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Atomistic and electronic structures of functional disordered materials revealed by a combination of quantum-beam measurements and computer simulations

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The advent of advanced quantum beam sources and instrumentation makes it feasible to use quantum-beam (synchrotron X-ray and neutron) techniques to investigate the structure of disordered materials in a quantitative manner. In particular, a combination of quantum-beam measurements and advanced simulation techniques allows us to study structures at both the atomistic and electronic levels. In this article, some of the recent work on solving the structure of functional disordered materials, which do not contain a glass former, are reviewed to discuss the relationship between structure and glass-forming ability as well as the relation between atomistic and electronic structures and functions. Furthermore, we consider the use of other quantum-beam-based techniques and the introduction of descriptors for disordered matter to reveal the ordering hidden in correlation functions.

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1. Introduction

The structure of glassy, liquid, and amorphous materials is still not well understood owing to their lack of distinct translational periodicity, which, in turn, is the result of disorder.^{1)–4)} In addition, multicomponent functional disordered materials make it complicated to understand the atomic structure and its relationship with functions, which is a key for the design of novel materials. A combination of synchrotron X-ray and neutron scattering is very powerful, because X-rays are sensitive to heavy elements while neutrons are important to probe light elements. In addition, advanced instrumentations at synchrotron X-ray and neutron sources cover scattering data in a wide momentum transfer Q [$= (4\pi/\lambda) \sin\theta$, where 2θ is the scattering angle and λ is the photon or neutron wavelength] range, yielding high real-space resolution (see section 2 for details). This is achieved by utilizing short wavelength (high-energy) photons and neutrons. Furthermore, a close link between quantum beam measurements and advanced computation allows us to reveal the structure of disordered materials at both the atomistic and electronic levels.^{5),6)} In particular, it is possible to reveal the structure beyond the nearest-neighbor correlation length, which has been hitherto challenging using a structure model, although careful inspections are required to assess the results of simulations because simulation models are not unique.

Here, we briefly describe the essential theory for a scattering experiment. Then the focus will be put on research on functional disordered materials, fast-phase-change materials,^{7)–11)} binary

oxide glasses^{12)–14)} synthesized by containerless processing,¹⁵⁾ and high-temperature oxide melts^{16),17)} at both the atomistic and electronic levels. In particular, materials that do not contain a glass former (i.e. when it is impossible to form a bulk glass by conventional methods), $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST), $\text{CaO-Al}_2\text{O}_3$, and ZrO_2 , are featured to discuss the relationship between structure and glass-forming ability (GFA), as well as the relationship between atomistic and electronic structures and functions in disordered materials. Moreover, we address future directions for probing the hidden order within disorder¹⁾ in correlation functions by using other quantum-beam-based techniques and the introduction of descriptors for disordered matter.

2. Scattering theory

In an X-ray or neutron scattering experiment on a disordered material containing n chemical species, structural information is contained in the total structure factor^{3)–5)}

$$S(Q) = 1 + \frac{1}{| \langle W(Q) \rangle |^2} \sum_{i=1}^n \sum_{j=1}^n c_i c_j w_i^*(Q) w_j(Q) [S_{ij}(Q) - 1] \quad (1)$$

where c_i is the atomic fraction of chemical species i ; $w_i(Q)$ is either a Q -dependent atomic form factor with dispersion terms in X-ray scattering or a Q -independent coherent scattering length in neutron scattering and is, in general, a complex number; $S_{ij}(Q)$ is the partial structure factor. $| \langle W(Q) \rangle |^2 = \sum_{i=1}^n \sum_{j=1}^n c_i c_j w_i^*(Q) w_j(Q)$. The superscripts X or N can be used to distinguish between the $S(Q)$ functions measured by X-ray and neutron scattering, respectively. The corresponding real-space information is contained in the total correlation function $T(r)$, which is obtained by the Fourier transform relation

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$$T(r) = 4\pi r \rho + \frac{2}{\pi} \int_{Q_{\min}}^{Q_{\max}} Q[S(Q) - 1] \sin(Qr) dQ \quad (2)$$

where r is a distance in real-space and ρ is the atomic number density. To obtain real-space information with sufficient resolution, it is necessary to measure $S(Q)$ up to the higher- Q region since a higher resolution in real space is achieved with a larger $Q_{\max}$.⁶⁾

3. Phase-change materials

Although data storage and distribution via the internet is becoming popular, DVD/Blu-ray (BD) systems are still indispensable media in our daily lives. Information is stored on a DVD/BD in the form of microscopic bits in a thin layer of a polycrystalline alloy (GST). The bits can have a disordered, amorphous structure (recorded) or an ordered, crystalline structure (erased). The phase change between the two phases lasts only tens of nanoseconds and is triggered by a laser pulse.¹⁸⁾ The combination of synchrotron radiation high-energy X-ray total scattering (HEXTS), element-specific anomalous X-ray scattering (AXS) measurements, and reverse Monte Carlo (RMC)/density function theory (DFT)-molecular dynamics (MD) simulations on amorphous GST has made it possible to determine the structures of both phases and allowed the establishment of a model to explain the rapid phase change and its high durability, particularly, the stability of the amorphous phase.

Figure 1(A) shows a comparison of the HEXTS total structure factors $S(Q)$ for crystalline (c -) GST and amorphous (a -) GST. $S(Q)$ for c -GST exhibits sharp Bragg peaks with a diffuse scattering pattern, while only the latter appears for a -GST. It was confirmed that $S(Q)$ for the RMC model (solid curve) is in good agreement with experimental data (open circles). The differential structure factors $\Delta S(Q)$ of a -GST for Sb and Te obtained from AXS measurements are shown in Fig. 1(B). As can be seen in the figure, there are distinct differences between the Sb- and Te-related data at $Q < 6 \text{ \AA}^{-1}$, suggesting that AXS data can distinguish Sb (atomic number of 51)-related correlation and Te (atomic number of 52)-related correlations beyond the nearest-neighbor distance. The differential structure factor of Sb, $\Delta S_{\text{Sb}}(Q)$, exhibits a first sharp diffraction peak (FSDP) at $Q \sim 1 \text{ \AA}^{-1}$. This peak is also observed in HEXTS data for both the amorphous and crystalline phases (owing to diffuse scattering present in c -GST), as shown in Fig. 1(A), although the FSDP is not prominent in comparison with that of a typical glass-forming materials such as SiO_2 glass (the origin of FSDP is discussed in section 5).⁶⁾

To investigate the atomic ordering formed by Ge–Te and Sb–Te bonds in detail, the connectivities of atoms were calculated for various maximum distances ($r_{\max}$) within which atomic pairs were considered to be connected. As can be seen in **Fig. 2(A)**, about 60% of the Ge–Te bonds form a continuous network when $r_{\max}$ is $3.2 \text{ \AA}$, while Sb–Te bonds do not form such a network when $r_{\max}$ is $3.2 \text{ \AA}$. This distance corresponds to the bond length determined by DFT-MD simulation.¹⁹⁾ The atomic configurations of Ge–Te and Sb–Te with bonds considered up to a distance of $3.2 \text{ \AA}$ are shown in Figs. 2(B) and 2(C), respectively. It is observed that Ge–Te bonds form a network, which stabilizes the amorphous phase, whereas Sb–Te bonds do not. Furthermore, Ge–Te bonds form large fractions of fourfold (highlighted in blue) and sixfold (highlighted in light blue) rings. On the other hand, about 70% of the Sb–Te pairs form a so-called pseudonetwork, as can be seen in Figs. 2(A) and 2(D), when $r_{\max}$ is $3.5 \text{ \AA}$ (in this case, the coordination numbers of Te around Ge ($N_{\text{Ge-Te}}$) and Sb ($N_{\text{Sb-Te}}$) are 4.1 and 3.1, respectively). In other words, the Sb–Te pseudonetwork becomes visible when the correlation distance is increased to $3.5 \text{ \AA}$, whereas such a feature cannot be observed for Ge–Te connectivity.

Figure 3 illustrates the phase-change process based on the structural features in a -GST found above. As highlighted in red in Fig. 3, Ge–Te bonds substantially contribute to the network comprising by fourfold rings. Therefore, Ge and Te can be recognized as network-forming elements that ensure the long-term stability of the amorphous phase at room temperature, although GeTe is not a network former. The Ge–Te network may remain in the crystalline phase, which explains the rapid crystallization. As highlighted in yellow in Fig. 3, the Sb–Te correlations beyond the nearest coordination distance can form a Sb–Te pseudonetwork. This unusual atomic ordering in terms of Sb–Te correlations is ascribed to the combination of two positively charged atoms (Ge, -0.22 electrons; Sb, 0.32 electrons; Te, 0.22 electrons¹⁹⁾) and allows the amorphous phase to form critical nuclei via the formation of Sb–Te bonds by small atomic displacements of antimony and tellurium atoms.

4. Atomistic and electronic structures in $\text{CaO-Al}_2\text{O}_3$ glasses

Understanding the atomistic and electronic structures and bonding upon glass formation is one of the most important topics in glass science. Glass formation in the $\text{CaO-Al}_2\text{O}_3$ system is an important phenomenon because it does not contain a typical

Fig. 1. Comparison between the experimental data (open circles) and the results of RMC modeling (solid curve). (A) X-ray total structure factors $S(Q)$ for c -GST and a -GST. (B) $\Delta S(Q)$ for a -GST measured at Sb and Te K absorption edges.¹¹⁾ $S(Q)$ for c -GST and $\Delta S(Q)$ for Sb are shifted upward by two units for clarity. X: Ge, Sb, Te.

Fig. 2. RMC-generated atomic configurations and connectivity of Ge-Te and Sb-Te in *a*-GST.¹¹⁾ (A) Connectivity of Ge-Te and Sb-Te for different values of $r_{\max}$. (B) Atomic configuration of Ge-Te (connectivity of Ge-Te for $r_{\max} = 3.2$ Å). (C) Atomic configuration of Sb-Te (connectivity of Sb-Te for $r_{\max} = 3.2$ Å). (D) Atomic configuration of Sb-Te (connectivity of Sb-Te for $r_{\max} = 3.5$ Å). The threefold, fourfold, fivefold, and sixfold rings are highlighted by red, blue, green, and light blue colors, respectively.

Fig. 3. Schematic drawing of phase-change process in *a*-GST. (A) highlights the Ge-Te network and (B) highlights the Sb-Te pseudonetwork. The sticks represent Ge-Te (red) and Sb-Te (yellow) bonds up to 3.2 Å and the dotted yellow lines show Sb-Te correlations of 3.2 to 3.5 Å in the amorphous phase.¹¹⁾

network former. The RMC modeling technique²⁰⁾ was combined with DFT to investigate the relationship between the atomistic/electronic structures and the GFA in the 50CaO–50Al₂O₃ (50CaO) and the 64CaO–36Al₂O₃ (64CaO) glasses. These compositions were chosen because the GFA of the 64CaO glass is much higher than that of the 50CaO glass, although composition difference is small. **Figures 4(A)–4(C)** show the neutron and X-ray total structure factors $S^{N,X}(Q)$ and the EXAFS $k^3\chi(k)$ data, respectively, of 50CaO glass and 64CaO glass as colored dots, together with the results of a DFT-RMC simulation as black curves. Difference for scattering data and for EXAFS data are small between the two compositions, implying that the short-range structure is similar in the compositions. Both the neutron and X-ray total structure factors show an FSDP at $Q \sim 2.2$ Å^{−1}, but the X-ray data show a sharper peak, because X-rays are more

sensitive to cation – cation correlation than neutrons. This manifests the ordering of the center of Al–O and Ca–O polyhedra. In addition, the height of the FSDP for the 64CaO glass is greater than that for the 50CaO glass in the X-ray data. The partial pair distribution functions $g_{ij}(r)$ of the above CaO–Al₂O₃ glasses obtained by DFT-RMC simulation show very small differences between the 50CaO glass and 64CaO glass. The Al–O coordination number $N_{\text{Al-O}}$ calculated up to 2.5 Å is 4.26 for the 50CaO glass and 4.14 for the 64CaO glass, and $N_{\text{Ca-O}}$ calculated up to 2.8 Å is 5.02 for the 50CaO glass and 4.92 for the 64CaO glass.

Figure 5 compares the distribution of –Al(Ca)–O–Al(Ca)–O–Al(Ca)– rings in the CaO–Al₂O₃ glasses. The 64CaO glass (high GFA) has a wide ring-size distribution, while the 50CaO glass (low GFA) has a very narrow ring size distribution. This trend can be understood in terms of the concept of topological order-disorder according to Gupta and Cooper.²¹⁾ This characteristic ring-size distribution, and particularly the formation of large rings, indicates the existence of a cage structure²²⁾ at the eutectic composition of 64CaO glass, which exhibits high viscosity in an undercooled liquid, yielding high GFA. Moreover, it is suggested that the topological disorder in the 64CaO glass is a signature of a stronger liquid²³⁾ than that of the 50CaO composition. This scenario can reasonably explain the high GFA of the 64CaO glass without the need for the presence of a traditional network former, as proposed in Zachariasen's original theory.²⁴⁾

Recently, the 'C12A7' (63.2CaO–36.8Al₂O₃):e[−] electride glass has been synthesized from a strongly reduced high-temperature melt by Kim et al.²²⁾ It is assumed that the removal of excess O atoms from AlO₅ and AlO₆ units in the C12A7 melt results in the formation of more extended cage structures in the electride version of the glass, which can host solvated electrons. To shed light on the formation of the electride glass, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) single-particle states of electrons were computed for the 64CaO glass by DFT calculations as illustrated in **Figs. 6(A)** and **6(B)**. The characters of the HOMO and LUMO states are considerably different: while the former is located across atoms and bonds [Fig. 6(A)], the latter is associated with a cavity (cage), forming a spin-paired state analogous to an F-center in a

Fig. 4. Neutron (A) and X-ray (B) total structure factors $S(Q)$ and EXAFS $k^3\chi(k)$ (C) data for 50CaO and 64CaO glasses. The EXAFS $k^3\chi(k)$ data were obtained by back Fourier transformation of the first correlation peak in [FT]. Circles, experimental data; curve, DFT-RMC model.¹⁴⁾

Fig. 5. Distribution of $-\text{Al}(\text{Ca})-\text{O}-\text{Al}(\text{Ca})-\text{O}-\text{Al}(\text{Ca})-$ rings in 50CaO and 64CaO glasses obtained by DFT-RMC simulation.¹⁴⁾

Fig. 6. Close-up visualizations of (A) HOMO and (B) LUMO single-particle electron states in the 64CaO glass. h_1 indicates the cavity (cage) occupied by the LUMO. Yellow and magenta represent the different signs of the wave-function nodes. (C) Simulation box and the electron spin density of the 64CaO glass with one oxygen removed at h_2 , i.e., with two additional electrons. (D) Cage structure around the spin density of one electron corresponding to the h_2 cavity [close-up of (C)]. Al, gray; Ca, green; O, red.¹⁴⁾

vacancy site of crystalline MgO [h_1 in Fig. 6(B)]. The computed HOMO–LUMO gap is 1.71 eV.

Since it is well known that DFT calculations at this level underestimate band gaps by approximately a factor of two, this

value is consistent with the typical insulating electronic behavior and transparent properties of the glass. Furthermore, our DFT-RMC model suggests that the first three cage-trapped LUMO states appear as impurity states below the onset of the conduction band. Following the idea of bipolaron states and conducting electride glass, we removed one oxygen atom from the h_2 site in Fig. 6(B), thus releasing two additional electrons from the Al/Ca cations in the system while keeping the total charge neutral, and then the structure was optimized for several spin configurations by DFT. In the spin-degenerate case, where there is no distinction concerning the “spin” of electrons, these electrons occupy a cavity vacated by the removed oxygen (marked as h_2), yielding a HOMO state similar to that of the LUMO state of the parent system. On the other hand, the removal of the spin degeneracy (triplet spin configuration) leads to a 0.97 eV more energetically favorable electronic configuration, where the two additional electrons have the same spin and are located in well-separated cavities [Fig. 6(C), h_1 and h_2]. This procedure was repeated for two, three, and four removed oxygen atoms (four, six, and eight additional electrons), and in all cases, the separated (solvated) electrons in individual cages were energetically more favorable than the F-center-like states (two electrons in one cavity). An example of the cage structure around a single electron (spin density) is presented in Fig. 6(D). These cases confirm that by removing oxygen from the standard stoichiometry, one can achieve local spin states in the 64CaO glass. Moreover, the gradual removal of O increases the number of impurity states within the electronic band gap, which leads to changes in conductivity due to a narrower band gap. Although this is a simulation of an early stage in the formation of electride glass, it is demonstrated that the combination of RMC modeling and DFT calculation is a powerful tool for understanding the structure of glass at both the atomistic and electronic levels.

5. Structure of non-glass forming oxide melt

The levitation method¹⁵⁾ allows enhanced glass formation owing to the elimination of extrinsic heterogeneous nucleation. It also enables experiments on high-temperature liquids and deeply undercooled liquids without contamination effects from containers. Furthermore, the use of levitation technique can improve the quality of X-ray and neutron scattering data, because it is possible to avoid scattering contributions from the container. Recently, the use of levitation to study liquids and the formation of glasses from liquids has been of particular interest in understanding the structure of non-glass-forming liquids and the process of glass formation. Levitation techniques have recently been used to investigate the structures of the high-temperature oxide melts

Fig. 7. (A) Total structure factors $S(Q)$ for l -ZrO₂ at 2600–2800°C together with $S(Q)$ derived from a DFT-MD simulation at 2800°C. Both the experimental and DFT-MD simulation data at 2800°C are shifted upward by one unit for clarity. (B) Total correlation functions $T(r)$ for l -ZrO₂ at 2600–2800°C.¹⁶⁾

Al₂O₃,¹⁷⁾ Y₂O₃,²⁵⁾ Ho₂O₃,²⁵⁾ La₂O₃,²⁵⁾ ZrO₂,^{16),25)} and UO₂.²⁶⁾ using high-quality data together with simulation techniques.

ZrO₂ is commonly used as a refractory material and nucleating agent in the production of glass ceramics, suggesting that liquid (l -) ZrO₂ is indeed a non-glass-forming liquid. **Figure 7(A)** shows the X-ray total structure factors $S(Q)$ for l -ZrO₂ at 2600–2800°C. The structural change between the liquid at 2800°C and the undercooled liquid at 2600°C is small. A sharp peak is observed at $Q = 2 \text{ \AA}^{-1}$. The X-ray total correlation functions $T(r)$ for l -ZrO₂ [Fig. 7(B)] also show small differences in the real space. The first correlation peak observed at about 2.1 Å is assigned to Zr–O correlation and the significant tail to ~3 Å implies the formation of asymmetrical ZrO_{*n*} polyhedra in the liquid. The second peak observed at about 3.7 Å can be assigned mainly to Zr–Zr correlation, and the contribution of O–O correlation is unclear owing to its small weighting factor for X-rays. The Zr–O correlation length of 2.1 Å is significantly longer than those of Si–O (~1.63 Å²⁷⁾ at 1600–2100°C) and Al–O (~1.78 Å¹⁷⁾ at 2127°C) owing to substantial differences between the ionic radii of silicon, aluminum, and zirconium ions. The increased cation–oxygen correlation length in l -ZrO₂ suggests that the oxygen coordination number around zirconium is higher than four because 2.1 Å is close to the sum of the ionic radii of oxygen (1.35 Å) and sixfold zirconium (0.72 Å). The intermediate-range structure of l -ZrO₂ is therefore made up of large, interconnected polyhedral units and is very different from those of l -SiO₂ and l -Al₂O₃. This suggests that the peak in $S(Q)$ observed at $Q = 2 \text{ \AA}^{-1}$ in Fig. 7(A) is not the FSDP, which is typically associated with intermediate-range ordering in disordered materials, meaning that there is no such ordering in l -ZrO₂.

The total structure factor $S(Q)$ obtained from the DFT-MD simulation at 2800°C is shown in Fig. 7(A) as a solid magenta curve. Additional insight into the intermediate-range ordering of l -ZrO₂, in comparison with that of l -SiO₂ and l -Al₂O₃, can be found by calculating the Bhatia–Thornton²⁸⁾ number–number partial structure factor $S_{NN}(Q)$, which indicates for the topological order in a system

$$S_{NN}(Q) = c_A^2 S_{AA}(Q) + 2c_A c_B S_{AB}(Q) + c_B^2 S_{BB}(Q) \quad (3)$$

where $S_{ij}(Q)$ is a Faber–Ziman partial structure factor²⁹⁾ and c_i denotes the atomic fraction of chemical species i . Furthermore, it is possible to compare data for three liquids without taking into account the difference in the sensitivity of cations to X-rays

Fig. 8. (A) Bhatia–Thornton number–number partial structure factor $S_{NN}(Q)$ for l -ZrO₂ at 2800°C derived from the DFT-MD simulation (bold curve)¹⁶⁾ in comparison with those for l -Al₂O₃ at 2127°C¹⁷⁾ and l -SiO₂ at 2100°C (dotted curve).²⁷⁾ The momentum transfer Q was scaled by r_{AX} (r_{AX} is the first coordination distance between A and X in the real-space function) to eliminate the effect of the size of cations. (B) Coordination number distribution of oxygen around the cations in l -ZrO₂ at 2800°C,¹⁶⁾ l -Al₂O₃ at 2127°C,¹⁷⁾ and l -SiO₂ at 2100°C.²⁷⁾ (C) Polyhedral connections in l -ZrO₂ at 2800°C,¹⁶⁾ l -Al₂O₃ at 2127°C,¹⁷⁾ and l -SiO₂ at 2100°C.²⁷⁾ CS, corner sharing of oxygen; ES, edge sharing of oxygen; FS, face sharing of oxygen.

because weighting factors for X-rays are eliminated in $S_{NN}(Q)$. **Figure 8(A)** shows $S_{NN}(Q)$ for l -ZrO₂ at 2800°C compared with those for l -Al₂O₃ at 2127°C¹⁷⁾ and l -SiO₂ at 2100°C.²⁷⁾ Only l -SiO₂ exhibits an FSDP at $Qr_{AX} = 2.7$ [r_{AX} is the atomic cation (A) – anion (X) distance in AX polyhedra]. The position Q_{FSDP} of the FSDP arises from an underlying real-space periodicity of $2\pi/Q_{FSDP}$ that originates, for example, from the formation of pseudo-Bragg planes with a finite correlation length of $2\pi/\Delta Q_{FSDP}$ in l -SiO₂,⁵⁾ as indicated by the bold curves in Fig. 8(A). On the other hand, neither l -Al₂O₃ nor l -ZrO₂ shows an FSDP in $S_{NN}(Q)$, although a small contribution arising from Zr–O and O–O correlations can be observed at $Qr_{AX} = 2.2$ in the l -ZrO₂ data. Since the Bhatia–Thornton $S_{NN}(Q)$ can eliminate the weighting

Fig. 9. (A) DOS and its projections onto atomic orbitals for the higher valence bands and conduction band, together with the Wannier function spreads. (B) Visualization of the HOMO state (KS orbital) in *l*-ZrO₂. Zr and O atoms are shown in cyan and red color, respectively. Yellow and blue isosurfaces denote different signs of the wavefunction nodes.¹⁶⁾

factors for X-rays, the absence of an FSDP in $S_{\text{NN}}(Q)$ for *l*-ZrO₂ is a signature of a non-glass-forming liquid. Another important feature in $S_{\text{NN}}(Q)$ is that both *l*-SiO₂ and *l*-Al₂O₃ exhibit a second principal peak (PP) at $Qr_{\text{AX}} = 3$ while the PP is not distinct in *l*-ZrO₂ data.

The coordination number distributions of *l*-SiO₂,²⁷⁾ *l*-Al₂O₃,¹⁷⁾ and *l*-ZrO₂ calculated from the structural models are shown in Fig. 8(B). SiO₄ tetrahedra are predominant in *l*-SiO₂, while *l*-Al₂O₃ comprises AlO₃, AlO₅, and AlO₆ units as well as fourfold Al. For *l*-ZrO₂, the most common configurations are ZrO₅, ZrO₆, and ZrO₇. Although ZrO₂ and Al₂O₃ have different stoichiometries, this comparison supports our view that the variety of oxygen coordination around cations in *l*-ZrO₂ is another characteristic feature of non-glass-forming behavior, because it can disturb the evolution of intermediate-range ordering.

To obtain structural features beyond the first coordination distance, a polyhedral connection analysis was performed for *l*-SiO₂, *l*-Al₂O₃, and *l*-ZrO₂. Figure 8(C) shows a comparison of the fractions of corner-sharing, edge-sharing, and face-sharing polyhedral units in the liquids. The corner sharing of oxygen is prevalent in *l*-SiO₂, which is a unique feature of glass forming liquids (GFLs) according to Zachariasen.²⁴⁾ However, both *l*-Al₂O₃ and *l*-ZrO₂ exhibit a considerable amount of oxygen edge sharing, implying that the variety of polyhedral connections is another characteristic feature of single-component non-glass-forming oxide liquids.

Electronic structure analysis was carried out in terms of the electronic density of states (DOS), Wannier functions (WFs), and effective charges for snapshots of the high-temperature phases of crystalline (*c*-) ZrO₂ and *l*-ZrO₂. The DOS (above -20 eV) of *c*- and *l*-ZrO₂ and its projections (P-DOS) for *l*-ZrO₂ are shown in Fig. 9(A). The P-DOS plots reveal that this part of the electronic spectrum is mainly associated with oxygen (O-2*p* orbitals) and that the Zr semicore states corresponding to the atomic Zr-4*s* and Zr-4*p* orbitals are deeper (below -20 eV, not shown). The zirconium *d*-component dominates in the conduction band of *l*-ZrO₂. The effect of a high temperature on the distorted ZrO_{*n*} polyhedra in *l*-ZrO₂ is evident as a broadening of the energy bands, and the gap between the valence and conduction bands disappears (the calculated band gap is 3.26 eV for *c*-ZrO₂). This feature is probably related to an indistinct PP in $S_{\text{NN}}(Q)$ for *l*-ZrO₂. The difference between the electronegativities of Zr (1.3) and O (3.5) indicates that the chemical bonding between the two elements is mainly ionic, and this is supported by the significant

weight of the oxygen P-DOS for the highest valence band. The effective charges calculated by the Bader method are +2.62*e* and -1.31*e* for Zr and O in *l*-ZrO₂, respectively, and reflect the ionic bonding. The atomic charges in *l*-ZrO₂ are very similar to those in the crystalline phase, which is in accordance with our previous studies on MgO-SiO₂¹³⁾ and CaO-Al₂O₃¹⁴⁾ glasses. The associated atomic volumes imply that the increased oxygen volume in *l*-ZrO₂ compensates for the decreased oxygen coordination, and this results in comparable atomic charges for the two phases. Similar behavior has been found for MgO-SiO₂ glass.¹³⁾ The maximally localized WF can be considered as a natural generalization of localized molecular orbitals in solids, and they provide valuable insight into chemical bonding. The WFs have been obtained from the occupied Kohn-Sham (KS) orbitals by a unitary transformation, where the spatial extension (spread) of the WF orbitals is minimized. For each WF orbital, the center of the WF indicates the most probable location of an electron (or an electron pair in the case of a spin-degenerate orbital), and the corresponding Wannier spread is a direct measure of the degree of localization. The distribution of Wannier spreads is shown in Fig. 9(A). The oxygen coordination is smaller ($N_{\text{O-Zr}} \sim 3$) and less regular in the liquid than in the crystal. There is considerable scatter in the spreads and the WFs are markedly less localized than the crystal, which has a value of ~ 2.9 .

The HOMO is also visualized in Fig. 9(B), where the KS orbital (HOMO) is delocalized over a group of atoms highlighted by a dashed circle, while the transformed WFs for HOMO and HOMO-1 (molecular orbitals) are each localized over one Zr-O bond. The WF shapes in these examples are very similar to those in the high-temperature phase of *c*-ZrO₂ but there are also cases with considerable deviation, as can be expected from the scatter of WF spreads [Fig. 9(A)].

The origin of the FSDP associated with the formation of intermediate-range ordering in oxide glasses and liquids remains controversial because the inherent disorder complicates the ability of AX polyhedral connections to form an A-X network. SiO₂ has exceptionally high GFA, and the origin of the FSDP in SiO₂ has often been studied. The results are summarized in Ref. 30. The random network model of Zachariasen,²⁴⁾ which was modified for an oxide glass in Refs. 31 and 32 (illustrated in Fig. 7 of Ref. 30), demonstrates that the intermediate-range ordering arises from the periodicity of boundaries between successive small cages in the network formed by connected, regular SiO₄ tetrahedra with shared oxygen atoms at the corners. It has also been suggested

Fig. 10. Atomic configurations and schematic illustrations of (a) *c*-SiO₂, (b) *l*-SiO₂, and (c) *l*-ZrO₂. The periodicity of the cage boundaries is highlighted by dashed lines and curves.¹⁶⁾

that the small cages are topologically disordered,²¹⁾ resulting in a broad distribution of ring sizes from threefold to twelvefold rings centered at sixfold rings.¹³⁾ This is reflected in $S_{NN}(Q)$ for *l*-SiO₂ [Fig. 10(A)], where the FSDP is broader than the corresponding Bragg peak in the crystalline phase (β -cristobalite, *c*-SiO₂), where only a sixfold ring contributes.

Figures 10(A) and 10(B) illustrate three-dimensional atomic configurations and schematic illustrations of *c*-SiO₂ and *l*-SiO₂, respectively. The crystalline phase exhibits only sixfold rings of six SiO₄ tetrahedra, resulting in long-range periodicity [dashed cyan lines in Fig. 10(A)]. However, some pseudo-Bragg planes [dashed cyan lines in the left panel of Fig. 10(B)] can be recognized in *l*-SiO₂. Although the introduction of different ring sizes can easily modify the crystalline topological order [Fig. 10(B)], the interconnection of regular SiO₄ tetrahedra with shared oxygen at corners only yields the broadened Bragg peak as the FSDP. As can be seen in Fig. 8(A), an FSDP is absent in $S_{NN}(Q)$ for *l*-ZrO₂. This is because the variety of short-range structural units with large oxygen coordination, ZrO₅, ZrO₆, and ZrO₇, and the large contribution of oxygen edge sharing prevent the formation of intermediate-range ordering. A similar feature can be expected in *l*-Y₂O₃ and *l*-La₂O₃ because their Faber-Ziman partial structure factors $S_{ij}(Q)$ do not contribute to the expected Q position of $\sim 1 \text{ \AA}^{-1}$ for an FSDP. Short-range structural disordering in *l*-ZrO₂ is further demonstrated in the three-dimensional atomic configuration and the schematic illustration of *l*-ZrO₂ [Fig. 10(C)]. The periodicity of boundaries (dashed lines) is suppressed by the edge sharing of oxygen associated with the formation of ZrO₅, ZrO₆, and ZrO₇. Although ZrO₂ forms a network structure by interconnecting AX polyhedra in the liquid phase, it is shown that the various short-range structural units and their connectivity cause disorder at the intermediate range and prevent the evolution of an FSDP for the liquid. These results demonstrate that the absence of an FSDP in $S_{NN}(Q)$ can be an important indicator of single-component non-glass-forming oxide liquids, but this does not necessarily apply similarly to other non-glass-forming liquids. The absence of an FSDP in $S_{NN}(Q)$ suggests that both *l*-Al₂O₃ and *l*-ZrO₂ are extremely fragile liquids.²³⁾ This suggestion is supported by a comparison with *l*-ZnCl₂, which is recognized as

an intermediate case between a strong and fragile liquid. *l*-ZnCl₂ has a well-defined but not sharp FSDP in $S_{NN}(Q)$ owing to the contribution of corner-sharing ZnCl₄ tetrahedra, while edge sharing also occurs.³³⁾ This behavior of a fragile glass former is very similar to that of *l*-GeSe₂, for which the FSDP in $S_{NN}(Q)$ is weak, and a considerable fraction of edge-sharing GeSe₄ tetrahedra contribute,³⁴⁾ as in glassy GeSe₂.³⁵⁾

6. Conclusions

In this article, we have reviewed recent studies on atomistic and electronic structures of functional disordered materials revealed by a combination of quantum-beam measurements and computer simulations. The results highlight the quality of the experimental information that can now be obtained, which has been made possible by a combination of advances in the instrumentation at X-ray synchrotron/neutron sources and modern computer simulations. This approach uncovers the relationship between atomistic and electronic structures of disordered materials and their functions as well as the relation between structure and glass-forming ability beyond the nearest-neighbor correlation length, which has been hitherto challenging.

Other quantum-beam diffraction-based techniques can be used to investigate the hidden structures of liquids and glasses. In the case of electron beams, fluctuation microscopy³⁶⁾ has recently been applied to study continuous random networks in comparison with inhomogeneous para-crystalline models for the intermediate-range order in amorphous Si,³⁶⁾ and Ångström beam electron diffraction (ABED) has been developed to probe the local atomic configurations and their assemblies in metallic glasses.^{37),38)} A combination of ABED and HEXTS has proved to be a powerful tool for investigating the atomic-scale disproportionation of amorphous silicon monoxide into silicon-like and silicon-dioxide-like regions, and their interface.³⁹⁾ The development of coherent X-rays at next-generation synchrotron radiation sources provides an important opportunity for the investigation of disordered materials. Woche et al.⁴⁰⁾ used coherent X-rays to investigate a colloidal glass of poly(methyl methacrylate) spheres and, by avoiding configurational and temporal averaging, hidden local symmetries were revealed by applying a cross-correlation analysis.

Understanding disordered matter is one of the most challenging topics in materials science, and hence the combination of experiments and computer simulations is indispensable to derive descriptors for disordered materials. In this review article, disordered materials, which do not contain a glass former, are featured and it is found that they do not show a prominent FSDP in diffraction data, although further investigation is required to determine whether this feature is unique or also applies to other disordered materials, as discussed in Ref. 16.

Salmon and coworkers recently reported the relationship between the coordination number and oxygen packing fraction for several oxide glasses and liquids.⁴¹⁾ Moreover, they attempted to classify peaks in the structure factor of several glasses and amorphous materials by normalizing Q with r_{AX} [see Fig. 8(A)], which provides us with crucial information from experimental data to uncover the origin of the FSDP and PP.⁴²⁾ Hiraoka and coworkers recently developed a novel topological analysis technique based on mathematics.⁴³⁾ A combination of novel experimental techniques and protocols to analyze data will probe the order within disorder¹⁾ hidden in correlation functions. Furthermore, these approaches and the establishment of a database of structure data, physicochemical properties, and simulation data will increase the capability of the materials informatics of disordered materials.

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