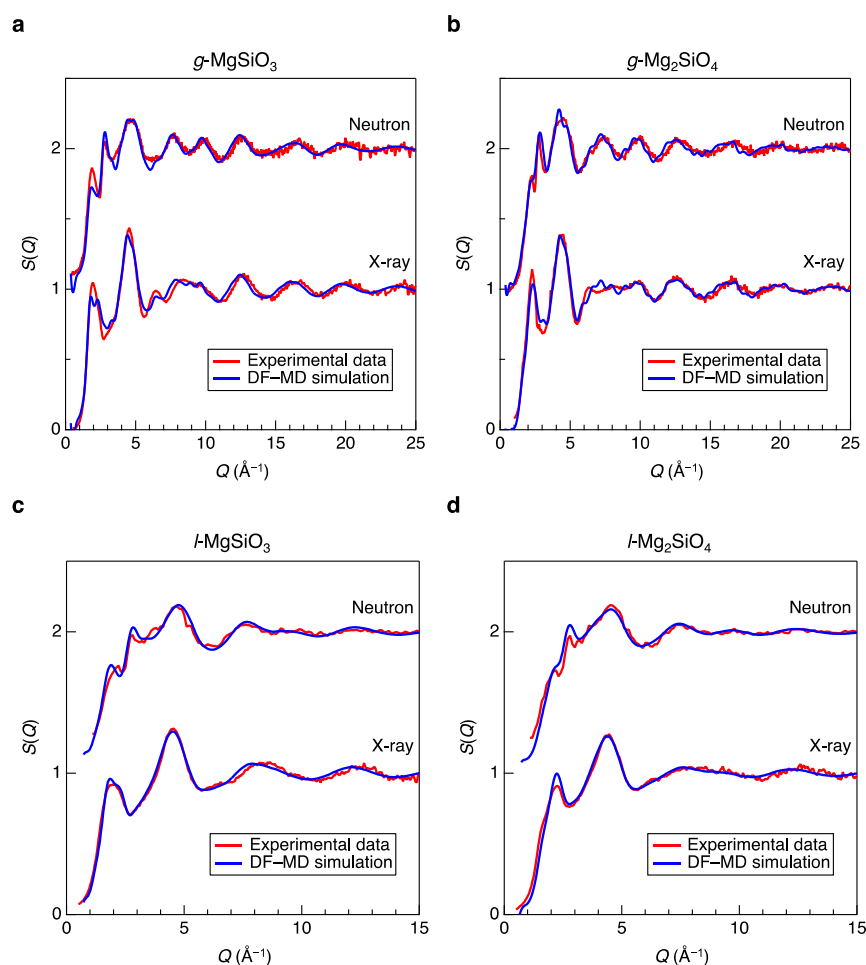


Figure 4. Neutron and X-ray total structure factors, $S(Q)$, for g,l -MgO–SiO₂ derived from DF–MD simulations (blue line) and experimental (red line) data. (a) Neutron (upper) and X-ray (lower) structure factors, $S(Q)$ for g -^{7,9} MgSiO₃. (b) Neutron (upper) and X-ray (lower) structure factors, $S(Q)$ for g -^{7,9} Mg₂SiO₄. (c) Neutron (upper) and X-ray (lower) structure factors, $S(Q)$ for l -MgSiO₃. (d) Neutron (upper) and X-ray (lower) structure factors, $S(Q)$ for l -Mg₂SiO₄.

are predominant silicate species. In this research, we focused on the ring statistics for –O–Si(Mg)–O– rings in MgO–SiO₂, and these data are shown in Figure 6b. Our ring statistics data are slightly different from those reported previously.⁹ We attribute this discrepancy to the different modeling approaches, i.e., RMC modeling in ref 9 vs a DF–MD simulation in our study. Fourfold rings are the dominant rings in all MgO–SiO₂. Intriguingly, all ring size distributions are very similar in Mg₂SiO₄, while g - and l -MgSiO₃ have larger-sized rings in comparison with c -MgSiO₃. It is suggested that g - and l -MgSiO₃ are topologically disordered,⁵⁰ which is a typical behavior of high GFA glass, while g - and l -Mg₂SiO₄ are topologically very similar to c -Mg₂SiO₄. Table 2 summarizes the results of the polyhedral connections and Q^n analyses for MgO–SiO₂. It is found that most of MgO–SiO₂ are within the corner-sharing motif for SiO₄–SiO₄ connectivities, although small fractions of edge-sharing are observed in g -Mg₂SiO₄ and liquid MgO–SiO₂. SiO₄–MgO_x connectivities for c -MgSiO₃ show a corner-sharing motif, too, but the fraction of edge-sharing is increased in g -MgSiO₃ and shows the maximum value in l -MgSiO₃ due to disorder. However, SiO₄–MgO_x connectivities in Mg₂SiO₄ show completely different behavior. The fraction of edge-sharing is increased in l -Mg₂SiO₄ in comparison with g -Mg₂SiO₄, but the fraction of that in c -Mg₂SiO₄ shows the maximum value. Moreover, the ratio of

corner-sharing and edge-sharing is exactly the same between SiO₄–MgO_x connectivities and MgO_x–MgO_x connectivities between c -Mg₂SiO₄ and g - and l -Mg₂SiO₄. The fraction of corner-sharing in MgO_x–MgO_x connectivities in c -Mg₂SiO₄ is smaller than that in g -Mg₂SiO₄ and l -Mg₂SiO₄. On the other hand, MgO_x–MgO_x connectivities in c -MgSiO₃ show only edge-sharing, while the g -MgSiO₃ shows a small fraction of edge-sharing in addition to corner-sharing and the fraction of edge-sharing slightly decreases in l -MgSiO₃. Thus, the behavior is quite different between MgSiO₃ and Mg₂SiO₄, and the latter shows similarity between c -Mg₂SiO₄ and g -/ l -Mg₂SiO₄ because it is noted that the SiO₄–SiO₄ connectivities are subtle in g -/ l -Mg₂SiO₄ owing to the breakdown of SiO₄ network.

Q^n distributions summarized in Table 2 provide us with connectivities of SiO₄ polyhedra. c -MgSiO₃ shows quite unique connectivity, because we can observe only Q^2 chain network. Indeed, it is demonstrated that SiO₄ tetrahedra form a corner-sharing chain network and MgO_x polyhedra form only an edge-sharing network, which form a layer structure in c -MgSiO₃. More than 50% of the Q^2 chain transforms into Q^1 and Q^3 in both g -MgSiO₃ and l -MgSiO₃, suggesting that the structural transformation between c -MgSiO₃ and g -/ l -MgSiO₃ requires quite significant structural modifications. On the other hand, c -Mg₂SiO₄ shows only Q^0 because the SiO₄ tetrahedra are isolated. Moreover, the fractions of Q^0 in g - and l -Mg₂SiO₄ are

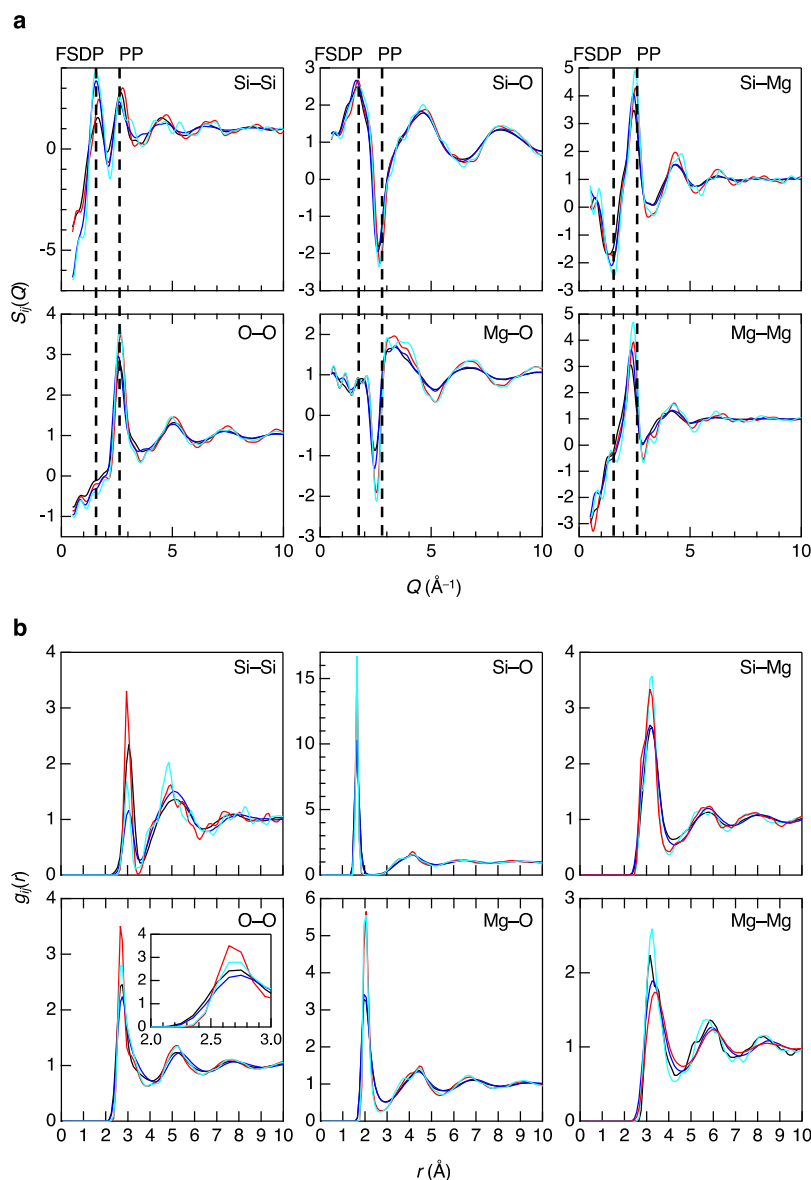


Figure 5. Partial structure for MgO–SiO₂ glasses and liquids. (a) Partial structure factors, $S_{ij}(Q)$. (b) Partial pair distribution functions, $g_{ij}(r)$. Black, *l*-MgSiO₃; red, *g*-MgSiO₃; blue, *l*-Mg₂SiO₄; cyan, *g*-Mg₂SiO₄. Dashed lines are a guide to the eyes.

decreased to less than 40% and Q^1 (Si₂O₇⁶⁻ dimers⁷) is dominant (43.8% in glass and 45.2% in liquid), while the fractions of Q^2 are about 16%. In addition, a small fraction of Q^3 (1.4%) and Q^4 (0.1%) is observed in *l*-Mg₂SiO₄. It is suggested from these behaviors that the transformation from *g*/*l*-Mg₂SiO₄ into *c*-Mg₂SiO₄ seems to be easier than that in MgSiO₃ because only the breakdown of chains or dimers is required while the formation of chains is required in the transformation from *g*/*l*-MgSiO₃ into *c*-MgSiO₃. The average Q^n values of MgO–SiO₂ are 2.00 (*c*-MgSiO₃), 2.03 (*g*-MgSiO₃), 2.02 (*l*-MgSiO₃), 0 (*c*-Mg₂SiO₄), 0.77 (*g*-Mg₂SiO₄), and 0.82 (*l*-Mg₂SiO₄). Both *g*- and *l*-SiO₂ with high GFA have the value of that average Q^n are almost 4.0, which suggested that the number of average Q^n is an indicator of GFA.

Figure 7a shows the Si-centric persistence diagrams, PD₁s. It is well-known that *g*-SiO₂ shows a prominent vertical profile along with the death axis at $b_k \sim 2.2$ Å² in both the Si-centric and O-centric PD₁s due to the formation of SiO₄ tetrahedral network with corner-sharing of oxygen atoms.^{51,52} Similar

profiles are only observed in the Si-centric PD₁ for *g*- and *l*-MgSiO₃ at $b_k \sim 2.4$ Å², but *c*-MgSiO₃ does not show such a profile since *c*-MgSiO₃ has only a Q^2 chain network, which is not three-dimensional. Mg₂SiO₄ does not show such a profile, either, because there is almost no Q^3 or Q^4 three-dimensional SiO₄ network. The O-centric PD₁s are shown in Figure 7b. The small death profiles are observed along with the diagonal in PD₁s because the death values reflect significantly high packing of oxygen atoms and high density. It is found that the death value is a maximum in *l*-MgSiO₃ (minimum density) and a minimum in *c*-MgSiO₃ (maximum density). Figure 7c shows Mg-centric PD₁s. The PD₁s for *g*-MgSiO₃ and *g*-Mg₂SiO₄ have a profile along with the death axis at $b_k \sim 3.0$ Å², which are the signature for the formation of the Mg–O network. The PD₁s for *c*-Mg₂SiO₄ have a profile at the same b_k position, while *c*-MgSiO₃ does not have such a profile because of the absence of well-defined three-dimensional Mg–O network. Moreover, it is suggested that all of the liquid data are very similar to glass data and that *c*-Mg₂SiO₄ data are very similar to *g*-Mg₂SiO₄,

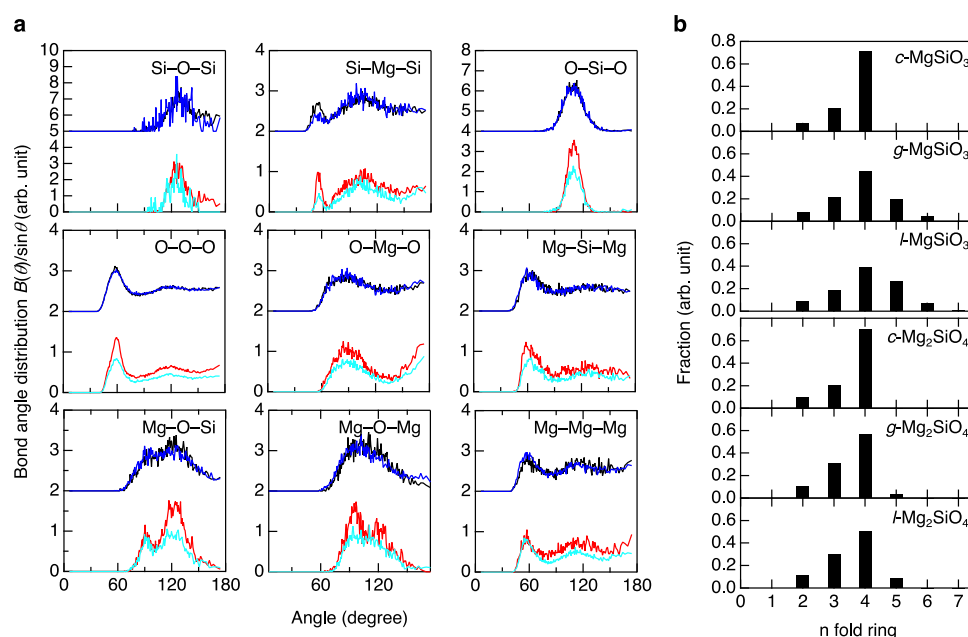


Figure 6. Analysis of intermediate-range structure in MgO–SiO₂. (a) BADs. (b) King ring size distributions for –O–Si(Mg)–O– rings. Black, *l*-MgSiO₃; red, *g*-MgSiO₃; blue, *l*-Mg₂SiO₄; cyan, *g*-Mg₂SiO₄.

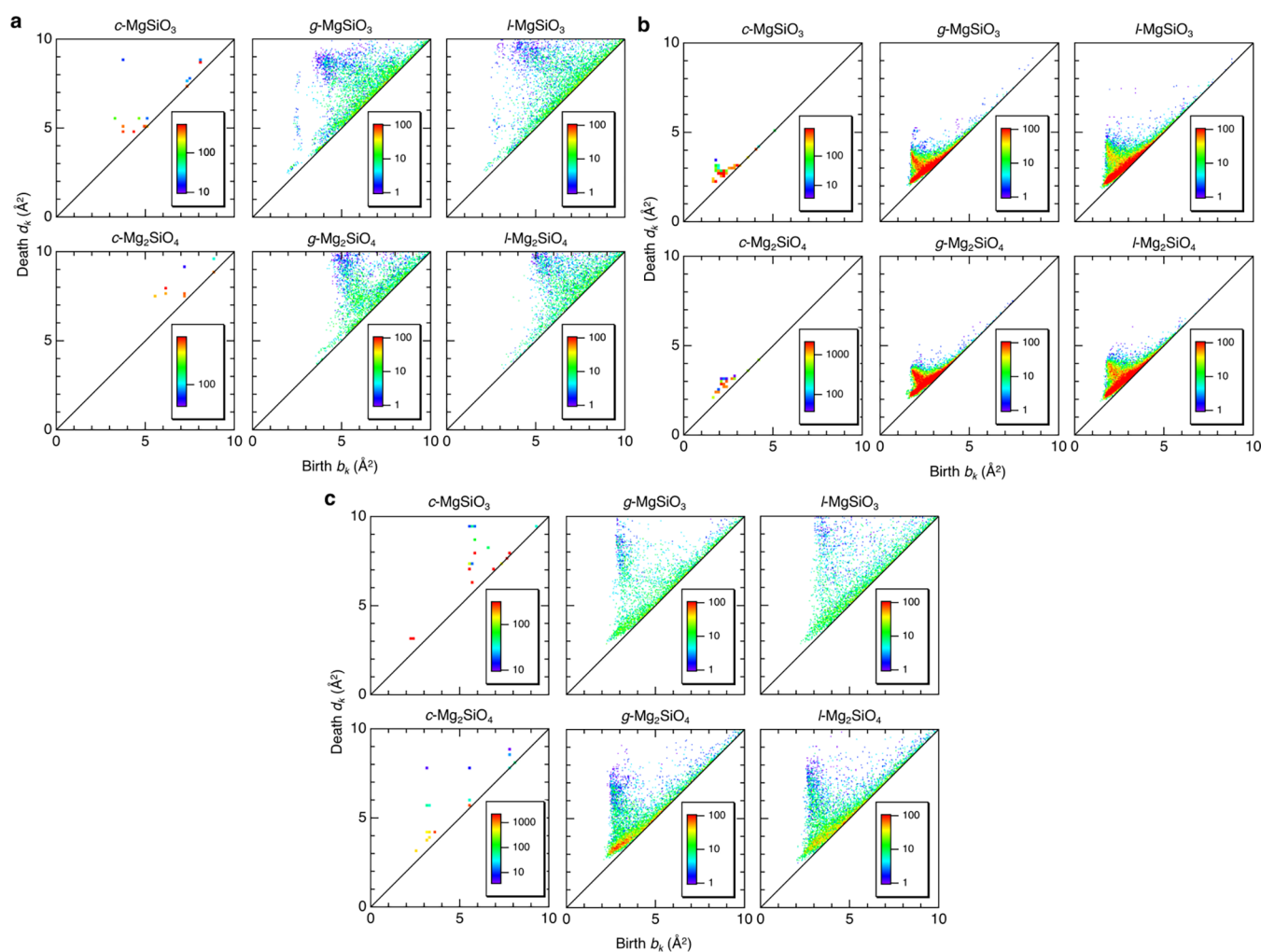


Figure 7. Topological analysis for MgO–SiO₂. (a) Si-centric PD₁, (b) O-centric PD₁, and (c) Mg-centric PD₁.

Table 2. Polyhedral Connections and Q^n Analyses for MgO–SiO₂

		polyhedral connections			Q^n				
		SiO ₄ –SiO ₄	SiO ₄ –MgO _x	MgO _x –MgO _x	Q^0	Q^1	Q^2	Q^3	Q^4
<i>c</i> -MgSiO ₃	corner	100	92.3	0	0	0	100	0	0
	edge	0	7.7	100					
	face	0	0	0					
<i>g</i> -MgSiO ₃	corner	100	82.7	65.9	4.9	22.6	44.1	21.4	7.0
	edge	0	17.3	30.7					
	face	0	0	3.4					
<i>l</i> -MgSiO ₃	corner	98.5	77.1	69.6	5.8	20.3	44.3	25.7	3.9
	edge	1.5	22.5	27.9					
	face	0	0.4	2.5					
<i>c</i> -Mg ₂ SiO ₄	corner	0	66.7	66.7	100	0	0	0	0
	edge	0	33.3	33.3					
	face	0	0	0					
<i>g</i> -Mg ₂ SiO ₄	corner	96.6	79.3	71.5	39.6	43.8	16.6	0	0
	edge	3.4	20.7	27.4					
	face	0	0	1.1					
<i>l</i> -Mg ₂ SiO ₄	corner	98.4	76.2	68.5	37.1	45.2	16.2	1.4	0.1
	edge	1.6	23.2	28.3					
	face	0	0.6	3.2					

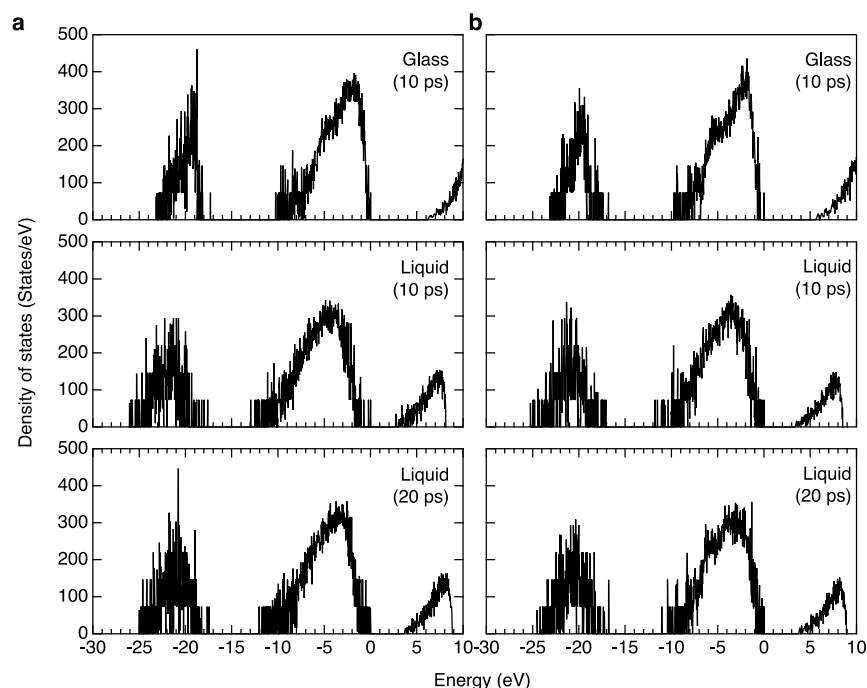


Figure 8. Electronic structure of MgO–SiO₂ glasses and liquids. Electron DOSs for (a) MgSiO₃ and (b) Mg₂SiO₄ glasses and liquids calculated by DF–MD simulations employing PBE0 (0.3).

but *c*-MgSiO₃ data are very different from *g*/*l*-MgSiO₃ data. This trend is consistent with ring size distributions, demonstrating that we can see similarity in homology in Mg₂SiO₄, but the homology of *c*-MgSiO₃ is quite different from that of *g*- and *l*-MgSiO₃.

Electronic Structures. Figure 8 shows electron density of states (DOS) for *g*- and *l*-MgO–SiO₂ calculated employing PBE0⁵³ with a fraction of exact exchange of $\alpha = 0.3$, which will be referred to as PBE0 (0.3) below. It is known that GGA–PBE underestimates the band gap, and we performed several benchmark tests for crystalline MgO, SiO₂ (α -quartz), MgSiO₃, and Mg₂SiO₄ (see Table S3) and confirmed that PBE0 (0.3) shows the best agreement with experimental data;

hence, we compare GGA–PBE (blue) and PBE0 (0.3) (red) in Figure S4. It is suggested from the DF–MD calculations that the lowest unoccupied molecular orbitals (LUMOs) are 3s orbitals and free electron-like state at the void sites near magnesium atoms (see Figure 9a for *g*-MgSiO₃ as a typical example and Figure S5 for *l*-MgSiO₃ and *g*/*l*-Mg₂SiO₄) arising from a decreased oxygen coordination, and the highest occupied molecular orbitals (HOMOs) are oxygen's 2p orbital states. These behaviors are in line with our previous study on CaO–Al₂O₃ glass⁵⁴ but very different from α -quartz, *c*-MgO, *c*-MgSiO₃, and *c*-Mg₂SiO₄, in which LUMOs and HOMOs are oxygen's 3s and 2p orbitals, respectively. Electron band gaps calculated by PBE0 (0.3) are found to be 7.97, 6.30, and 2.71

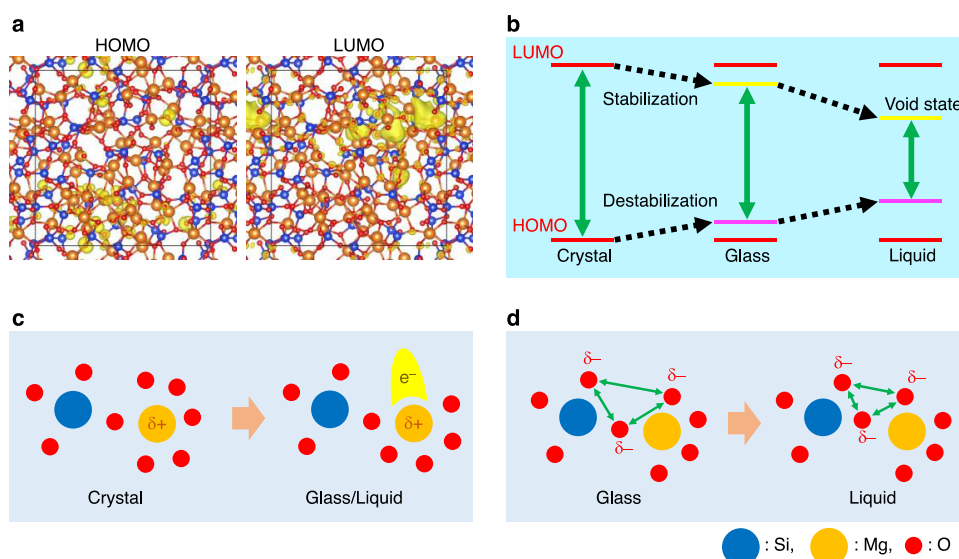


Figure 9. Behaviors of HOMO and LUMO in MgO-SiO_2 . (a) Isosurface plots of the partial charge density around the HOMO and the LUMO levels for $g\text{-MgSiO}_3$. (b) Schematic illustration for HOMOs and LUMOs in crystals, glasses, and liquids. (c) Schematic illustration of LUMO in glasses and liquids. (d) Schematic illustration for electron repulsions in liquids.

(10 ps)/3.69 (20 ps) eV, for c -, g -, and $l\text{-MgSiO}_3$ and 8.37, 5.64, and 3.43 (10 ps)/3.81 (20 ps) eV, for c -, g -, and $l\text{-Mg}_2\text{SiO}_4$. Note that liquid data have more fluctuations due to the high temperature. It is found that band gap values become small in the order of crystal, glass, and liquid (see Figure 9b) and the band gap of $g\text{-Mg}_2\text{SiO}_4$ is narrower than that of $g\text{-MgSiO}_3$. We discuss these behaviors in Figure 9. The LUMO levels of glasses can be stabilized due to void site arising from a decreased oxygen coordination from six in the crystals to five in the glasses (Figure 9c). The LUMO levels of the liquid can be more stabilized due to the high temperature. HOMO can be destabilized in glasses due to inherent structural disorder, especially between oxygen atoms. This feature is enhanced in the liquid due to high temperature (see Figure 9d) manifested by decreased minimum oxygen–oxygen atomic distances shown in the inset of Figure 5b.

CONCLUSIONS

In this article, we have discussed the atomic and electronic structures of MgSiO_3 and Mg_2SiO_4 to understand the network topology and relationship between structure and GFA. The density measurement at the ISS confirmed that our previous estimated density for $l\text{-Mg}_2\text{SiO}_4$ is very close to experimental data. The packing of oxygen atoms in Mg_2SiO_4 is larger than that in MgSiO_3 , and that of the glasses is larger than that of the liquids. Diffraction measurements and DF–MD simulations demonstrated that the packing of oxygen atoms is an important structural descriptor to understand the difference between MgSiO_3 and Mg_2SiO_4 and between glass and liquid. The analysis of electronic and topological structures reasonably explained the behaviors of electron band gaps and topological similarity in crystals, glasses, and liquids. These results suggest that an electronic state does not change quite a lot between MgSiO_3 and Mg_2SiO_4 , also the topological similarity between crystalline (c)- and g -(l -) Mg_2SiO_4 is the signature of low GFA and high GFA g -(l -) MgSiO_3 shows a unique glass topology, which is different from $c\text{-MgSiO}_3$. This means the atomic structure in terms of network topology is an important factor to understand GFA. We demonstrated that systematic

comparison among crystal, glass, and liquid is important to understand the nature and glass and liquid. The utilization of containerless techniques and understanding of behavior of oxygen atoms, as well as network topology, provide us with crucial information to discuss glass-forming ability.

ASSOCIATED CONTENT

Data Availability Statement

The data sets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.3c05561>.

Experimental and computational details; density data of $l\text{-}x\text{MgO}-(100-x)\text{SiO}_2$; X-ray total structure factors, $S(Q)$, for $l\text{-}x\text{MgO}-(100-x)\text{SiO}_2$; pair function analysis; electron density of states; Isosurface plots of the partial charge density; coordination numbers obtained by pair function analysis; coordination number obtained by DF–MD; electron band gaps of GGA–PBE and PBE0 (PDF).

AUTHOR INFORMATION

Corresponding Author

Shinji Kohara – Center for Basic Research on Materials, National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0047, Japan; orcid.org/0000-0001-9596-2680; Email: KOHARA.Shinji@nims.go.jp

Authors

Yuta Shuseki – Graduate School of Engineering, Kyoto University, Kyoto 615-8520, Japan; Center for Basic Research on Materials, National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0047, Japan; orcid.org/0000-0003-4835-2841

Tomoaki Kaneko – Department of Computational Science and Technology, Research Organization for Information Science and Technology (RIST), Tokyo 105-0013, Japan

Keitaro Sodeyama – Center for Basic Research on Materials, National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0047, Japan; orcid.org/0000-0002-9228-0729

Yohei Onodera – Center for Basic Research on Materials, National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0047, Japan

Chihiro Koyama – Human Spaceflight Technology Directorate, Japan Aerospace Exploration Agency (JAXA), Tsukuba, Ibaraki 305-8505, Japan

Atsunobu Masuno – Graduate School of Engineering, Kyoto University, Kyoto 615-8520, Japan; Center for Basic Research on Materials, National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0047, Japan

Shunta Sasaki – Graduate School of Science and Technology, Hirosaki University, Hirosaki, Aomori 036-8561, Japan

Shohei Hatano – Graduate School of Science and Technology, Hirosaki University, Hirosaki, Aomori 036-8561, Japan

Motoki Shiga – Unprecedented-Scale Data Analytics Center, Tohoku University, Sendai, Miyagi 980-8578, Japan; Graduate School of Information Science, Tohoku University, Sendai, Miyagi 980-8579, Japan; RIKEN Center for Advanced Intelligence Project, Tokyo 103-0027, Japan

Ipppei Obayashi – Center for Artificial Intelligence and Mathematical Data Science, Okayama University, Okayama 700-8530, Japan

Yasuaki Hiraoka – Institute for the Advanced Study of Human Biology (WPI-ASHBi), Kyoto University, Kyoto 606-8303, Japan

Junpei T. Okada – Institute for Materials Research, Tohoku University, Sendai, Miyagi 980-8577, Japan

Akitoshi Mizuno – National Institute of Technology, Hakodate College, Hakodate, Hokkaido 042-8510, Japan; orcid.org/0000-0002-5238-1971

Yuki Watanabe – Advanced Engineering Services Co., Ltd., Tsukuba, Ibaraki 305-0032, Japan

Yui Nakata – Advanced Engineering Services Co., Ltd., Tsukuba, Ibaraki 305-0032, Japan

Koji Ohara – Faculty of Materials for Energy, Shimane University, Matsue, Shimane 690-8504, Japan; orcid.org/0000-0002-3134-512X

Motohiko Murakami – Department of Earth Sciences, ETH Zürich, Zürich 8092, Switzerland

Matthew G. Tucker – Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States; orcid.org/0000-0002-2891-7086

Marshall T. McDonnell – Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, United States; orcid.org/0000-0002-3713-2117

Hirohisa Oda – Human Spaceflight Technology Directorate, Japan Aerospace Exploration Agency (JAXA), Tsukuba, Ibaraki 305-8505, Japan

Takehiko Ishikawa – Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency (JAXA), Tsukuba, Ibaraki 305-8505, Japan

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acs.jpca.3c05561>

Author Contributions

S.K. designed the research. A.M. prepared the samples. Y.S., S.K., C.K. A.M., Y.W., Y.N. H.O., and T.I. measured density of

$\text{I-Mg}_2\text{SiO}_4$. Y.S., S.K., Y.O., C.K., A.M., S.S., S.H., Y.W., and K.O. performed X-ray diffraction measurements. S.K., Y.O., C.K., J.T.O. A.M., Y.N., M.G.T., and M.T.M. performed neutron diffraction measurements. T.K. and K.S. conducted DF–MD simulations. Y.S., S.K., T.K., K.S., Y.O., M.S., I.O., Y.H., M.M. H.O., and T.I. analyzed data. Y.S. and S.K. wrote the paper, with comments provided by all authors.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The synchrotron radiation experiments were performed with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (proposal nos. 2018A1096 and 2022A1074). The neutron data were collected on the NOMAD instrument at the Spallation Neutron Source, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory. This research was supported by JSPS Grant-in-Aid for Transformative Research Areas (A) “Hyper-Ordered Structures Science” Grant Numbers 20H05878 (to M.S. and S.K.), 20H05881 (to S.K. and Y.O.), 20H05882 (to T.I.), 20H05884 (to M.S.), and KAKENIH Grant Number 19K05648 (to Y.O.)). Discussion with Yuji Higo is gratefully appreciated.

REFERENCES

- (1) Mysen, B.; Richet, P. *Silicate Glasses and Melts*, Second ed.; Elsevier, 2019.
- (2) Angell, C. A. Formation of glasses from liquids and biopolymers. *Science* **1995**, *267*, 1924–1935.
- (3) Xie, L.; Yoneda, A.; Yamazaki, D.; Manthilake, G.; Higo, Y.; Tange, Y.; Guignot, N.; King, A.; Scheel, M.; Andrault, D. Formation of bridgmanite-enriched layer at the top lower-mantle during magma ocean solidification. *Nat. Commun.* **2020**, *11*, 548.
- (4) Price, D. L. *High-Temperature Levitated Materials*; Cambridge University Press, 2010.
- (5) Tangeman, J.; Phillips, B. L.; Novrotsky, A. Vitreous forsterite (Mg_2SiO_4): Synthesis, structure, and thermochemistry. *Geophys. Res. Lett.* **2001**, *28*, 2517.
- (6) Yi, C. D.; Okuno, M.; Morikawa, H.; Marumo, F. Structure analysis of MgSiO_3 glass. *J. Non-Cryst. Solids* **1983**, *55*, 131–141.
- (7) Kohara, S.; Suzuya, K.; Takeuchi, K.; Loong, C. K.; Grimsditch, M.; Weber, J. K. R.; Tangeman, J. A.; Key, T. S. Glass formation at the limit of insufficient network formers. *Science* **2004**, *303*, 1649–1652.
- (8) Wilding, M. C.; Benmore, C. J.; Tangeman, J. A.; Sampath, S. Coordination changes in magnesium silicate glasses. *Europhys. Lett.* **2014**, *67*, 212–218.
- (9) Kohara, S.; Akola, J.; Morita, H.; Suzuya, K.; Weber, M. C.; Benmore, C. J. Relationship between topological order and glass forming ability in densely packed enstatite and forsterite composition glasses. *Proc. Natl. Acad. U. S. A.* **2011**, *108*, 14780–14785.
- (10) Shimoda, K.; Tobu, Y.; Hatakeyama, M.; Nemoto, T.; Saito, K. Structural investigation of Mg local environments in silicate glasses by ultra-high field ^{25}Mg 3QMAS NMR spectroscopy. *Am. Mineral.* **2007**, *92*, 695–698.
- (11) Sen, S.; Tangeman, J. Evidence for anomalously large degree of polymerization in Mg_2SiO_4 glass and melt. *Am. Mineral.* **2008**, *93*, 946–949.
- (12) Shimoda, K.; Nemoto, T.; Saito, K. Local structure of magnesium in silicate glasses: A ^{25}Mg 3QMAS NMR study. *J. Phys. Chem. B* **2008**, *112*, 6747–6752.
- (13) Sen, S.; Maekawa, H.; Papatheodorou, G. N. Short-range structure of invert glasses along the pseudo-binary join MgSiO_3 – Mg_2SiO_4 : Results from ^{29}Si and ^{25}Mg MAS NMR spectroscopy. *J. Phys. Chem. B* **2009**, *113*, 15243–15248.
- (14) Kalampounias, A. G.; Nasikas, N. K.; Papatheodorou, G. N. Glass formation and structure in the pseudobinary system: From

- degraded networks to ioniclike glasses. *J. Chem. Phys.* **2009**, *131*, 114513.
- (15) McGreevy, R. L.; Pusztai, L. Reverse Monte Carlo simulation: a new technique for the determination of disordered structures. *Mol. Simul.* **1988**, *1*, 359–367.
- (16) Waseda, Y.; Toguri, J. M. The structure of molten binary silicate systems CaO–SiO₂ and MgO–SiO₂. *Metall. Trans. B* **1977**, *8*, 563–568.
- (17) Wilding, M. C.; Benmore, C. J.; Weber, J. K. R. In situ diffraction studies of magnesium silicate liquids. *J. Mater. Sci.* **2008**, *43*, 4707–4713.
- (18) Tamaru, H.; Koyama, C.; Saruwatari, H.; Nakamura, Y.; Ishikawa, Y.; Takada, T. Status of the electrostatic levitation furnace (ELF) in the ISS-KIBO. *Microgravity Sci. Technol.* **2018**, *30*, 643–651.
- (19) Fabrichnaya, O. B. Thermodynamic modelling of melting in the system FeO–MgO–SiO₂–O₂ at pressure of 1 bar. *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.* **2000**, *24*, 113–131.
- (20) Ohara, K.; Onodera, Y.; Murakami, M.; Kohara, S. Structure of disordered materials under ambient to extreme conditions revealed by synchrotron x-ray diffraction techniques at SPring-8—recent instrumentation and synergic collaboration with modelling and topological analyses. *J. Phys.: Condens. Matter* **2021**, *33*, 383001.
- (21) Ohara, K.; Onodera, Y.; Kohara, S.; Koyama, C.; Masuno, A.; Mizuno, A.; Okada, J. T.; Tahara, S.; Watanabe, Y.; Oda, H.; et al. Accurate synchrotron hard X-ray diffraction measurements on high-temperature liquid oxides. *Int. J. Microgravity Sci. Appl.* **2020**, *37*, No. 370202.
- (22) Kohara, S.; Itou, M.; Suzuya, K.; Inamura, Y.; Sakurai, Y.; Ohishi, Y.; Takata, M. Structural studies of disordered materials using high-energy x-ray diffraction from ambient to extreme conditions. *J. Phys.: Condens. Matter* **2007**, *19*, No. 506101.
- (23) Neufeld, J.; Feynson, M.; Carruth, J.; Hoffmann, R.; Chipley, K. K. The nanoscale ordered materials diffractometer NOMAD at the spallation neutron source SNS. *Nucl. Instrum. Meth. B* **2012**, *287*, 68–75.
- (24) Faber, T. E.; Ziman, J. M. A theory of the electrical properties of liquid metals III. The resistivity of binary alloys. *Philos. Mag.* **1965**, *11*, 153–173.
- (25) Greben, O.; J  v  ri, P.; Temleitner, L.; Pusztai, L. A new version of the RMC++ Reverse Monte Carlo programme, aimed at investigating the structure of covalent glasses. *J. Optoelectron. Adv. Mater.* **2007**, *9*, 3021–3027.
- (26) CP2K Download site, <http://www.cp2k.org/>. Access date 2020/4/5.
- (27) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (28) Goedecker, S.; Teter, M.; Hutter, J. Separable dual-space Gaussian pseudopotentials. *Phys. Rev. B* **1996**, *54*, 1703–1710.
- (29) PHASE0 download site, <http://azuma.nims.go.jp/>. Access date 2020/5/17.
- (30) Vanderbilt, D. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Phys. Rev. B* **1990**, *41*, 7892–7895.
- (31) Troullier, N.; Martins, J. L. A straightforward method for generating soft transferable pseudopotentials. *Solid State Commun.* **1990**, *74*, 613–616.
- (32) Perdew, J. P.; Ernzerhof, M.; Burke, K. Rationale for mixing exact exchange with density functional approximations. *J. Chem. Phys.* **1996**, *105*, 9982–9985.
- (33) Le roux, S.; Jund, P. Ring statistics analysis of topological networks: new approach and application to amorphous GeS₂ and SiO₂ systems. *Comput. Mater. Sci.* **2010**, *49*, 70–83.
- (34) Hiraoka, Y.; Nakamura, T.; Hirata, A.; Escobar, E. G.; Matsue, K.; Nishiura, Y. Hierarchical structures of amorphous solids characterized by persistent homology. *Proc. Natl. Acad. Sci. USA* **2016**, *113*, 7035–7040.
- (35) Obayashi, I. *HomCloud*; Hiraoka Laboratory, Advanced Institute for Materials Research, Tohoku University: Japan, 2018. https://www.wpi-aimr.tohoku.ac.jp/hiraoka_lab/homcloud/index.en.html. Access date 2020/7/10.
- (36) Morimoto, N.; Koto, K. The crystal structure of orthoenstatite. *Z. Krist.-Cryst. Mater.* **1969**, *129*, 65–83.
- (37) Smyth, J. R.; Hazen, R. M. The crystal structures of forsterite and hortonolite at several temperatures up to 900 °C. *Am. Mineral.* **1973**, *58*, 588–593.
- (38) Tomlinson, J. W.; Heynes, M. S. R.; Bockris, J. O'M. The structure of liquid silicates. Part 2.—Molar volumes and expansivities. *Trans. Faraday Soc.* **1958**, *54*, 1822–1833.
- (39) Price, D. L.; Moss, S. C.; Reijers, R.; Saboungi, M. L.; Susman, S. Intermediate-range order in glasses and liquids. *J. Phys. C Solid State Phys.* **1988**, *21*, L1069–L1072.
- (40) Salmon, P. S.; Martin, R. A.; Mason, P. E.; Cuello, G. J. Topological versus chemical ordering in network glasses at intermediate and extended length scales. *Nature* **2005**, *435*, 75–78.
- (41) Salmon, P. S.; Zeidler, A. Ordering on different length scales in liquid and amorphous materials. *J. Stat. Mech. Theory E* **2019**, *2019*, 114006.
- (42) Salmon, P. S.; Moody, G. S.; Ishii, Y.; Pizzey, K. J.; Polidori, A.; Salanne, M.; Zeidler, A.; Buscemi, M.; Fischer, H. E.; Bull, C. L.; Klotz, S.; Weber, R.; Benmore, C. J.; MacLeod, S. G. Pressure induced structure transformations in amorphous MgSiO₃ and CaSiO₃. *J. Non-Cryst. Solids* **2019**, *3*, No. 100024.
- (43) Cormier, L.; Cuello, G. J. Mg coordination in a MgSiO₃ glass using neutron diffraction coupled with isotopic substitution. *Phys. Rev. B* **2011**, *83*, No. 224204.
- (44) Comier, L.; Hennet, L.; Lelong, G.; Cuello, G. J.; Bytchkov, A. Structure from glass to melt: a case study along the MgSiO₃–CaSiO₃ join using neutron and X-ray diffraction. *C. R. Geosci.* **2022**, *354*, 15–34.
- (45) Onodera, Y.; Takimoto, Y.; Hijiya, H.; Taniguchi, T.; Urata, S.; Inaba, S.; Fujita, S.; Obayashi, I.; Hiraoka, Y.; Kohara, S. Origin of the mixed alkali effect in silicate glass. *NPG Asia Mater.* **2019**, *11*, 75.
- (46) Zeidler, A.; Salmon, P. S.; Skinner, L. B. Packing and the structural transformations in liquid and amorphous oxides from ambient to extreme conditions. *Proc. Natl. Acad. USA* **2014**, *111*, 10045–10048.
- (47) Koyama, C.; Tahara, S.; Kohara, S.; Onodera, Y.; Sm  br  ten, D. R.; Selbach, S. M.; Akola, J.; Ishikawa, T.; Masuno, A.; Mizuno, A.; et al. Very sharp diffraction peak in nonglass-forming liquid with the formation of distorted tetraclusters. *NPG Asia Mater.* **2020**, *12*, 43.
- (48) Hashimoto, H.; Onodera, Y.; Tahara, S.; Kohara, S.; Yazawa, K.; Segawa, H.; Murakami, M.; Ohara, K. Structure of alumina glass. *Sci. Rep.* **2022**, *12*, 516.
- (49) Sun, K.-H. Fundamental condition of glass formation. *J. Am. Ceram. Soc.* **1947**, *30*, 277–281.
- (50) Gupta, P. K.; Cooper, A. R. Topologically disordered networks of rigid polytopes. *J. Non-Cryst. Solids* **1990**, *123*, 14–21.
- (51) Onodera, Y.; Kohara, S.; Tahara, S.; Masuno, A.; Inoue, H.; Shiga, M.; Hirata, A.; Tsuchiya, K.; Hiraoka, Y.; Tsuchiya, K.; et al. Understanding diffraction patterns of glassy, liquid and amorphous materials via persistent homology analyses. *J. Ceram. Soc. Jpn.* **2019**, *127*, 853–863.
- (52) Onodera, Y.; Kohara, S.; Salmon, P. S.; Hirata, A.; Nishiyama, N.; Kitani, S.; Zeidler, A.; Shiga, M.; Masuno, A.; Inoue, H.; et al. Structure and properties of densified silica glass: characterizing the order within disorder. *NPG Asia Mater.* **2020**, *12*, 85.
- (53) Perdew, P. J.; Ernzerhof, M.; Burke, K. Rationale for mixing exact exchange with density functional approximations. *J. Chem. Phys.* **1996**, *105*, 9982–9985.
- (54) Akola, J.; Kohara, S.; Ohara, K.; Fujiwara, A.; Watanabe, Y.; Masuno, A.; Usuki, T.; Kubo, T.; Nakahira, A.; Nitta, K.; Uruga, T.; et al. Network topology for the formation of solvated electrons in binary CaO–Al₂O₃ composition glasses. *Proc. Natl. Acad. USA* **2013**, *110*, 10129–10134.