Ring-originated anisotropy of local structure ordering in amorphous and crystalline silicon dioxide

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Rings consisting of chemically-bonded atoms are essential topological motifs in the structural order of network-forming materials. Here, we propose two analysis methods based on rings: (1) quantitative characterization of ring shapes and (2) evaluation of the local structure order around rings. In the first method, we quantify the geometric shape of a ring using a set of our proposed indicators, namely, the roundness and roughness, in addition to the conventional ring size. Our findings reveal that the structure of amorphous silica consists of distorted rings, some of which resemble polymorphisms in silica crystals. The second method is based on a spatial correlation function, which describes three-dimensional atom densities around rings. It allows us to visualize the anisotropy of the local structure order around rings in amorphous silica. Furthermore, through a comparative analysis of the amorphous silica models made with different constraints, we show that the local anisotropy originates from centrally located rings. Moreover, we demonstrate that the anisotropy contributes to building the intermediate-range structure order in the amorphous silica characterized by the first sharp diffraction peaks observed in diffraction experiments.

I. INTRODUCTION

Amorphous materials exhibit a disordered structure due to the lack of translation periodicity. Meanwhile, the formation of short-range order can be observed in the pair distribution function (PDF) obtained by X-ray diffraction (XRD) and neutron diffraction (ND) measurements. For some amorphous materials, these diffraction experiments also provide evidence of a structural order on a length scale larger than the atomic bond length, that is, the intermediate range. Amorphous silica (SiO$_2$) is a representative material with an intermediate-range structural order, which has a variety of crystalline polymorphs. It is well known that the short-range order of amorphous and crystalline SiO$_2$ under ambient conditions is based on a regular SiO$_4$ tetrahedron. The interconnection of tetrahedra with corner-sharing oxygen atoms forms a network structure. The formation of intermediate-range order is often discussed in terms of the first sharp diffraction peaks (FSDP) observed in diffraction data. The origin of FSDP in amorphous SiO$_2$ has long been debated. It is currently well known that the length scale of FSDP is $\sim 4\AA (2\pi/\Delta q_{\text{FSDP}})$. $q = (4\pi/\lambda) \sin \theta$ with the scattering angle $2\theta$ and X-rays or neutrons wavelength $\lambda$ with the coherence length of $\sim 10$ Å ($= 2\pi/\Delta q_{\text{FSDP}}$, where $\Delta q_{\text{FSDP}}$ is the width of FSDP). However, structural order analysis based on PDF has limitations caused by the rapid decrease in the atomic pair correlation peaks on the intermediate-range scale. Moreover, structural units, building intermediate-range orders, are larger complexes than chemical bonds, which cannot be identified by pairwise correlation analysis. Therefore, revealing the structural orders hidden in pairwise correlations in amorphous materials remains challenging. Nonetheless, an important first step forward consists in uncovering the relationship between structural orders and material properties, which would enable the forging of a new path for designing novel functional materials.

Structural models of glass, which are based on the network structure consisting of the corner-sharing tetrahedral motif, as found in SiO$_2$, help investigate the intermediate range structural orders in amorphous materials. The first structural model for glass was the crystallite model, which described glass as an aggregate of small crystallites, proposed in 1835 by Frankenheim. The crystallite model is also called the discrete crystalline model, which presumes that crystalline clusters are embedded in the glass matrix, based on the relatively sharper feature of the FSDP in the diffraction data.

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However, this model has been shown inappropriate because the estimated lattice constants of the crystallites are larger than those of $\beta$-cristobalite, leading to a discrepancy between the observed and calculated densities. Subsequently, a continuous crystal [11] and quasi-crystal models [3] have been proposed. Meanwhile, a continuous random network model was first proposed by Zachariasen in 1932 [12], in which short-range structural units in glass were connected randomly. Zachariasen also addressed the relationship between the structure and glass-forming ability and proposed four rules for the formation of glass. Zachariasen’s rules are widely used, although they are only based on chemical bonds, such as the coordination number. Several structural models have followed, which assumed larger structural units, such as the layer model [13] and periodic boundaries of void (or cage) models [8, 14].

The structural order of an atomic configuration given by experimental measurements or theoretical computations can be analyzed using mathematical tools of homology and topology to characterize the voids in the atomic configuration and chemical bond networks [9]. Persistent homology (PH) is a novel topological analysis tool capable of exhaustively detecting voids (i.e., cavities or holes) in atomic configurations of amorphous materials [15, 16], using an efficient computational algorithm without considering chemical bonds. First, the computation of PH replaces each atomic coordinate with a sphere and continuously increases the radius from zero to a sufficiently large value. Next, pairs of radii, at which a void in a specific location appears (birth) and disappears (death), are recorded. Finally, a scatter plot of the birth-death plane, called the persistence diagram (PD), is visualized to capture the shape of the voids at multiple scales. Following a landmark study of metallic glasses by Hirata et al. [17], Hiraoka et al. applied PD to amorphous materials [18]. Another approach for network topology is conventional ring (closed-path) analysis, in which rings are enumerated by shortest-path algorithms, providing ring size distributions in the structures of amorphous materials [18, 22]. It is worth noting that the atomic geometry information detected by ring analysis differs from that obtained by PH because the latter identifies voids without searching for atomic bonds. PDs enable elucidating not only the size of voids but also their shapes by evaluating the distance between birth and death scales, even though they are insensitive to chemical bonds. Recently, Onodera et al. reported structural orderings related to ring transformation in densified silica glass by independent analysis of PD and conventional ring-size analyses to take advantage of both approaches [23].

Here, we propose extensions from conventional ring analysis for structural order analysis: (1) quantitative characterization of ring shapes and (2) a spatial correlation function around rings to visualize local structure orders. The advantage of our approach is that it enables a direct combination of the size, shape, and spatial distribution of rings based on both atomic configuration and network topology. The direct approach is effective for deeply understanding intermediate-range structure orders because crucial topological structures formed by chemical bonds are embedded in the atomic configuration. Our methods are applied to analyze amorphous and crystalline silica for a deeper understanding of the structural orders around rings.

II. STRUCTURE ORDER ANALYSIS BASED ON RINGS

To reveal the contribution of the network topological order to the intermediate-range structure order, we propose two analysis methods based on rings: (1) ring shape characterization (Fig. 1) and (2) spatial correlation analysis around rings (Fig. 2).

A. Ring shape characterization

Our first proposed procedure characterizes the shape of a ring through computation of the eigenvector and eigenvalue of the covariance matrix of atomic coordinates (so-called, the point cloud) in the ring, as shown in Fig. a. This procedure first selects a ring enumerated from a network consisting of atoms and chemical bonds (Fig. 1(a)) and then translates atomic coordinates to match the origin with the ring’s center (Fig. 1(b)). Next, the eigenvectors and eigenvalues of the coordinates’ covariance matrix are computed (Fig. 1(c)). The first eigenvector is computed as the direction in which the variance of the point cloud is the largest. Under the restriction that the first and second eigenvectors are orthogonal with each other, the second eigenvector is computed by maximizing the variance of the point cloud in the vector. The third eigenvector is computed as the vector orthogonal with the first and second eigenvectors. As their eigenvalues are proportional to the variances along with these vectors, they can be used to measure the ring shape. This approach uses eigenvectors, which are second-order information. It is equivalent to approximating a ring by an ellipsoid, in which the first and second eigenvectors are directions to the major and minor axes of the ellipse approximating the ring, whereas the third eigenvector is the normal vector of the plane of the ellipse. We propose two shape indicators for a ring: roundness and roughness, as illustrated in Fig. 1(d), both of which are computed from eigenvalues. Assuming a square root of the three eigenvalues, $s_1$, $s_2$, and $s_3$, the first indicator “roundness”, which is defined as $r_c = s_2/s_1$, evaluates how close the ring is to a perfect circle. The roundness value for a perfect circle is 1. The second indicator “roughness”, defined as $r_l = s_3/\sqrt{s_1 \cdot s_2}$, evaluates the flatness of the ring. Examples in Fig. 1(e) demonstrate that roundness and roughness appropriately evaluate these ring shapes, which cannot be evaluated by the conventional ring size nor PH analyses.
From 3rd vector
From 2nd vector

Ring size 6 6 8 9 11
Roundness 0.82 1.00 0.98 0.50 0.95
Roughness 0.24 0.19 0.15 0.28 0.42

FIG. 1. Computation procedure of ring shape characterizations. (a) Rings observed from top and side views. (b) Point cloud of atoms in the ring. (c) The 1st, 2nd, and 3rd eigenvectors and eigenvalues of the covariance matrix of the point cloud. (d) Ring shape measurements: roundness and roughness, both of which are computed from eigenvalues. (e) Examples of ring characterizations by ring size, roundness, and roughness for various rings along with observations from the direction of the 2nd and 3rd eigenvectors.

B. Spatial correlation function around rings

The second proposed procedure (Fig. 2) is used to visualize how the symmetry and/or anisotropy of a ring significantly contribute to local structural orderings in the intermediate-range scale. In contrast, the bond lengths and bond angles offer limited information in the case of amorphous materials. First, our procedure enumerates all the rings (Fig. 2(a)) and then computes the eigenvectors and eigenvalues for each, similarly to the ring shape characterization (Fig. 2(b)). Next, it aligns the origin, x-, y-, and z-axes in the new coordination system of the spatial correlation function by the ring center, major axis (the first eigenvector), minor axis (the second eigenvector), and normal vector (the third eigenvector) of a ring, respectively (Fig. 2(c)). For each Si and O atom, a histogram of spatial atom counts is computed by summing the spatial histogram of the atom over all enumerated rings (Fig. 2(d)). The spatial correlation functions for Si and O atoms around the rings are finally obtained by normalizing the atom counts in these histograms by $d_w^3 N_{\text{rings}} N_{\text{atoms}} V_{\text{box}}$, where $V_{\text{box}}$ is the volume of the simulation box, $N_{\text{rings}}$ is the number of enumerated rings, $N_{\text{atoms}}$ is the number of Si or O atoms included in the structure model, and $d_w$ is the bin width of the histogram. Normalization is necessary to compare struc-
III. ANALYSIS OF AMORPHOUS AND CRYSTALLINE SILICA

A. Structure models

In this study, we focus on amorphous and crystalline materials with corner-sharing tetrahedral motifs, a structural model of amorphous silica (α-SiO$_2$), along with those of five crystalline polymorphs of silica: α-tridymite 25, α-cristobalite 26, β-cristobalite 27, α-quartz 28, and coesite 29 (see Appendix A for data IDs and structure statistics).

We generated a large-scale structure model of α-SiO$_2$ by classical molecular dynamics (MD) simulation of a melt-quenching procedure, followed by refinement using the reverse Monte Carlo (RMC) 30 technique to reproduce XRD and ND data. Here, the side length of the simulation box for the model was assumed to be approximately 100 Å to ensure accurate statistics and suppress artifacts caused by the periodic boundary condition (see Appendix B for the detailed procedure). Hereafter, we refer to the generated structure as the MD-RMC model.

The X-ray and neutron total structure factors, $S(q)$, of the MD-RMC model showed good agreement with the experimental data. The coordination numbers around Si and O atoms, of over 99 % in the first coordination distance of the generated model, are four and two, respectively. It is confirmed that a well-known network structure, which consists of SiO$_4$ tetrahedral, sharing O atoms at the corner for SiO$_2$ ($N_{Si-O} = 4$, $N_{O-Si} = 2$), is formed in our MD–RMC model. The detailed structural statistics of α-SiO$_2$ are summarized in Appendix A.

B. Ring shape characterizations

Among various well-known ring definitions, such as the Guttman ring 18, King ring 20, and primitive ring...
FIG. 4. Isomorphic primitive rings in crystalline SiO$_2$: $\beta$-cristobalite, $\alpha$-cristobalite, $\alpha$-tridymite, $\alpha$-quartz, and coesite.

[21, 22], we selected the latter for our investigations. The primitive ring is defined as a closed loop whose all node pairs have the shortest path only along the loop. In other words, no node pair in a primitive ring has shorter paths in the external ring. Primitive rings are, therefore, essential components in a network structure forming amorphous material. The primitive criterion enumerates larger rings compared to Guttman's and King's criteria. As a first step, our analysis exhaustively enumerates rings in each network of the structural models using our in-house Python package, which is based on the shortest path algorithms described in Appendix C. Fig. 3(a) shows distributions of ring sizes, i.e. the numbers of Si atoms in a ring, in amorphous and crystalline materials. Among the crystalline materials, $\beta$- and $\alpha$-cristobalite and $\alpha$-tridymite are topologically ordered because they have only six-fold rings. In contrast, $\alpha$-quartz and coesite have rings of different sizes. Note that the ring size of coesite is widely distributed, as in the amorphous material shown in the bottom panel, indicating that the structure of coesite is topologically disordered owing to its high density. The ring size of $\alpha$-SiO$_2$ is also widely distributed, with the peak of the ring size distribution located at approximately six or seven, which is close to those of $\beta$- and $\alpha$-cristobalite and $\alpha$-tridymite.

For these structural models, we applied our proposed ring-shape characterizations, as summarized in Fig. 1. Figures 3(b) - (c) show our proposed indicators of ring shape, i.e. roundness and roughness, in crystalline and amorphous silica materials. It was found that $\beta$-cristobalite has only six-fold rings with the largest roundness and smallest roughness compared to the other crystals. Thus, the symmetry of the rings in $\beta$-cristobalite is the highest among crystalline materials. In contrast, $\alpha$-cristobalite is less symmetric, although its symmetry is higher than that of $\alpha$-quartz and coesite. The latter exhibited the lowest symmetry, which is in line with the results of persistent homology analysis [9, 23]. The order of roughness shows an opposite behavior to roundness, suggesting that the roughness indicator also reflects the symmetries of the rings.

We emphasize that a set of three eigenvalues of a ring can be used as an indicator of the ring's shape. It is similarly worth noting that enumerating isomorphic rings is also useful for crystalline materials because these values are identical if the ring shapes are identical. The isomorphic rings identified in crystalline SiO$_2$ and their shape characterizations are summarized in Fig. 4 and Table I.

FIG. 5. Distribution of ring characteristic indicators (roundness and roughness) of amorphous and crystalline SiO$_2$.

| Name          | ID  | Ring size | Roundness | Roughness |
|---------------|-----|-----------|-----------|-----------|
| $\beta$-cristobalite | A6-1 | 6         | 1.00      | 0.19      |
| $\alpha$-cristobalite | B6-1 | 6         | 0.82      | 0.24      |
| $\alpha$-tridymite | C6-1 | 6         | 0.99      | 0.20      |
|               | C6-2 | 6         | 0.91      | 0.29      |
|               | C6-3 | 6         | 0.85      | 0.29      |
| $\alpha$-quartz | D6-1 | 6         | 0.86      | 0.55      |
|               | D8-1 | 8         | 0.77      | 0.13      |
|               | D8-2 | 8         | 0.76      | 0.22      |
|               | D8-3 | 8         | 0.65      | 0.44      |
|               | D8-4 | 8         | 0.55      | 0.59      |
| coesite       | E4-1 | 4         | 0.92      | 0.19      |
|               | E4-2 | 4         | 0.89      | 0.16      |
|               | E6-1 | 6         | 0.75      | 0.24      |
|               | E8-1 | 8         | 0.98      | 0.15      |
|               | E9-1 | 9         | 0.50      | 0.28      |
|               | E9-2 | 9         | 0.45      | 0.44      |
|               | E10-1| 10        | 0.58      | 0.10      |
|               | E11-1| 11        | 0.95      | 0.42      |
|               | E11-2| 11        | 0.84      | 0.43      |
|               | E12-1| 12        | 0.71      | 0.22      |
|               | E12-2| 12        | 0.71      | 0.29      |
Both $\beta$- and $\alpha$-cristobalite have only one isomorphic ring, whereas $\alpha$-tridymite, $\alpha$-quartz, and coesite have three, five, and eleven isomorphic rings, respectively. This indicates that the number of isomorphic rings in a crystalline material is a measure of its symmetry. It consequently reveals that $\beta$-cristobalite and coesite exhibit the highest and lowest symmetries, respectively.

The bottom panels in Fig. 3(b)-(c) show the computed results for $\alpha$-SiO$_2$. Similar to the ring size distribution, roundness and roughness are broadly distributed. This indicates that various rings are included in $\alpha$-SiO$_2$. The ring-shape evaluation with two-dimensional distributions of both measures is shown in Fig. 5. Characterized results for crystalline materials are represented by symbols due to the limited number of isomorphic rings. The figure shows that the peak positions of the roundness-roughness distributions in $\alpha$-SiO$_2$ are close to ring B6-1 in $\alpha$-cristobalite and C6-3 in $\alpha$-tridymite. This points towards the resemblance between the major rings in $\alpha$-SiO$_2$ and those in $\alpha$-cristobalite and $\alpha$-tridymite. The broad distribution of the shape indicators in $\alpha$-SiO$_2$, covering those of all isomorphic rings in crystalline materials, highly suggests that the distribution in $\alpha$-SiO$_2$ is a mixture of isomorphic rings in crystalline materials and their variants.

C. Spatial correlation functions around rings

The influence of ring symmetries on the local structure ordering was evaluated using our proposed spatial correlation function. Fig. 6 shows three-dimensional surfaces of large spatial correlations for crystalline and amorphous models, in which the surfaces of Si and O atoms are colored blue and red, respectively. As can be seen in Fig. 6 (a), correlations in $\beta$-cristobalite have parallel planes along the $z$-axis and concentric circles on the $x$-$y$ plane, suggesting that these atomic configurations are highly oriented and are surprisingly identical. These directional orderings are due to only one isomorphic ring (six-fold ring) with large roundness and small roughness. In contrast, the correlation function for $\alpha$-tridymite (Fig. 6 (b)) seems to be noisy compared to that of $\beta$-cristobalite (Fig. 6 (a)). This is because $\alpha$-tridymite has three isomorphic rings, of which the first ring (C6-1, see Fig. 4) with large roundness and small roughness is symmetric whereas the other two are less symmetric. We notice that coesite (Fig. 6 (e)) is the most disordered due to the variety of isomorphic rings, most of which are not symmetric. Another visualization of the spatial correlation functions by cross-section mapping is presented in Appendix 14. We computed the correlation function for each isomorphic ring as summarized in Appendix 14. This demonstrates that rings with small roughness form planes parallel to the center ring (along $z$-axis), which seem to be pseudo-Bragg planes from the point of view.
of diffraction. In contrast, rings with large roughness disrupt their planes. This indicates that flat and symmetric rings are essential components for structural ordering, whereas non-symmetric rings disrupt structural ordering. We also emphasize that the direction along the $z$-axis (the normal vector) is essential for creating pseudo-Bragg planes. This also means that anisotropic structure orders exist around the rings in crystalline SiO$_2$.

Fig. 7(f) shows the spatial correlation function for the $\alpha$-SiO$_2$ model. These diagrams exhibit a ring around the center, which is the average of all primitive rings. The $x-y$ plane also shows that the averaged ring shape in $\alpha$-SiO$_2$ is not a perfect circle, but rather an eclipse, which is consistent with the results of the roundness analysis in

![Fig. 7. Comparison of the spatial correlations cross-section mappings of Si atoms from the $x$, $y$, and $z$-axis directions in $\alpha$-SiO$_2$ with those in a crystalline SiO$_2$. The blue density indicates a spatial correlation of Si atom in $\alpha$-SiO$_2$, whereas the green region indicates spatial positions where the correlation of Si atom is larger than the threshold in a crystalline material of (a) $\beta$-cristobalite, (b) $\alpha$-cristobalite, (c) $\alpha$-tridymite, (d) $\alpha$-quartz, and (e) coesite. (f) Colorbar indicating the spatial correlation of $\alpha$-SiO$_2$. The threshold for crystalline SiO$_2$ is 2.0.

![Fig. 8. Comparison of spatial correlations cross-section mappings of O atoms from the $x$, $y$, and $z$-axis directions in $\alpha$-SiO$_2$ with those in a crystalline SiO$_2$. The red density indicates a spatial correlation of the O atom in $\alpha$-SiO$_2$ whereas the green region indicates spatial positions where the correlation of the O atom is larger than the threshold in a crystalline material of (a) $\beta$-cristobalite, (b) $\alpha$-cristobalite, (c) $\alpha$-tridymite, (d) $\alpha$-quartz, and (e) coesite. (f) Colorbar indicating the spatial correlation of $\alpha$-SiO$_2$. The threshold for crystalline SiO$_2$ is 2.0.]
This is also shown in the cross-sectional mapping in Appendix D. As can be seen in these figures, the center ring is surrounded by multiple shells in the amorphous model. The shells of the O and Si atoms are alternately located from the center owing to the O-Si–O–Si linkage. In addition, these figures show planes parallel to the center ring in the upper and lower parts of the ring along the \( z \)-axis. They also show partially parallel planes along the \( y \)-axis, which is parallel to the \( x \)-axis (the major axis of the rings), as shown in the middle panel of Fig. 6. However, they do not exhibit such planes along the \( x \)-axis. It can be concluded that amorphous SiO\(_2\) has anisotropic structural order around the rings owing to the anisotropic shapes of the rings. In particular, the normal vector (i.e., orthogonal to the ring’s plane) of a ring is the essential direction, contributing to the formation of intermediate-range structural orders exhibited in the diffraction data.

We further investigated the consistency between the spatial correlation functions of the amorphous and crystalline models. Fig. 8 shows correlation functions of the O atom, in which spatial correlations of the amorphous model and those of crystalline models are colored red and green, respectively. The rightmost diagrams (\( x-y \) plane) show that the averaged ring of the amorphous model is similar to that of \( \alpha \)-cristobalite (Fig. 7(b) and Fig. 8(b)), which is consistent with the roundness of rings in Fig. 8(b). The averaged ring shape of \( \alpha \)-tridymite (Fig. 7(c) and Fig. 8(c)) is rather similar, whereas that of \( \beta \)-cristobalite (Fig. 7(a) and Fig. 8(a)) is different, both of which are consistent with these roundness. The upper and lower planes made by the large correlation regions for \( \alpha \)-SiO\(_2\), which are pseudo-Bragg planes, are also consistent with those for \( \alpha \)-cristobalite, \( \alpha \)-tridymite, and \( \beta \)-cristobalite. The correlation functions for \( \alpha \)-quartz (Fig. 7(d) and Fig. 8(d)) and coesite (Fig. 7(e) and Fig. 8(e)) also have regions partly similar to those for \( \alpha \)-SiO\(_2\), although they look globally rather different. The anisotropic nature of the \( \alpha \)-SiO\(_2\) amorphous model is consistent with the analysis results for crystalline SiO\(_2\), especially with \( \beta \)- and \( \alpha \)-cristobalite and \( \alpha \)-tridymite.

### D. Comparing amorphous models with various structure orderings

A series of analyses revealed an anisotropic local structure order in the amorphous silica (\( \alpha \)-SiO\(_2\)) model, whereas isotropic halo rings were observed in reciprocal space by macroscopic diffraction data. A transition from anisotropic to isotropic order seems to prevail in the change from microscopic to macroscopic viewpoints.

![Cross-section mappings of spatial correlations of \( \alpha \)-SiO\(_2\) models](image)

**Fig. 9.** Cross-section mappings of spatial correlations of \( \alpha \)-SiO\(_2\) models: (a) Rand-Coord, (b) Rand-Tetra, (c) Rand-RMC and (d) MD-RMC. (e) Color indicator, a region with blue/red color indicates a large density of Si/O atoms. The cross-section thickness \( t \) is 1 \( \AA \). Green arrows indicate pseudo-Bragg planes, related to the intermediate-range structure order.

We would like to stress that the anisotropic local structure originates from rings, which is an essential topological motif in network-forming materials. Here, we discuss the influence of the anisotropic local structural order on the degree of structural order in amorphous structures through the comparison of some additional amorphous models.

For further validation of our analyses, we generated three additional amorphous structure models from a random configuration. The same number of atoms and the same size of the simulation box were used for these additional models. The first model (so-called, Rand-Coord) was generated from a random configuration followed by a hard-sphere Monte Carlo (HSMC) simulation under two
The third model (so-called, Rand-RMC) used the Rand-Tetra model as the initial atomic configuration, which was then generated by the RMC simulation to reproduce the X-ray and neutron S(\(q\)) data. Structural statistics, such as structure factors, coordination numbers, bond angles, and ring characters are summarized in Appendix E. This structured summary demonstrates that the randomly initialized models (i.e., Rand-Coord, Rand-Tetra, and Rand-RMC) are more disordered compared to the MD-RMC model. Among the structure factors, only Rand-RMC and MD-RMC exhibit FSDP because RMC fits the structure factors. Overall, the structural orders of these amorphous models are quite different, although all models form a network of chemical bonds.

Fig. 9 shows the spatial correlation functions of (a) Rand-Coord, (b) Rand-Tetra, (c) Rand-RMC, and (d) MD-RMC. It shows that all models exhibit anisotropic structural orders around the rings. This indicates that the anisotropy is related only to the network formation of amorphous materials. A clearer shell structure was observed in the MD-RMC model compared to the other models. This is due to the ring size distribution of MD-RMC, which is concentrated at six (see Appendix E for details), whereas the distributions of the other three models are broadly distributed. Thus, the correlation functions computed using only six-fold rings, shown in Fig. 10, present more clear shell structures in all models. The correlation functions for Rand-RMC and MD-RMC in Figs. 9 (c)-(d) and Figs. 10 (c)-(d) exhibit parallel planes above and below rings along the z-axis indicated by green arrows. This relates to the intermediate-range structure orders exhibited by FSDP in diffraction experiments. These figures demonstrate that the anisotropy of structural orders around rings is essential for building intermediate-range structural orders.

IV. CONCLUSIONS

In the present study, we proposed two analysis methods for the structural orders of rings and those around rings, based on ring shapes in network-forming materials. Our proposed analysis of crystalline and amorphous SiO2 first demonstrated that the distribution of ring shape characteristics is a strong tool for analyzing amorphous models of SiO2. The roundness-roughness distribution revealed that the major rings in amorphous SiO2 are similar to those in two crystals, α-cristobalite and α-tridymite, whose mass densities are similar to those of amorphous SiO2. It was also revealed that the rings in α-quartz and coesite are included as minor rings in amorphous SiO2. This indicates that various rings found in crystalline polymorphs are necessary to form bulk amorphous materials [31]. Furthermore, the spatial correlation analysis revealed that the anisotropic nature of structure orders was found in both crystalline SiO2 with different polymorphisms and amorphous SiO2. Moreover, the analysis revealed pseudo-Bragg planes parallel to the rings in amorphous SiO2, which are consistent with restrictions: the closest atom–atom distance and the coordination number. The closest distance restriction can avoid unreasonable spikes in the partial pair distribution functions. The coordination number restriction forces Si atoms to coordinate to four O atoms, whereas O atoms are coordinated to two Si atoms within a Si–O cutoff distance of 1.90 Å. The second structure model (so-called, Rand-Tetra) used the aforementioned Rand-Coord model as the initial atomic configuration and was then generated by implementing HSMD with restrictions on the coordination numbers and the O–Si–O bond angle distribution to create a network structure, which consists of regular SiO4 tetrahedra sharing O atoms at the corner.
those for three crystals: α-cristobalite, α-tridymite, and β-cristobalite. Our findings showed that rings with low roughness tend to construct planes parallel to the central rings, as revealed by the ring shape characterization of isomorphic rings on crystalline materials. To validate the applicability of our approaches, three SiO₂ structure models with different ordering degrees were prepared. The corresponding anisotropic local environments, as described above, were confirmed in all models. Although the actual degree of order for amorphous SiO₂ is still arbitrary, even if it satisfies the experimental structure factors, it is fair to say that amorphous SiO₂ has anisotropic local structures based on our verification. We assume that the observed pseudo-Bragg planes, which presumably generate the first sharp diffraction peak, correlate with the intermediate-range structural orders in amorphous SiO₂.

Our proposed approach is demonstrated useful for analyzing generic network-forming materials, not limited to SiO₂. Analyzing other network-forming materials using our methods and a comprehensive comparison of these results should provide further information to understand intermediate-range structural orders in network-forming materials.

Appendix A: Structure statistics of crystalline and amorphous model

The densities and data IDs of the crystalline SiO₂ models are summarized in Tables [I] and [II]. In all crystalline models, the coordination numbers of all Si atoms are four, while those of all O atoms are two. On the other hand, in the amorphous MD-RMC model, the coordination number of 99.8 % of Si atoms is four, whereas that of 99.9 % of O atoms is two.

Fig. [I] shows bond angle distributions of (a) Si–O–Si, (b) O–Si–O, and (c) Si–Si–Si. These figures suggest that the angles of the O–Si–O bonds in all crystalline and amorphous models are concentrated at approximately 109.47° (= cos⁻¹(−1/3)), indicating that the SiΟ₄ tetrahedra in all models are nearly equal to those of the regular tetrahedron. On the other hand, the Si–O–Si bond angles in low-density structures, such as β-cristobalite and α-tridymite, include a 180° angle, which is nearly linear. Those in α-SiΟ₂, in which the mass density is close to these two crystals, also have a large number of such bonds, as indicated by the left-tailed distribution (having a larger density than the peak position). This suggests that α-SiΟ₂ has a structure similar to that of β-cristobalite and α-tridymite. The distributions of Si–O–Si shifted to smaller values with increasing mass densities in the crystalline models. Note that the coesite, with the highest density among crystalline SiΟ₂, has Si–O–Si bonds with an angle of 180°, whereas α-cristobalite and α-quartz do not include such a bond. In contrast, the variances in the angles of the Si–Si–Si bond become large with increasing mass densities for crystalline models. It is inversely proportional to the structural order because the variance inversely reflects the symmetry of the SiΟ₄ tetrahedra.

The X-ray and neutron total structure factors S(q) of α-SiΟ₂ are shown in Figs. [II](a)-(b) together with the results of MD–RMC model. It is confirmed that the agreement between the MD and RMC model and the experimental data is excellent. The partial structural factors are shown in Figs. [II](c)-(e). The coordination numbers around Si and O atoms, of over 99 % in the first coordination distance of the generated MD-RMC model, are four and two, respectively. It was confirmed that the MD-RMC model forms a network structure, sharing O atoms at the corners of the SiΟ₄ tetrahedra. The bond angle distributions of the crystalline and amorphous models of MD-RMC are shown in the bottom panels of Fig. [II]. The distribution of O–Si–O for α-SiΟ₂ (MD-RMC) has a peak around 109.47° (= cos⁻¹(−1/3)), indicating that the SiΟ₄ tetrahedra are nearly regular. Because the distribution of Si–Si–Si also has a peak at approximately 109.47, the SiSi₄ tetrahedra are also close to regular.

Appendix B: Generation of a structure model of amorphous silica

Structural models of amorphous silica were generated by a melt quenching procedure in classical molecular dynamics (MD) simulation using the LAMMPS code followed by reverse Monte Carlo (RMC) techniques to fit the diffraction measurements of the synthesized materials. MD simulations and RMC were implemented using LAMMPS code [22] and RMC++ code [33], respectively. In the MD simulation of amorphous silica (α-SiΟ₂), the simulation box was set to a cube with a length for each axis of 100 Å. The density of this system is 2.2 g/cm³. Thus, it had 66,156 atoms (22,052 Si atoms and 44,104 O atoms) within the NVT ensemble. A time step of 1 fs was used in the Verlet algorithm. The interactions were described by pair potentials with short-range Born-Mayer repulsive and long-range Coulomb terms:

\[ \phi_{ij} = B_{ij} \exp \left( -\frac{r}{\rho_{ij}} \right) + \frac{e^2 Z_i Z_j}{4 \pi \varepsilon_0 r}, \] (B1)

where \( r \) is the interatomic distance between the atoms \( i \) and \( j \). \( B_{ij} \) and \( \rho_{ij} \) define the magnitude (10⁻¹⁶ J) and softness (Å) of the Born-Mayer term, respectively. \( Z_i \) is the effective charge on atom \( i \) (\( Z_{O2} = 2.4 \) and \( Z_{Si} = -1.2 \)), \( e \) is the elementary charge, and \( \varepsilon_0 \) is the permittivity of a vacuum. The coefficients used in the simulation \( B_{ij} = 21.39 \times 10^{-16} \) and \( \rho_{ij} = 0.174 \) Å for an atom pair of Si and O, and \( B_{ij} = 0.6246 \times 10^{-16} \) and \( \rho_{ij} = 0.362 \) Å for an atom pair of O atoms. The interactions between the Si atoms were ignored. The atomic configuration was initialized at random, and the system was equilibrated at 4,000 K for 100,000 steps. Then, it was cooled to 300 K for 5,000,000 steps and annealed at 300 K for 100,000 steps. The generated model was refined via RMC modeling using XRD and ND measurements. We call this the
TABLE II. Atom density of crystalline SiO$_2$. The abbreviations of database names are COD (Crystallography Open Database), AMCSD (American Mineralogist Crystal Structure Database), and ICSD (Inorganic Crystal Structure Database).

| Name           | Mass Density (g/cm$^3$) | Number density (#atoms/Å$^3$) | Database and ID   |
|----------------|-------------------------|-------------------------------|-------------------|
| β-cristobalite | 2.21                    | 0.0665                        | AMCSD #0017665    |
| α-cristobalite | 2.33                    | 0.0701                        | COD #9009686      |
| α-tridymite    | 2.21                    | 0.0665                        | ICSD #40895       |
| α-quartz       | 2.65                    | 0.0796                        | COD #9005017      |
| coesite        | 2.92                    | 0.0878                        | COD #9000803      |

TABLE III. Statistics on atoms in α-SiO$_2$ models (MD-RMC, Rand-Coord, Rand-Tetra and Rand-RMC).

| Name | Mass density (g/cm$^3$) | Number density (#atoms/Å$^3$) | The length of simulation box (Å) | The number of Si atoms | The number of O atoms |
|------|-------------------------|-------------------------------|---------------------------------|------------------------|-----------------------|
| α-SiO$_2$ | 2.20                      | 0.0662                         | 100.00                          | 22,052                 | 44,104                |

FIG. 11. Triplet correlations evaluated by bond angle distribution of (a) O–Si–O, (b) Si–O–Si, and (c) Si–Si–Si in crystalline and amorphous SiO$_2$.

Appendix C: Ring enumeration

Under the assumption that the first coordination distance is less than 2.0 Å for Si–O, a network for each structure model of SiO$_2$ was generated. A primitive ring is defined as a ring that cannot be decomposed into two smaller rings [21, 22]. This is equivalent to the condition that no shorter path exists between nodes in the ring that goes through any nodes in the external ring. Thus, primitive rings can be efficiently enumerated based on shortest path algorithms. The enumeration algorithm first computes the distances of the node pairs in the network using the shortest path algorithm. Next, node pairs whose distances in the network are less than the threshold, which should be set to half of the maximum size of the primitive rings, are enumerated. Subsequently, all the shortest paths between the enumerated node pairs are enumerated. Ring candidates are generated by connecting two different shortest paths that do not share internal nodes. After inspecting the primitive criterion for the generated candidates and removing candidates that did not satisfy the criterion, the ring enumeration algorithm was terminated. The ring enumerations in this study were implemented using our in-house Python package, which will be made available as an open-source package after this manuscript has been published.
in the upper and lower parts of the ring along the 
The figure also shows planes parallel to the central ring 
tures, where the O and Si atoms are alternately located.
hibit a ring around the center. The shape is not a perfect 
circle, which is the same as in the roundness/roughness 
experiment data and simulated structure model of MD-RMC, 
respectively. (c) Partial structure factors, $S_{ij}(q)$, for MD-
RMC model.

**Appendix D: Cross-section mappings of spatial correlation functions**

To visualize the distribution of the spatial correlation functions of the crystalline and amorphous SiO$_2$ models, corresponding cross-section mappings at approximately $x = 0$, $y = 0$, or $z = 0$ were computed by integrating the correlation function over the cross-section thickness $t$. The cross-sectional thickness $t$ was set to 2 Å for the crystalline models and 1 Å for the amorphous model. The computed maps are presented in Fig. 12. In these diagrams, the blue and red regions exhibit high densities of Si and O atoms, respectively, as indicated by the color indicator (Fig. 12g). These mappings also show that $\beta$-, $\alpha$-cristobalite, and $\alpha$-tridymite have parallel planes, whereas $\alpha$-quartz and coesite appear to be disordered. Cross-sectional mappings for the amorphous model $a$-SiO$_2$ are shown in Fig. 12f. The mappings exhibit a ring around the center. The shape is not a perfect circle, which is the same as in the roundness/roughness analysis. The mappings also exhibit multiple shell structures, where the O and Si atoms are alternately located. The figure also shows planes parallel to the central ring in the upper and lower parts of the ring along the z-axis.

To understand the relationship between the ring shapes and local structural orders, we computed the correlation function for each isomorphic ring in crystalline SiO$_2$. The computed cross-sectional mappings of the correlation functions are shown in Fig. 12. This demon-
strates that rings with low roughness, such as C6-1, D8-2, and E4-1, make planes parallel to the center ring (along z-axis), which seem to be pseudo-Bragg planes from the point of view of diffraction. This suggests that the symmetry of the rings and diffraction peaks is highly relevant. For example, the correlation function of ring A6-1 in $\beta$-cristobalite, whose roundness and roughness are 1.00 and 0.19, respectively, is highly ordered. Similarly, the correlation function of ring C6-1 in $\alpha$-tridymite, whose roundness and roughness are 0.99 and 0.20, respectively, is also highly ordered. These results indicate that flat and symmetric rings are essential components for structural ordering, whereas non-symmetric rings disrupt structural ordering. It is worth mentioning that $\alpha$-tridymite exhibits both ordered and less-ordered structures, where they can be separated by identifying isomorphic rings.

**Appendix E: Structure statistics of amorphous models with different structural restrictions**

Fig. 15 shows structure factors by (a) X-ray and (b) neutron diffraction and (c)-(e) partial structure factors of four amorphous models: Rand-Coord, Rand-Tetra, Rand-RMC, and MD-RMC. Fig. 15a)-(b) demonstrate that Rand-RMC and MD-RMC exhibit FSDP at around $q = 1.5$ Å$^{-1}$, which is not the case for Rand-Coord and Rand-Tetra. In Figs. 15c)-(e), partial structure factors of only MD-RMD model has sharp principal peaks (PPs) at around $q = 2.8$ Å$^{-1}$.

Figure 16 shows coordination number distributions of these four models. In random initialization models (i.e., Rand-Coord, Rand-Tetra, and Rand-RMC), the coordination numbers of only approximately 95% of Si atoms are four, while those of approximately 97% of O atoms are two. These percentages were smaller than those of the MD-RMC model. Fig. 17 and Fig. 18 show bond angle distributions, ring characters, respectively. These figures show that the random initialization models are more broadly distributed than those of the MD-RMC model. In particular, the distributions of the ring sizes of the random initialization models are quite different from those of the MD-RMC model. Overall, these structural statistics demonstrate that the MD-RMC model is the most structurally ordered among the models.

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indicator, a region with blue/red color indicates a large density of Si/O atoms. The cross-section thickness $\beta$-cristobalite, (b) FIG. 13. Cross-section mappings of spatial correlation functions from direction of $x, y, z$-axis for crystalline SiO$_2$: (a) $\beta$-cristobalite, (b) $\alpha$-cristobalite, (c) $\alpha$-tridymite, (d) $\alpha$-quartz, (e) coesite, and amorphous: (f) a-SiO$_2$ (MD-RMC). (g) Color indicator, a region with blue/red color indicates a large density of Si/O atoms. The cross-section thickness $t$ was set to 2 Å for crystalline and 1 Å for amorphous materials.

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FIG. 14. Cross-section mappings of spatial correlation around isomorphic rings in crystalline SiO$_2$. IDs of isomorphic rings are identical to Table I.
FIG. 15. Quantum beam diffraction data for amorphous materials. Total structure factors, $S(q)$, by (a) X-ray and (b) neutron for α-SiO$_2$ models: Rand-Coord, Rand-Tetra, Rand-RMC and MD-RMC. Partial structure factors, $S_{ij}(q)$ of (c) Si-Si atom pair, (d) Si-O atom pair, and (e) O-O atom pair.
FIG. 16. Distribution of coordination numbers of (a) Si atom and (b) O atom in $\alpha$-SiO$_2$ models: Rand-Coord, Rand-Tetra, Rand-RMC, and MD-RMC.

FIG. 17. Triplet correlations evaluated by bond angle distribution of O–Si–O, Si–O–Si and Si–Si–Si in $\alpha$-SiO$_2$ models: Rand-Coord, Rand-Tetra, Rand-RMC, and MD-RMC.
FIG. 18. Ring characterizations of α-SiO$_2$ models: Rand-Coord, Rand-Tetra, Rand-RMC and MD-RMC. Relative counts of rings as a function of (a) ring size, (b) roundness, and (c) roughness.