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

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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 SiO_2 system. There is structural phase transformation from tetrahedra (SiO_4) to octahedra (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 (SiO2), Structure, the peak splitting.

1. Introduction

Silica (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. 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 SiO_2 material. Zachariasen [1] predicted that the structure of SiO_2 in amorphous and liquid state comprised mainly by 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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the O-Si-O and Si-O- Si bond angles in SiO_x units. The Si-O-Si bond angle in the SiO_2 glass is about 144°. The result of the high-energy X-ray diffraction for amorphous SiO_2 presented the Si-O-Si bond angle is 147°. By the ^{17}O NMR spectrum analysis of SiO_2 glass, the mean Si-O-Si bond angle is 144 ° [1]. By using MD simulation, network structure of SiO_2 is built from basic structural units SiO_4 at low pressure. Under compression, there is transformation from SiO_4 structure to SiO_6 structure via SiO_5 unit. At high pressure, structure of SiO_2 is a mixture of SiO_x (x=4,5, 6) units [3-5]. At all temperature and ambient pressure, structure of SiO_2 is mainly SiO_4 units that form tetrahedra network. The fraction of SiO_5 is very negligible. Thus, SiO_5 units are the same as structural defects in SiO_2 [6-8]. The properties of silica depend on the change of fraction of SiO_x units as well as the type of linkages and the spatial distribution of SiO_x units. Therefore, the studying of structure of SiO_2 at different temperature and pressure conditions is necessary. In this paper, we use MD simulation and visualization of MD data to investigate 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 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 (44.65×44.65×44.65 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 SiO4 units to SiO6 units via SiO5 units (figure 2). Note that, there is splitting of the first peak of Si-Si PRDF (located at r1 = 2.70 and r2 = 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 SiO2 is comprised mainly by SiO4 basic structural units (SiO4 means that Si atom is surrounded by four O atoms at the nearest-neighbor distance). The fraction of SiO4 units is 99% but the fraction of SiO5 and SiO6 units is negligible. As increasing pressure, the fraction of SiO4 decrease strongly, the fraction of SiO6 units increases. At high pressure, the structure of SiO2 is comprised mainly by SiO6 units. Thus, there is structural phase transformation from SiO4 tetrahedra to SiO6 octahedra network under compression. The SiOx (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_2 glass at different pressures is visualized in figure 3. We found that, the SiO_x 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_x units are showed in table 1.
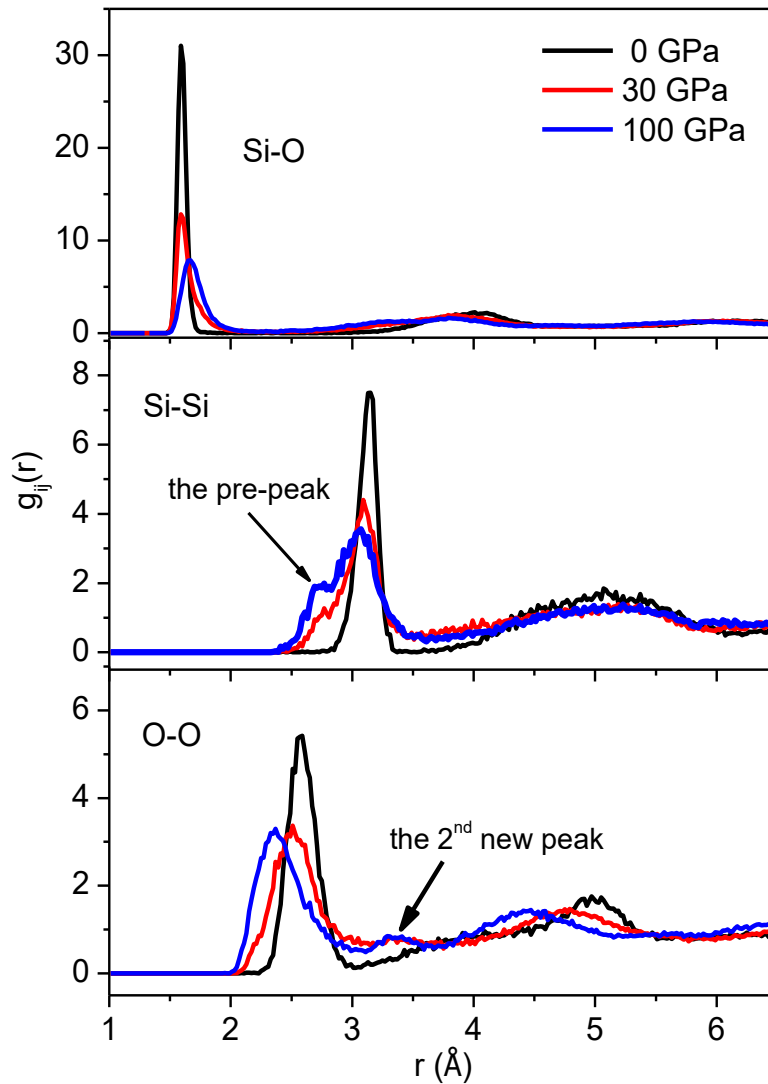

Figure 1. The dependence of the pair radial distribution functions of SiO_2 glass on pressures

Table 1. The number of oxygen corner-sharing (N_c), edge-sharing (N_e) and face-sharing (N_f) atoms in SiO_2 system.

P (GPa)	0	30	100
N_c (%)	99.65	66.67	17.20
N_e (%)	00.35	30.85	70.85
N_f (%)	00.00	02.48	11.95

Figure 2. The dependence of coordination number on pressures.

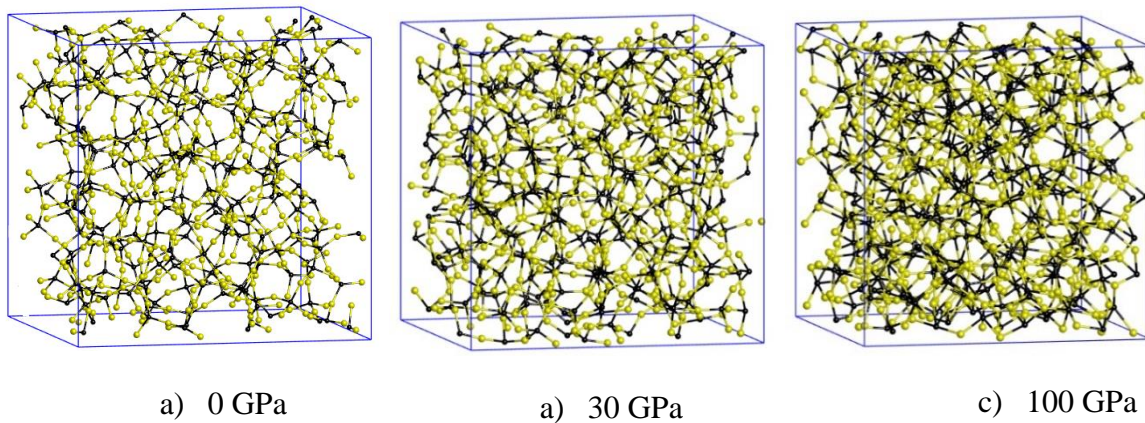a) 0 GPa   a) 30 GPa   c) 100 GPa

Figure 3. The network structure of SiO₂ glass at different pressures.

The result shows that at 0 GPa, links between two adjacent 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 SiO_x units are mainly the fraction of edge-sharing bonds. As above mentioned, the structure of SiO₂ is mainly build by SiO_4 tetrahedra units at 0 GPa and SiO_6 octahedra units at 100 GPa. It means that links between two

adjacent SiO_4 units are mainly corner-sharing bonds, meanwhile links between two adjacent SiO_5, 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.
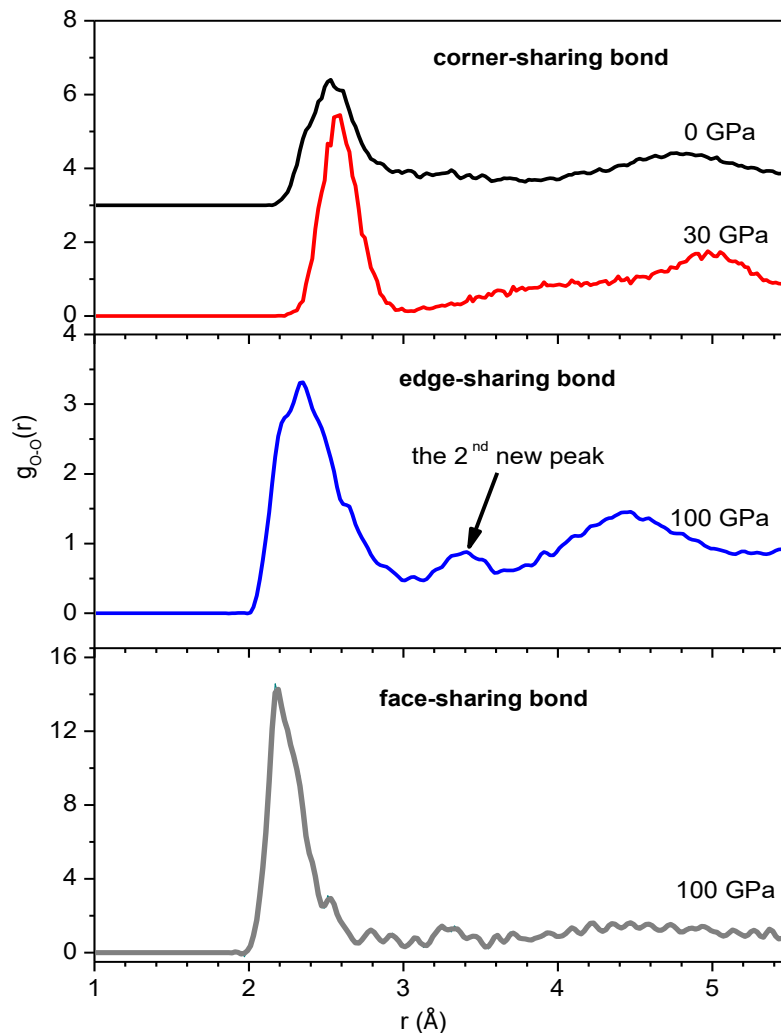

Figure 4. The O-O pair radial distribution functions of oxygen corner-, edge- and face-sharing atoms.
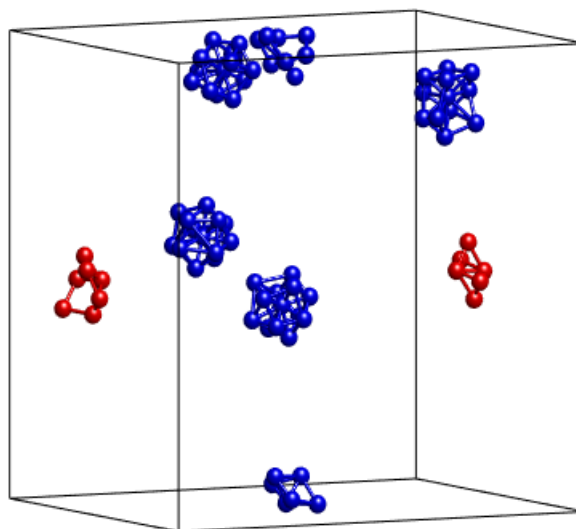
Figure 5. The fcc O atoms in blue color and hcp O atoms in red color at 100 GPa.

4. Conclusion

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

(i) The structure of SiO_2 is built by SiO_x (x=4,5,6) basic structural units, meanwhile, the structure of SiO_2 is comprised mainly by SiO_4 units at low pressure and SiO_6 units at high pressure. There is structural phase transformation from tetrahedra (SiO_4) to octahedra (SiO_6) network structure via SiO_5 units.

(ii) The 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

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