



# Correlation between Structure Characteristics and Pair Radial Distribution Function in Silica Glass under Compression

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Received 28 November 2018

Revised 25 December 2018; Accepted 26 December 2018

**Abstract:** We have studied structure of silica glass at different pressures and temperature of 300K by using Molecular Dynamics simulation (MD) method. The model consists of 6000 atoms (2000 Si, 4000 O atoms) with the periodic boundary condition. We applied the Morse-Stretch potentials which describe the pairwise interactions between ions for  $\text{SiO}_2$  system. There is structural phase transformation from tetrahedra ( $\text{SiO}_4$ ) to octahedra ( $\text{SiO}_6$ ) network structure. There is splitting in the Si-Si pair radial distribution function (PRDF) at high pressure (100 GPa). The original of this splitting relates to the edge- and face-sharing bonds. The new second peak of the O-O PRDF at the high pressure originates from oxygen atoms of the edge-sharing bonds. Thus, there is rearrangement of O atoms. O atoms have tendency to more order arrangement that leads to form some oxygen hcp and fcc structure in the model at high pressure.

**Keywords:** Molecular Dynamics simulation (MD), Silica ( $\text{SiO}_2$ ), Structure, the peak splitting.

## 1. Introduction

Silica ( $\text{SiO}_2$ ) is one of the most intensively investigated materials due to its importance in high technology materials (ceramic, semiconductor, solar cell) and geophysical sciences.  $\text{SiO}_2$  is typical network-forming oxide that studied for a long time by both experiments (X-ray diffraction, neutron diffraction, nuclear magnetic resonance, ...) and simulations. These studies have shown that under different temperature and pressure conditions, the change of network structure have a great influence on the physical properties of the  $\text{SiO}_2$  material. Zachariasen [1] predicted that the structure of  $\text{SiO}_2$  in amorphous and liquid state comprised mainly by  $\text{SiO}_4$  basic structural units that are linked together to form network structure at different temperature. This prediction is confirmed by Mozzi and Warren through X-ray diffraction [2]. The short- range order structure are determined by calculation of the coordination number, the radial distribution function of the Si-Si, Si-O and O-O pairs, distribution of

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<https://doi.org/10.25073/2588-1124/vnumap.4304>

the O-Si-O and Si-O-Si bond angles in  $\text{SiO}_x$  units. The Si-O-Si bond angle in the  $\text{SiO}_2$  glass is about  $144^\circ$ . The result of the high-energy X-ray diffraction for amorphous  $\text{SiO}_2$  presented the Si-O-Si bond angle is  $147^\circ$ . By the  $^{17}\text{O}$  NMR spectrum analysis of  $\text{SiO}_2$  glass, the mean Si-O-Si bond angle is  $144^\circ$  [1]. By using MD simulation, network structure of  $\text{SiO}_2$  is built from basic structural units  $\text{SiO}_4$  at low pressure. Under compression, there is transformation from  $\text{SiO}_4$  structure to  $\text{SiO}_6$  structure via  $\text{SiO}_5$  unit. At high pressure, structure of  $\text{SiO}_2$  is a mixture of  $\text{SiO}_x$  ( $x=4,5,6$ ) units [3-5]. At all temperature and ambient pressure, structure of  $\text{SiO}_2$  is mainly  $\text{SiO}_4$  units that form tetrahedra network. The fraction of  $\text{SiO}_5$  is very negligible. Thus,  $\text{SiO}_5$  units are the same as structural defects in  $\text{SiO}_2$  [6-8]. The properties of silica depend on the change of fraction of  $\text{SiO}_x$  units as well as the type of linkages and the spatial distribution of  $\text{SiO}_x$  units. Therefore, the studying of structure of  $\text{SiO}_2$  at different temperature and pressure conditions is necessary. In this paper, we use MD simulation and visualization of MD data to investigate  $\text{SiO}_2$  system. The aim of this work is to clarify the correlation between structure characteristics and pair radial distribution function, explain the splitting of Si-Si PRDF and the second peak of O-O PRDF in Silica glass under compression.

## 2. Calculation method

We used MD simulation method and employed the Morse–Stretch potential to construct MD models for  $\text{SiO}_2$ . Details about potential parameters can be found in reference [9]. The MD initial configuration is generated by randomly placing 6000 atoms (2000 Si, 4000 O atoms) in cubic box ( $44.65 \times 44.65 \times 44.65$  Å) with periodic boundary condition. To remove the effect of remembering initial configuration, the sample is heated up to 6000 K and relaxed after  $2.10^4$  MD steps to reach the equilibrium. Then, the sample was cooled down to the designed temperature and pressure (300K and 0 GPa, denoted M1 model) and relaxed in a long time. After that, the models at different pressures (0, 30 and 100 GPa) were constructed by compressing M1 model. Next, these models were relaxed for  $10^6$  MD steps in NPT ensemble to reach the best equilibrium. The structural characteristics of considered models are determined by averaging over 1000 configuration during the last  $2.10^4$  MD steps.

## 3. Result and discussion

The result of pair radial distribution functions is given in figure 1. The result is consistent with previous simulations and experimental data [10-15]. For Si-O pair, the position of the first peak at 1.60 Å. Under compression, the first peak shifts to the right at 1.68 Å. Conversely, the first peak of Si-Si and O-O pair shift to the left under compression. It means that the bond length of Si-O is longer, the bond length of Si-Si and O-O is shorter. These is explained by the transformation from  $\text{SiO}_4$  units to  $\text{SiO}_6$  units via  $\text{SiO}_5$  units (figure 2). Note that, there is splitting of the first peak of Si-Si PRDF (located at  $r_1 = 2.70$  and  $r_2 = 3.10$  Å) and appearance the new second peak of the O-O PRDF (located at 3.4 Å). The cause of these interesting results will be more analyzed and clarified in the following section. The figure 2 showed the dependence of coordination number on pressures. It showed that, at low pressure, the structure of  $\text{SiO}_2$  is comprised mainly by  $\text{SiO}_4$  basic structural units ( $\text{SiO}_4$  means that Si atom is surrounded by four O atoms at the nearest-neighbor distance). The fraction of  $\text{SiO}_4$  units is 99% but the fraction of  $\text{SiO}_5$  and  $\text{SiO}_6$  units is negligible. As increasing pressure, the fraction of  $\text{SiO}_4$  decrease strongly, the fraction of  $\text{SiO}_6$  units increases. At high pressure, the structure of  $\text{SiO}_2$  is comprised mainly by  $\text{SiO}_6$  units. Thus, there is structural phase transformation from  $\text{SiO}_4$  tetrahedra to  $\text{SiO}_6$  octahedra network under compression. The  $\text{SiO}_x$  ( $x=4,5,6$ ) basic structural units are linked each other by common oxygens to form continuous random network in three-dimensional space.

The network structure of SiO<sub>2</sub> glass at different pressures is visualized in figure 3. We found that, the SiO<sub>x</sub> units are connected each other by sharing one, two or three oxygens and these ones corresponding to the corner-, edge- or face-sharing bonds. The bond statistics corner-, edge- and face-sharing bonds between two adjacent SiO<sub>x</sub> units are showed in table 1.

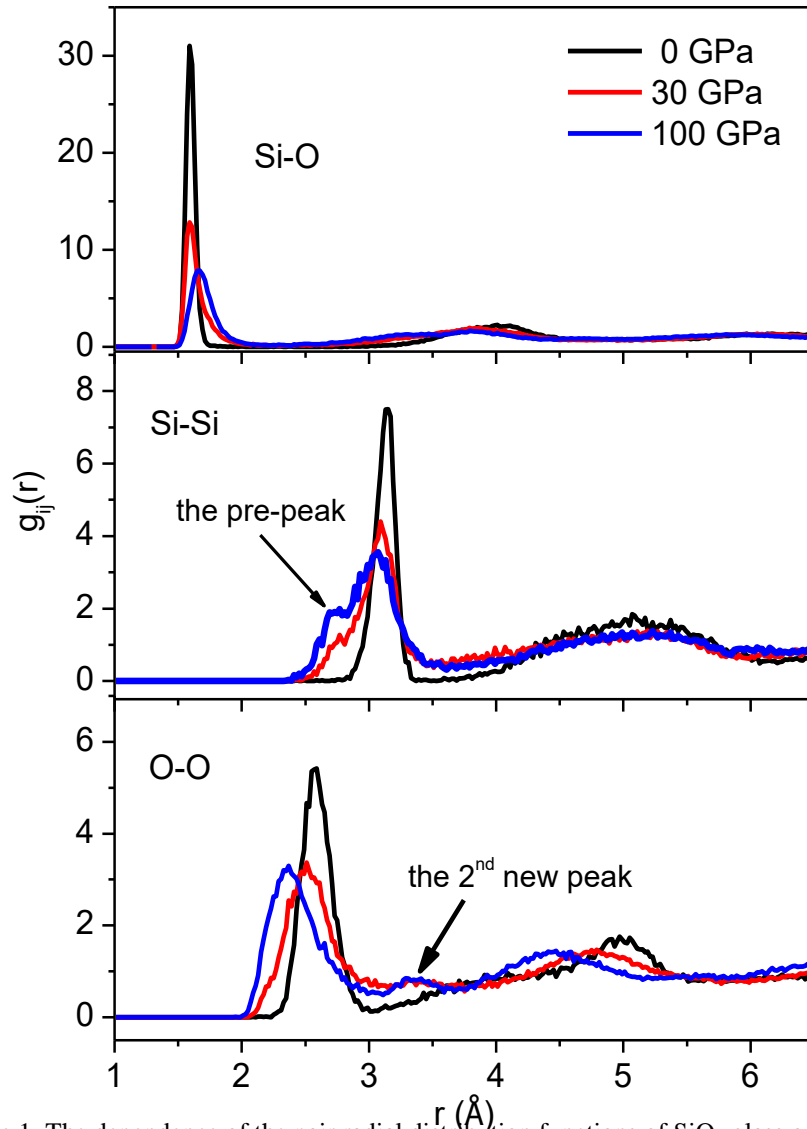


Figure 1. The dependence of the pair radial distribution functions of SiO<sub>2</sub> glass on pressures

Table 1. The number of oxygen corner-sharing (N<sub>c</sub>), edge-sharing (N<sub>e</sub>) and face-sharing (N<sub>f</sub>) atoms in SiO<sub>2</sub> system.

P (GPa)	0	30	100
N <sub>c</sub> (%)	99.65	66.67	17.20
N <sub>e</sub> (%)	00.35	30.85	70.85
N <sub>f</sub> (%)	00.00	02.48	11.95

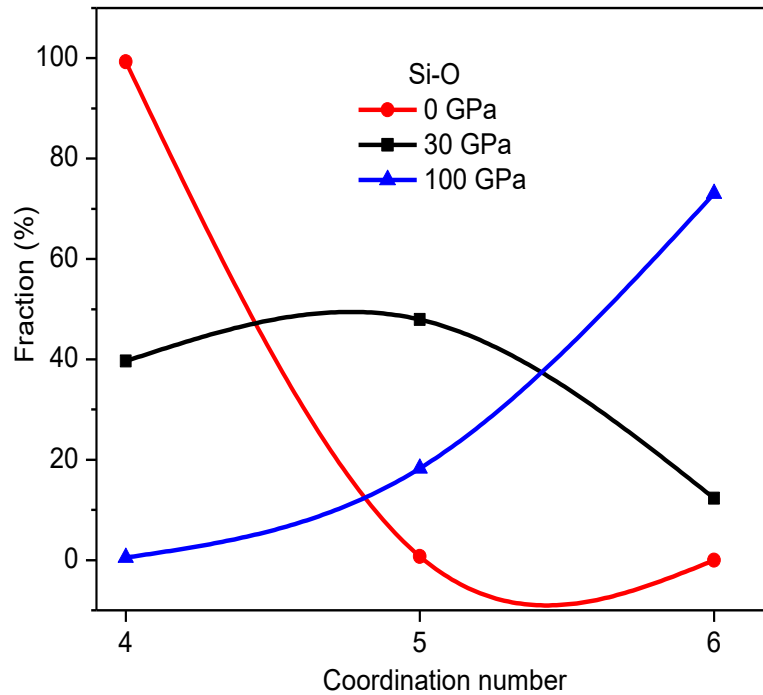


Figure 2. The dependence of coordination number on pressures.

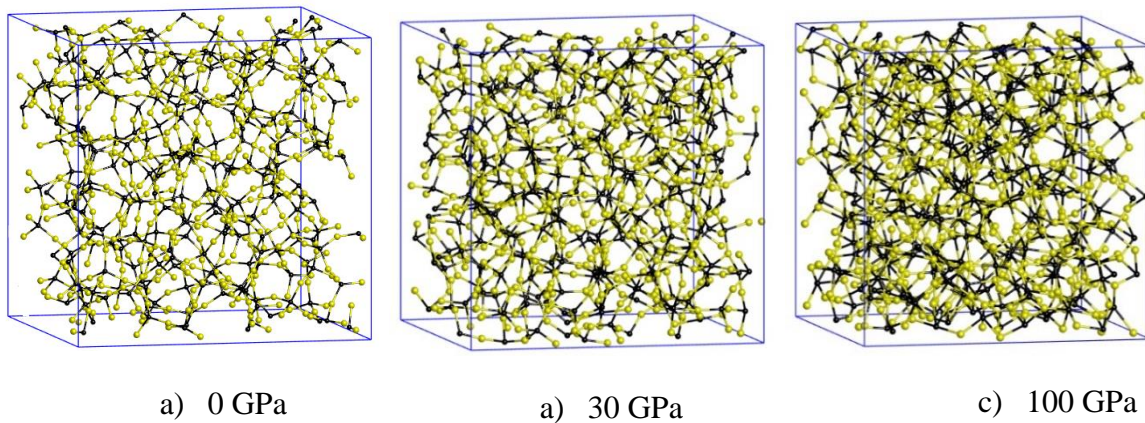


Figure 3. The network structure of  $\text{SiO}_2$  glass at different pressures.

The result shows that at 0 GPa, links between two adjacent  $\text{SiO}_x$  units are mainly corner-sharing bonds (99.65 %). When pressure increases, the fraction of corner-sharing bonds decreases, the fraction of edge- and face-sharing bonds increases. At high pressure, links between two adjacent  $\text{SiO}_x$  units are mainly the fraction of edge-sharing bonds. As above mentioned, the structure of  $\text{SiO}_2$  is mainly build by  $\text{SiO}_4$  tetrahedra units at 0 GPa and  $\text{SiO}_6$  octahedra units at 100 GPa. It means that links between two

adjacent  $\text{SiO}_4$  units are mainly corner-sharing bonds, meanwhile links between two adjacent  $\text{SiO}_5$ ,  $\text{SiO}_6$  units are mainly edge-, face- sharing. Thus, the first peak splitting in the Si-Si PRDF at  $r_1 = 2.70$  and  $r_2 = 3.10$  Å at 100 GPa relates to the edge-, face-sharing bonds. Next, we focus on explaining the origin of appearance of the second new peak in O-O PRDF at 100 GPa. We calculated and analyzed the O-O PRDF of oxygen corner-, edge- and face-sharing atoms. This result is presented in figure 4.

For the O-O PRDF of oxygen corner- and face-sharing atoms, they have only single peak that located at about 2.50 Å and 2.26 Å, respectively. However, the new second peak is observed in the O-O PRDF of oxygen edge-sharing atoms. This demonstrated that oxygen edge-sharing atoms cause the second peak of the O-O PRDF located at 3.40 Å. Moreover, we found that, with further increasing pressure, both of Si and O sublattices have a slight change. Meanwhile Si sublattice is more easily compressed than O sublattice at high pressure. O atoms have tendency to more order arrangement that leads to form some hexagonal close-packed (hcp) and faced centered cubic (fcc) structure of oxygen atoms in the model at high pressure. This result is visualized in figure 5.

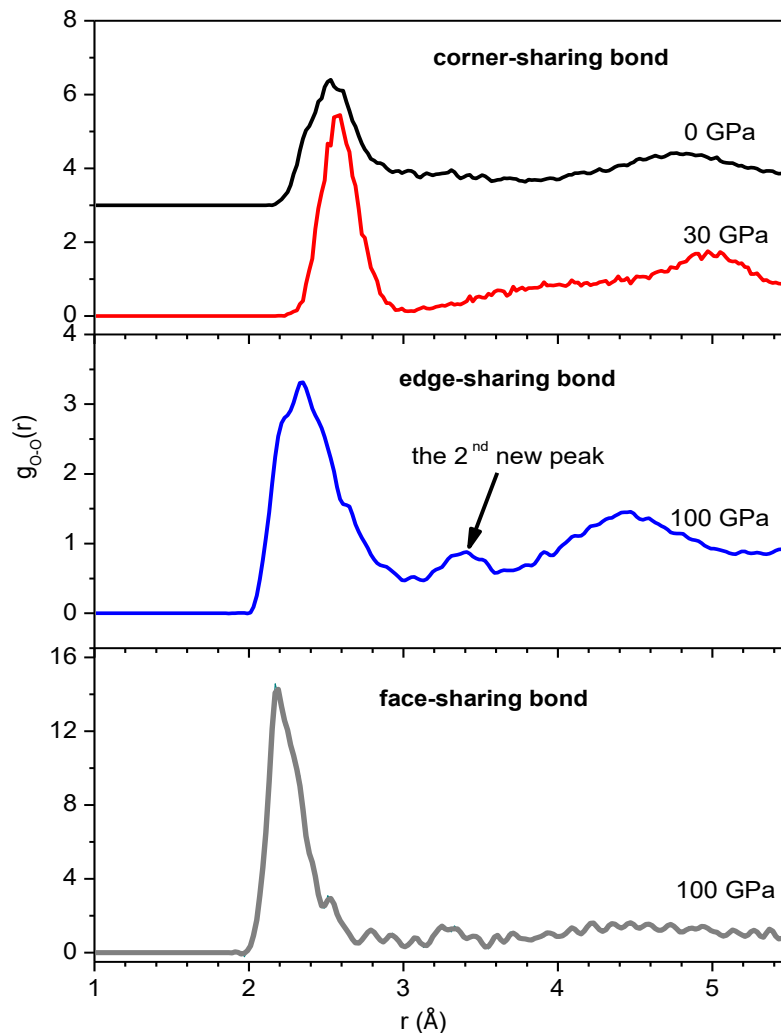


Figure 4. The O-O pair radial distribution functions of oxygen corner-, edge- and face-sharing atoms.

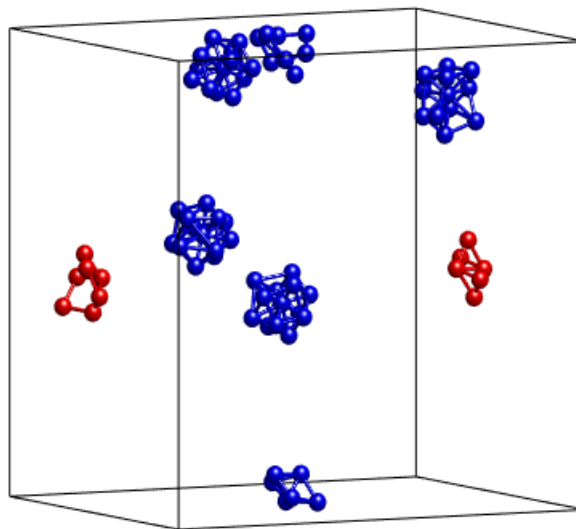


Figure 5. The fcc O atoms in blue color and hcp O atoms in red color at 100 GPa.

#### 4. Conclusion

In this paper, we have obtained the main results as following:

(i) The structure of  $\text{SiO}_2$  is built by  $\text{SiO}_x$  ( $x=4,5,6$ ) basic structural units, meanwhile, the structure of  $\text{SiO}_2$  is comprised mainly by  $\text{SiO}_4$  units at low pressure and  $\text{SiO}_6$  units at high pressure. There is structural phase transformation from tetrahedra ( $\text{SiO}_4$ ) to octahedra ( $\text{SiO}_6$ ) network structure via  $\text{SiO}_5$  units.

(ii) The  $\text{SiO}_x$  units are connected each other by the corner-, edge- and/or face-sharing bonds.

(iii) The splitting in the Si-Si PRDF at high pressure due to the edge- and face-sharing bonds and oxygen edge-sharing atoms cause the second peak of the O-O PRDF.

(vi) Under compression, O atoms have tendency to more order arrangement that leads to form some hcp and fcc structure of O atoms in the model at high pressure.

#### Acknowledgements

This research is funded by the Vietnamese Ministry of Education and Training project (B2018-BKA-57)

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