

*Research article***On the mechanism of helium permeation through silica glass****Shangcong Cheng***

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Abstract: Although the densities of crystal quartz and vitreous silica differ only by about 17% (2.65 and 2.20 g/cm³, respectively), the helium permeability of silica glass is six orders more elevated than that of crystal quartz. This vast difference has puzzled researchers for decades considering that silica glass and quartz crystal have the same chemical composition. This work discusses the mechanism of high helium permeation through silica glass. It briefly reviews the experimental data and its contradictions with the continuous random network theory. A recently proposed nanoflake model for silica glass structure is utilized to explain the origin of glass permeation to helium. According to the nanoflake model, the formation of nanoflakes not only brings a one-dimensional medium-range ordering structure into silica glass but simultaneously creates regions where van der Waals bonds replace the oxygen-silicon covalent bonds. It is the weakness of van der Waals bonds that causes the helium mobility in these areas to increase.

Keywords: permeation; helium gas; silica glass; sodium silicate glass; medium-range structure; van der Waals bond; nano-fissures; nanoflake model

1. Introduction

Glass permeability to gases, especially to helium, has been extensively studied [1–4]. These studies were originally motivated by the usage of glass to make various types of vacuum systems. To design and maintain an efficient vacuum system, it is necessary to know the actual rates of gas permeation through the wall material and the permeation mechanism. The significantly different permeation property of silica glass, compared to crystalline solids, received considerable attention. Substantial experimental data on the permeation properties of various glasses were accumulated

through many decades of studying [3–14]. However, a satisfactory structural model that reveals the origin of the observed permeation properties has yet to be developed.

This work aims to use the recently proposed nanoflake model [15,16] to explain the high permeation of helium through vitreous silica. The nanoflake model differs from the popular continuous random network (CRN) theory [17–19] in that it emphasizes the formation of a medium-range ordering structure in the glass cooling process. Since the model was proposed in 2017, it has explained various properties of glasses, including the viscosity behaviors of glasses in a wide temperature range, the step change in the glass heat capacity, anomalous density behavior, and the mechanical strength and brittleness of various glasses [20,21]. A valuable structural model of silica glass should be all encompassing and be able to explain most properties of glass. The intention of this work is to check if the nanoflake model can provide an explanation for the high permeability of silica glass to helium gas.

2. A brief review of studies on the permeation of He through silica glass

Since the early twentieth century, there have been many investigations on the penetration of silica glass by light gases. In 1926, H. Elsey reported that silica glass has the property of passing helium but stopping air at room temperature when the pressure is about 100 atmospheres [5]. As silica glass is apparently a compact solid, Elsey's results surprised many researchers and stimulated more investigations on the permeability of various solids, including crystals, metals, and glasses [6–14,22,23].

In 1953, F. Norton used a mass spectrometer as an analytical tool and a means for gas permeation measurements [6]. Compared with the early study, the sensitivity and accuracy of the measurement were significantly improved. Norton published experimental data on the permeation velocity of helium through nine types of glasses in the temperature range from -80 to 600 °C. These data are shown in Figure 1, which is a plot of the logarithm of the permeation velocity K , $\text{Log}_{10}K$, against the reciprocal of the absolute temperature, $1000/T$. These data indicate that the permeation of helium through glass is very sensitive to glass composition. The permeation may be reduced by many orders of magnitude by introducing non-glass formers into the glass composition. The general conclusion is that the lower the percentage of glass formers with more glass modifiers, the lower the permeation velocity. In the 1970s, J. E. Shelby carried out further study on binary glass systems of $\text{Na}_2\text{O-SiO}_2$ and $\text{K}_2\text{O-SiO}_2$. Shelby's data are consistent with the previous observation [10,11].

Norton also stated that the passage of helium through glass is related to glass being less closely packed. The density of silica glass at 2.20 g/cm^3 is about 17% less than that of quartz at 2.65 g/cm^3 [6]. In contrast to silica glass, a single quartz crystal with the same chemical composition does not pass measurable quantities of helium through its lattice at ordinary temperatures [6,22]. Experimental results obtained by L. Rayleigh and Norton show that the permeation velocity of crystalline quartz is many millions of times lower than that of silica glass [6,7,22,23]. In Figure 1, point A represents the permeation velocity at temperature 100 °C for silica glass; point Q represents the lowest permeation velocity in the scale of Figure 1 at the same temperature. The difference in permeation velocity between points A and Q is about six orders of magnitude. The measured permeation velocity for a single quartz is even lower than that of point Q and is out of the scale range in Figure 1 [23]. To explain the vast difference in permeation velocity between silica glass and crystal quartz, Norton relied on the popular continuous random network theory (CRN) proposed by Zachariasen and Warren, as illustrated in Figure 2 [14,16].

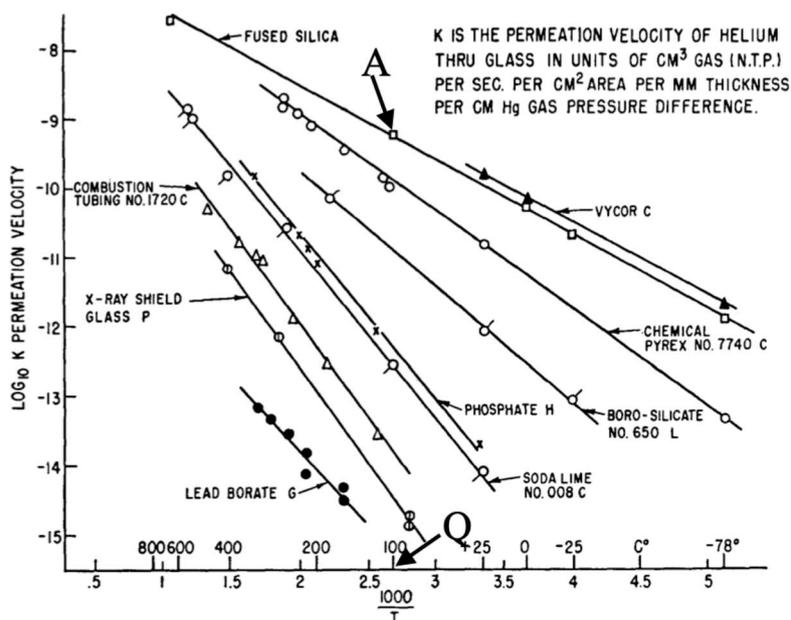


Figure 1. Permeation velocity K of helium diffusing through various glasses. The logarithm of permeation velocity $\log_{10}K$ is plotted against the reciprocal of the absolute temperature, $1000/T$. The temperature ranges from -80 to 600 °C (Reproduced from Ref. [7] with permission).

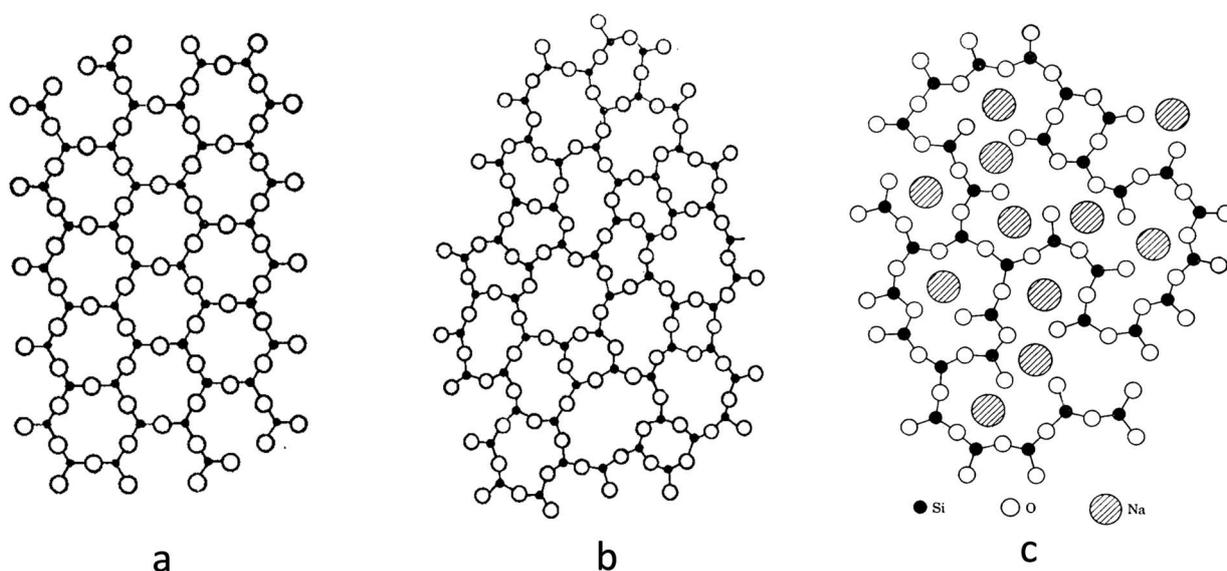


Figure 2. Illustration of two-dimensional atomic arrangement: (a) in crystalline silica, (b) in a glass according to the CRN theory and (c) in a soda silicate glass according to the CRN theory (Reproduced from Ref. [6] with permission).

Figure 2a represents the atomic arrangements in crystal silica in two dimensions. The material possesses symmetry and periodicity. The “holes” in the network (6-membered ring) are too small for helium to penetrate. The form of atomic arrangements in glass is different from crystalline materials. In the glass network, there are many larger “holes” (due to the presence of 7 or larger membered rings)

than in the regular crystal structure. This is shown in Figure 2b. It is possible that these sizeable random openings account for the increased helium permeation in silica glass. In Figure 2c, Na ions, which are present in sodium silicate glass, are inserted into these cavities. These added non-glass formers plug the openings, and reduce the helium permeation rate to levels below that of pure silica glass.

Although Norton's explanation as described above is based on the popular CRN theory, it is not convincing. The differences in hole sizes between the six-membered ring in silica crystal and seven or eight-membered rings in silica glass is about 20%–30%. The difference is relatively insignificant and could not be expected to account for the huge variation of permeation rate by six orders. Norton's hypothesis also does not explain why the helium permeation rate of sodium silicate glass with the plugged large openings is still many orders higher than that of single-crystal quartz. The experimental data suggest that Na ions may reduce the size of the channels for helium permeation and that the permeation channels may not be the large "holes" as described in Figure 2b. Thus, the popular CRN theory might have missed some important structural features of silica glass that distinguish it from crystal silica.

A few years after Norton published the experimental data of helium permeation through various glasses, in 1956, K. B. McAfee designed a particular device to investigate other possible permeation mechanisms of glasses [8].

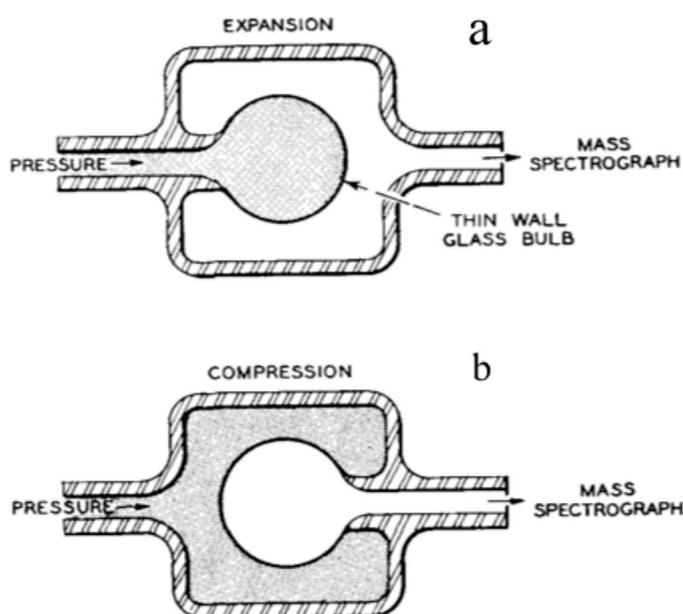


Figure 3. Pyrex glass tube, used in McAfee's experiments. Both radial tension in (a) and radial compression in (b) could be produced (Reproduced from Ref. [8] with permission).

McAfee's setup is shown in Figure 3. A Pyrex glass tube was mounted inside a metal tube. Helium or another gas was applied to the inside or outside of the shell of the glass tube, which produces radial tension or radial compression in the glass, respectively. Gas diffusing through the Pyrex glass was collected and passed into a consolidated electrodynamic analytical mass spectrometer. McAfee found that under remarkably high stress (about 73 lb/in² on the chart), the diffusion constant increased to 10 times that of the original value. Theoretical calculation shows that the diffusion constant should not change this much if the glass sample dilates from stress at the atomic scale [8]. The significantly higher

observed permeation velocity under tension indicates possible opening of flaws or voids within the glass. Based on the results of this study, McAfee concluded that the most acceptable glass model should consist of randomly oriented submicroscopic flaws or voids in the glass structure.

In 1960, C. C. Leiby and C. L. Chen published their permeation velocity data of helium and other gases through Vycor glass and silica glass [9], which also supported McAfee's arguments that the high permeation velocity of silica glass is due to flaws or voids in the internal structure. Leiby and Chen found that the gas solubilities, permeabilities, and activation energies in Vycor glass and silica glass seemed identical. Although this may be expected as the two glasses have approximately the same density and composition, their manufacturing processes are entirely different. In forming Vycor glass, a sodium borosilicate glass is heat treated to separate into two phases. The borate-rich phase is subsequently leached out with acid, leaving a honeycomb matrix of silica with channels. The silica matrix is then heated to a sintering temperature at which it shrinks to approximately two-thirds of its previous size. Although Vycor glass exhibits no apparent porosity in this finished state, the very nature of its manufacturing process leads to the belief that finished Vycor may still possess innumerable submicroscopic voids of molecular dimensions and that these voids may be responsible for the large permeation velocities. Based on the apparent similarity of permeation processes in Vycor glass and silica glass and the manufacturing mode of Vycor glass, Leiby and Chen augured that it is possible that "channels" or "voids" play an essential role in the diffusion of gases in a wide variety of glasses.

The hypothesis that glasses contain a random collection of atomic-sized fissures or openings contradicts with the CRN theory since the latter asserts that the structure of silica glass is a homogeneous SiO_2 tetrahedra network. The experimental results obtained by McAfee as well as by Leiby and Chen cannot be explained by the CRN theory. In the 1980s, N. Greaves applied an extended X-ray absorption fine structure spectroscopy (EXAFS) technique to the study of very local structures of elements in glasses. Based on these studies, Greaves proposed the modified random network (MRN) model [24–26]. In this model, the local environments of modifiers like Na_2O in glasses are incorporated in a complementary way with the network formers like SiO_2 . The overall structure contains two interlacing sublattices. The MRN is different from CRN model in Figure 2c and distinguished by percolation channels for modifying components like Na_2O . The MRN model explains the permeability of soda silicate and other diffusion-related properties of oxide glasses well and can be viewed as an improved CRN model. However, the MRN model is only relevant for silicate glasses containing alkali or other elements as modifiers. It does not provide the presence of any channels in pure silica for helium permeation and cannot explain the high helium permeability of silica glass. This work uses the recently proposed nanoflake model for silica glass to reveal the origin of helium permeation through pure silica glass and other silicate glasses.

3. Nanoflake model for the medium-range structure of silica glass

Recent studies on the structure and properties of silica glass have revealed the formation and evolution of medium-range ordering structures in silica glass [15,16]. The core knowledge gained from these studies is the recognition of two different temperature regions in the glass transition process. For pure silica glass, these two temperature regions are separated by a critical temperature T_c of 1470 °C, which is the polymorphic inversion temperature between crystal β -cristobalite and β -tridymite. In the high-temperature region above T_c up to the melting temperature T_m , SiO_4 tetrahedra form embryonic clusters of β -cristobalite in the supercooled liquid. If the cooling rate is sufficiently low, these clusters

may grow to form crystal nuclei and further to form larger crystal particles. The β -cristobalite nucleus is octahedral in shape, as shown in Figure 4a. 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, which is the structure of (111) plane of β -cristobalite, as shown in Figure 2a [15]. The side view of the facets is shown in Figure 4b. The two-layer structure in Figure 4b has a thickness of about 0.8 nm. The oxygen on the top layer in Figure 4b only bonds with one Si in the structure. As the crystal nucleus grows, it will bond with another Si in a new layer. However, if the cooling rate is high, the embryonic clusters may enter the low-temperature zone before becoming crystal nuclei, and the embryonic clusters' pathway to β -cristobalite nuclei would be blocked. In the lower temperature region, the structural evolution is governed by thermodynamics, and a one-dimensional ordering structure on the clusters' facets called “nanoflake” is formed [15]. Looking along the direction perpendicular to the facets of the embryonic particle, the structure is not organized into regular 6-membered rings. Instead, it consists of various membered rings, which are the same as described in Zachariassen's CRN theory, as shown in Figure 2b. Figure 4c shows the side view of the nanoflakes. 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 one-dimensional ordering structure formed in the low-temperature region after adjusting for the orientation of the SiO_4 tetrahedra on the topmost and bottommost layers. Adjacent nanoflakes are not parallel but intersect each other to form clusters. The shape of clusters is approximately octahedral with edges about 1.9 nm in length. The clusters are randomly orientated and distributed in the system such that bulk isotropy is preserved [15]. Silicon-oxygen bonds and van der Waals bonds connect the clusters with outside structures. The silicon-oxygen bonds may be provided by oxygen atoms located on the edges and vertexes of the clusters. Oxygen atoms not situated on the borders may interact with outside structures by the van der Waals force, which is significantly weaker than chemical bonding [27]. Van der Waals bonds create spaces in the neighborhoods of nanoflakes where there are no silicon-oxygen bonds to connect the facets with structures outside the clusters. These spaces can appear as fissures in the structure. The thickness of this space is comparable to the size of SiO_4 tetrahedra and should be close to 0.3 nm. Its width is near the size of the nanoflake, which is close to 2 nm. It has been recently reported that the replacement of Si–O covalent bonds by Van der Waals bonds increases the distance between the nanoflakes and their surrounding structures, and the slight volume enlargement associated with the formation of nanoflakes is the origin of the anomalous density behavior of silica glass [21].

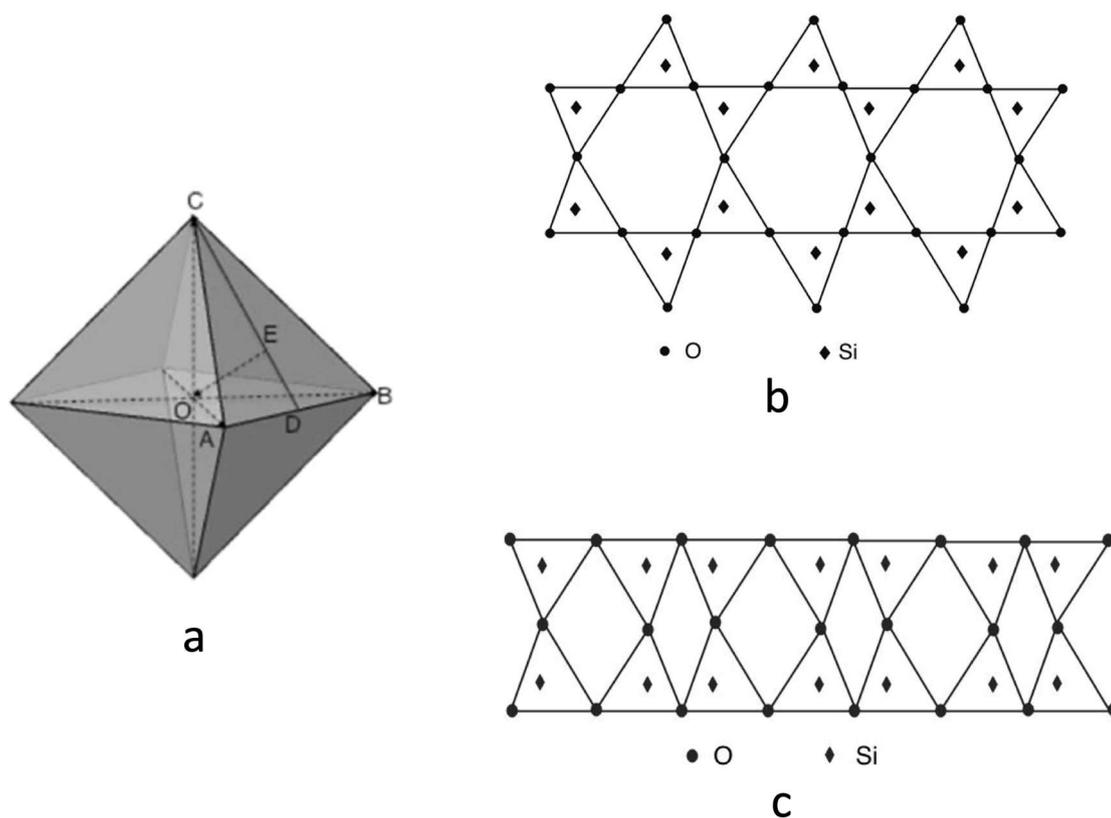


Figure 4. (a) Schematic figure of octahedral cristobalite nucleus. (b) Side view of facet structure of β -cristobalite nucleus. (c) Side view of the nanoflake (Reproduced from Ref. [15] with permission).

4. The origin of helium permeation through silica glass based on the nanoflake model

The structural model and its formation process described in the previous section demonstrate that the formation of nanoflakes not only brings a one-dimensional ordering structure into silica glass but also simultaneously creates nanosized fissures in the structure. Since the clusters are randomly distributed everywhere inside glass, the nanosized fissures are also randomly distributed everywhere inside the system. This structural picture is consistent with McAfee's as well as Leiby and Chen's experimental results [8,9]. The silica glass structure based on the nanoflake model is significantly different from the CRN model shown in Figure 2b. The clusters in the nanoflake model are only 1 or 2 nm in size and have a one-dimensional ordering structure on their facets. The spaces between the clusters are occupied by more disordered structures. However, as described in the previous section, the formation of ordering structure is accompanied by creation of fissures close to the facets. These fissures provide channels for gas to pass through.

Since the fissures are very thin, only the smallest gas molecule, helium with diameter of about 0.28 nm [28,29], can be passed at a relatively high rate. The permeation rates for larger gas molecules such as argon, oxygen, and nitrogen are very low and hard to detect [7]. In contrast to silica glass, the single quartz crystal has no such fissures in its structure, thus the permeation of helium through quartz is many orders of magnitude lower than that of silica glass.

In the case of soda silicate glass, the locations of Na cations in the structure depend on Na₂O concentration in the glass [20]. In the composition range below 25.5 wt.% Na₂O, Na cations are not involved in the internal structure of clusters and are distributed on the clusters' surfaces or spaces between clusters. Since sodium ions can bond with oxygen ions on the surface of clusters to form a stable structure, they can prevent the orientation change of SiO₄ tetrahedra on the top surface of facets and reduce the size of the fissures in the neighborhood of nanoflakes. Therefore, more Na cations in the sodium silicate glass lead to lower helium permeation through the glass.

5. Discussion and conclusions

A fundamental principle in materials science is that the physical properties of a material must correlate with its internal structure. If the fissures distributed inside the glass structure are the source causing the high permeation rate of helium through silica glass, then such structure must influence some other mechanical properties of silica glass. For example, the fracture strength of silica glass can be used to illustrate how the molecular-sized fissures influence other properties. Based on the popular CRN theory, every oxygen-silicon bond is part of the structural network and contributes to the strength of the glass. The estimated theoretical strength of silica glass is more than 10 Gpa, a few orders higher than the practically measured value [2]. This disagreement was previously explained by using Griffith's theory, which assumed the presence of tiny cracks or flaws in the glasses [30]. Although many researchers have attempted to prove Griffith's concept, evidence contradicting Griffith's concept has been reported [31]. Griffith's idea may not fully resolve the puzzle concerning the strength of silica glass as the measured value is much lower than the theoretical estimation.

Contrary to the CRN theory, this research has revealed the presence of molecular-sized fissures in silica glass that lack an oxygen-silicon covalent bond. The nanoflakes interact with the outside structures through oxygen-silicon covalent bonds and van der Waals bonds, with the latter being significantly weaker. This discovery, coupled with the random distribution of fissures in the internal structure, provides a compelling explanation for the significantly lower strength of silica glass than that calculated by the CRN theory. The findings highlight the importance of understanding the internal structure of materials in predicting their physical properties.

The research not only sheds light on the strength of silica glass but also suggests potential implications for other abnormal properties of silica glass. Unusual compressibility, low thermal expansion, and other properties of silica glass might also be related to the existing fissures in the structure. These findings open up new avenues for understanding and manipulating the properties of silica glass, with potential applications in various industries. More details about these structural correlations with other abnormal properties of silica glass will be discussed in future research.

One interesting feature of silica glass is the dependence of its properties on cooling rate. The cooling rate in the high-temperature region from melting temperature T_m to the critical temperature T_c influences the number of embryonic clusters. The total number of clusters varies inversely with the cooling rate. Thus, the number of fissures in fast cooling silica glass is less than that in slow cooling silica glass. Accordingly, the permeation rate of helium through silica glass with fast cooling is expected to be lower than that of slow cooling glass. This prediction should be experimentally verified in the near future.

In conclusion, the recently proposed nanoflake model supports the hypothesis of McAfee, Leiby and Chen suggested more than 60 years ago that silica glass contains a random collection of atomic-sized

fissures and openings. These fissures and openings provide the passage in the glass structure and are the origins of high permeation of helium through the silica glass.

Use of AI tools declaration

The author declares that no Artificial Intelligence (AI) tools were used in the creation of this article.

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Conflict of interest

The author declares no conflict of interest.

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