

The Origin of the First Sharp Diffraction Peak of Silica Glass

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ABSTRACT

The first sharp diffraction peak (FSDP) in diffraction data of silica glass is a prominent feature, occurring at the value of scattering vector $Q = 15 \text{ nm}^{-1}$. Although, it is widely accepted that FSDP correlates well with the medium-range structure of glass materials, the structural origin of FSDP has remained an outstanding issue. This work will first briefly review a newly proposed nanoflake model for the medium-range structure of silica glass. Then, based on the nanoflake model, it is suggested that the FSDP of silica glass is caused by a nano-layer structure formed by SiO_4 tetrahedra. This layer structure is different from the (111) plane of β -cristobalite crystal with an oxygen atom layer in the middle connecting the top and bottom layers of SiO_4 tetrahedra. This work also discusses the origin of the observed shoulder of FSDP at 7.5 nm^{-1} . It is predicted that the intensity variation of both peaks at 15 nm^{-1} and 7.5 nm^{-1} reflects the rearrangements of silica glass network in the cooling process.

Keywords

Silica glass, First sharp diffraction peak, Continuous random network theory, Medium-range ordering structure, Nanoflake model, Cooling rate, Critical temperature.

Introduction

Silica glass is the most important glass-forming substance. Understanding its structure is fundamental to deciphering the structure of all other silicate glasses. The most popular hypothesis for silica glass structure is the continuous random network theory (CRN), based on the original idea of Zachariasen and X-ray diffraction studies by Warren [1-4]. Although the CRN model is presented in many textbooks, it has to be regarded as a first-order approximation of the glass structure [5]. Despite the theory is hardly questioned for its depiction of near-range structure of a SiO_4 tetrahedron and long-range structure as random network, the medium-range structure of silica glass is remained as very controversial. One of promising experimental data in studying the medium-range structure of silica glass is the First Sharp Diffraction Peak (FSDP) in the diffraction data (X-ray or neutron). The FSDP of silica glass is a prominent feature, occurring at the modulus of the scattering vector $Q = |\mathbf{Q}| = 15 \text{ nm}^{-1}$. Since the radial distribution function (RDF) obtained from the Fourier transformation of the

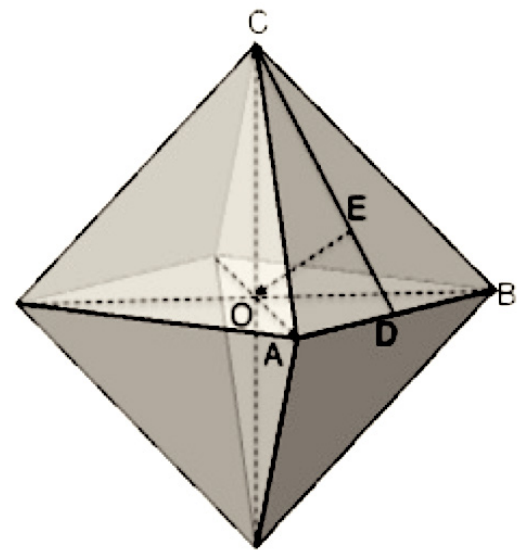
scattering data does not depend much on including FSDP in the Fourier transform, the intensive peak is believed to be caused mostly by the medium-range structure of glass [6]. Understanding the medium-range structure of glass materials is the key to revealing the nature of glass state and glass transition, and it has attracted substantial attention from the glass scientific community [7-13]. Despite several decades of study, there is still no consensus on the exact form of the medium-range structure that produces the FSDP of silica glass.

An interesting characteristic of FSDP is that the scattering angle position of the peak closely matches that of a strong diffraction peak of the corresponding crystalline phase [14]. For chalcogenide glasses, such as As_2S_3 , GeSe_2 , layers similar to two-dimensional layers of the corresponding crystals are believed to be the origin of FSDP [15-17]. However, the concept of layers in tetrahedral framework of silica glass seems not to be acceptable, since there are no such atomic layers in the three-dimensional structure of silica glass [6,17]. Alternatively, various other proposals on the origin of FSDP for silica glass, such as, interstitial voids and quasi-Bragg planes, have been suggested. The details of these explanations can be found in several articles [9,14,18].

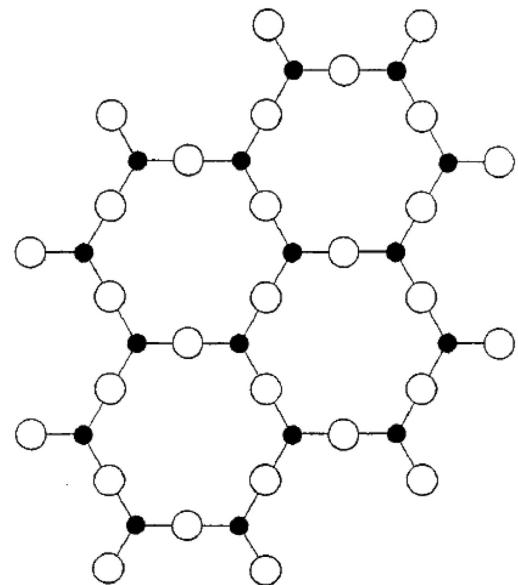
This work proposes that the FSDP of silica glass could be explained by the recently published nanoflake model of silica glass [13,19]. Based on the new medium-range structural model, the FSDP of silica glass is caused by two-dimensional nano-layers, similar to that of chalcogenide glasses.

Medium-Range Structure of Silica Glass Based on Nanoflake Model

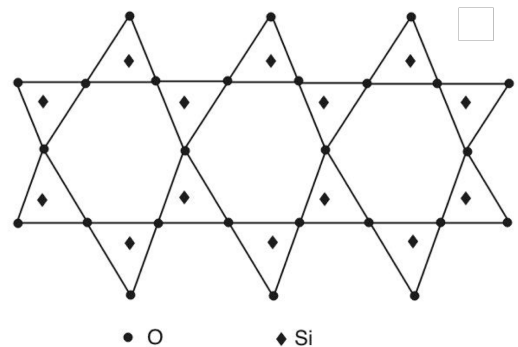
Recently, based on detailed analysis of X-ray diffraction data and comparing the formation process of vitreous silica with that of β -cristobalite crystal, a new nanoflake model for medium-range structure in vitreous silica has been proposed [13,19]. In the nanoflake model frame, there are two different temperature regions in the glass transition process. For pure silica, these two temperature regions are separated by a critical temperature T_c of 1470°C, which is the β -cristobalite and β -tridymite phase transition temperature. In the high-temperature region above T_c up to the melting temperature T_m , SiO_4 forms embryonic clusters of β -cristobalite in the supercooled liquid. Subsequent evolution of these embryonic clusters depends on the cooling rate. In the cases of low cooling rate, these clusters may grow to form crystal nuclei and subsequently larger crystal particles. The β -cristobalite nucleus is octahedral in shape, as shown in Figure 1(a) [13]. In the direction perpendicular to the facets of the nuclei particles, the structure is a 2-dimensional crystal, and all Si-O bonds form 6-membered rings. This is the structure of (111) plane of β -cristobalite, as shown in Figure 1(b). The side view of the facets is shown in Figure 1(c). It can be seen that the two-layer structure in Figure 1(c) has a thickness of about 0.8 nm. As the crystal nucleus grows, it will bond with other SiO_4 to form new layers. However, in the cases of high cooling rates, the embryonic clusters may enter the low-temperature zone before crystal nuclei can form, and the embryonic clusters' pathway to β -cristobalite nuclei would be blocked. In the lower temperature region, further structural evolution is still governed by thermodynamics. To reduce the free energy of the system, a local one-dimensional ordering structure on the clusters' facets called “nanoflake” is formed. Along the direction perpendicular to the facets of the embryonic particle, instead of organizing into regular 6-membered rings, the structure consists of various membered rings, which is the same as that described in Zachariasen’s continuous random network theory. This is shown in Figure 1(d) [1,2]. The side view of the nanoflakes is shown in Figure 1(e). It can be seen that there is an oxygen atom layer in the middle of the structure, connecting the top and bottom layers of SiO_4 tetrahedra. The nanoflake is a stabilized one-dimensional ordering structure formed in the low-temperature region after adjusting for the orientation of SiO_4 tetrahedra on the topmost and bottom layers. Adjacent nanoflakes are not parallel but intersect each other to form clusters. The shape of clusters is approximately octahedral with an edge length of about 1.9 nm [13]. The clusters are randomly orientated and distributed in the system such that bulk isotropy is preserved.



(a)



(b)



(c)

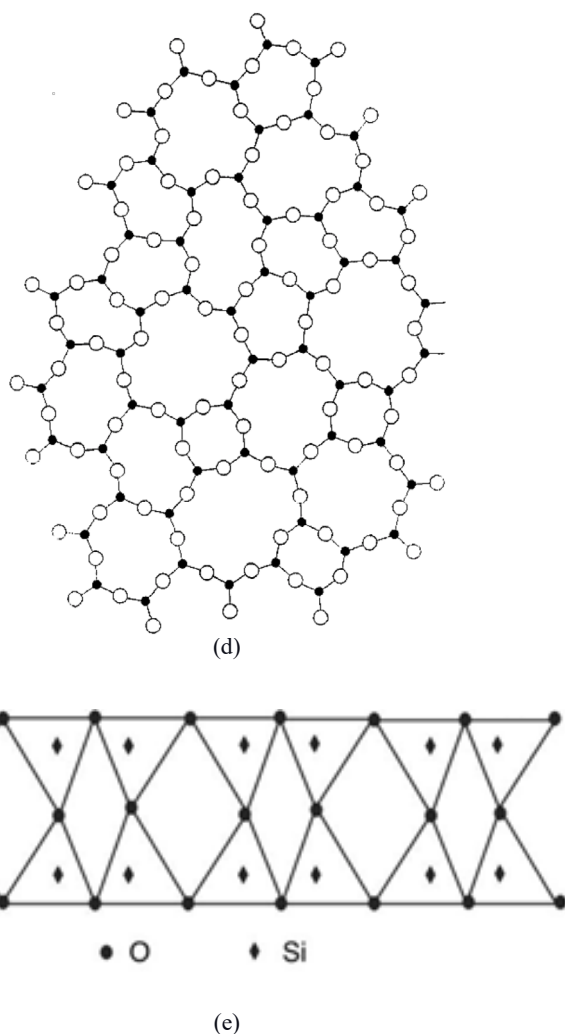


Figure 1: Structural difference between silica glass and β -cristobalite in the nanometer scale. (a) Schematic figure of octahedral cristobalite nucleus. (b) and (c) Plan view and side view of facet structure of β -cristobalite nucleus. (d) and (e) Plan view and side view of nanoflake.

The structural origin of FSDP for silica glass

Figure 2 is the classic raw X-ray data of silica glass from B. E. Warren [20], showing the FSDP at $Q = 4\pi\sin\theta/\lambda = 15 \text{ nm}^{-1} = 1.5 \text{ \AA}^{-1}$, where θ is the half scattering angle and λ is the wavelength of the probing radiation. The FSDP in Figure 2 can be related, via reciprocal relation, to a distance R of approximately 4.2 \AA in real space using the expression $R = 2\pi/Q$. This distance is longer than the first Si to O distance of 1.62 \AA , the second O to O distance of 2.65 \AA , and the third Si to Si distance of 3.12 \AA . The FSDP diffraction feature of silica glass represents a build-up of molecular arrangement with a basic period of about 4.2 \AA .

From Figure 1(e), the side view of nanoflake, the spacing between two layers in the nanoflake can be calculated from the size of SiO_4 tetrahedron and is found to be about 4.2 \AA . Since the structural geometry of the nanoflake matches the distance related with FSDP of silica glass, it is reasonable to assume that nanoflakes are the structural origin of the FSDP for silica glass. As the above

analysis indicates, the origin of the FSDP for silica glass might be the layers in nanoflakes; the layer structure should be observed in the high-resolution transmission electron microscope (HRTEM) as fringes. Each nanoflake is expected to generate two nearly parallel fringes about 1 to 2 nm long, and the spacing between the two fringes should be about 0.4 nm in HRTEM images. Such fringes, shown in Figure 3, in carefully prepared TEM specimens of high-purity silica glass, have already been reported [13]. The TEM results provide directly observed experimental evidence that the ordered medium-range structure, as described by the nanoflake model, indeed exists in silica glass, and such ordered medium-range structure could be the origin of FSDP of silica glass.

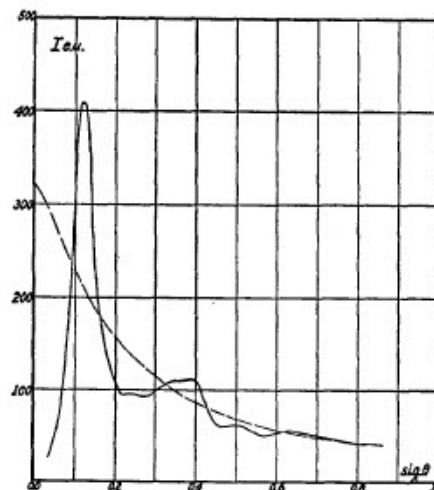


Figure 2: Experimental X-ray scattering data obtained from silica glass. X-ray intensity curve for vitreous silica in e.u. per SiO_2 ; dashed line, independent scattering per SiO_2 . The unit of Q is \AA^{-1} . Reproduced from Ref. 20.

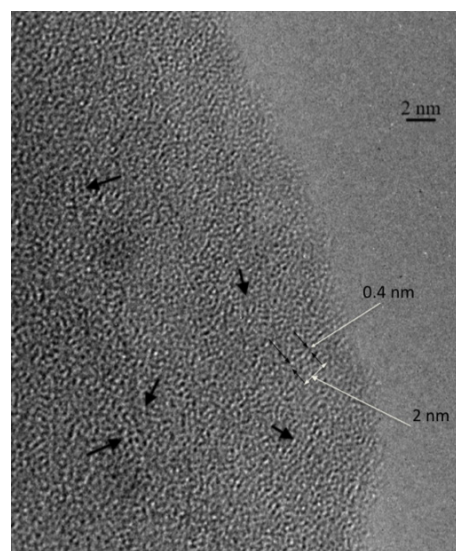


Figure 3: HRTEM image of silica glass. There are nearly parallel fringes about 1 to 2 nm long. According to the proposed nano-flake model, two parallel fringes represent one flake. The locations of some flakes are indicated by the thick arrows. The spacing and size of one flake are indicated by the thin arrows.

Discussions and Conclusion

It is reported that at the foot of the FSDP of silica glass, a shoulder at 7.5 nm^{-1} is clearly observed [21]. Although the intensity of the shoulder is significantly lower than that of the peak at 15 nm^{-1} , it can be recognized in the log-log plot of the X-ray scattering intensity, as indicated by an arrow shown in Figure 4. The correlated length for the small peak is close to 0.84 nm , which is equal to approximately twice the spacing of two layers in nanoflake. The structural origin of the shoulder at 7.5 nm^{-1} appears to relate to the structure just outside the nanoflakes.

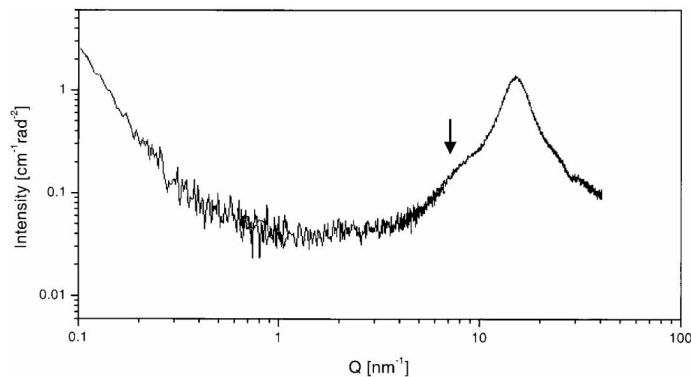


Figure 4: Log-log plot of the X-ray scattering intensity from silica at room temperature, plotted up to $Q = 32 \text{ nm}^{-1}$. The shoulder at 7.5 nm^{-1} is pointed by an arrow. Reproduced from Ref. 21.

As discussed in previous section, if the cooling rate is higher than the critical one, embryonic clusters in silica will enter the low-temperature zone before becoming crystal nuclei. The structural evolution of these clusters follows the path governed by thermodynamics. To reduce the system's free energy, nanoflakes are formed by adjusting the orientation of SiO_4 tetrahedra on the top-most and bottom-most layers. As shown in Figure 5, two SiO_4 tetrahedra, represented by ΔACD and ΔDEF are bonded face-to-face to create a stable structure in the nanoflake structure. Before forming the stable bond, SiO_4 tetrahedra represented by ΔABC and ΔEFG . The distance between point B and G is 0.84 nm , which is precisely twice the spacing of two layers in nanoflake of 0.42 nm . Therefore, the origin of the small peak located at 7.5 nm^{-1} is correlated with the structures in the pre-formation of nanoflakes. As the temperature in the silica glass-forming process decreases from the critical temperature T_c of 1470°C , the population of nanoflakes increases. Thus, one can not only predict that the intensity of FSDP increases with a decrease in temperature, but also predict that the intensity of the small peak at 7.5 nm^{-1} will vary in the opposite direction. It will decrease with a decrease in temperature.

The intensity of the small peak at 7.5 nm^{-1} may be very sensitive to impurities in silica glass. For example, a certain amount of hydroxyl in silica glass may enhance the intensity of the peak at 7.5 nm^{-1} , as reported in the reference [21]. The reason could be that additional hydrogen ions in the silica glass can bind with oxygen to form a stabilized structure. An example is the oxygen located at

point B in Figure 5. As this oxygen atom bonds with hydrogen, the SiO_2 tetrahedron represented by ABC becomes a stable structure without change in orientation. Therefore, hydrogen can keep more oxygen atoms in their positions to contribute to the peak intensity at 7.5 nm^{-1} . Future experiments may check these predictions.

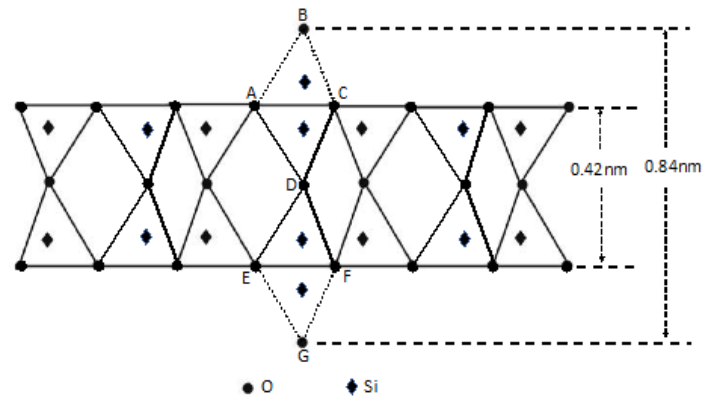


Figure 5: Side view of the nanoflake's layered structure. ΔABC and ΔEFG represent the positions and orientations of two SiO_4 tetrahedra before forming a stable bonding.

In conclusion, the information on the medium-range structure in silica glass obtained from the X-ray scattering technique is crucial. The recently proposed nanoflake model suggests that the FSDP of silica glass may be caused by an internal nano-sized planar-layer structure similar to that of chalcogenide glasses. The structural origins of the FSDP of silica glass located at 15 nm^{-1} and the observed shoulder of FSDP at 7.5 nm^{-1} are related to the formation of the medium-range ordering structure. The intensity variation of both peaks may be used to monitor the chemical bonding adjustments in the silica glass cooling process.

Acknowledgments

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