

Polyamorphism of Amorphous SiO₂ under Compression Based on Two-State Model

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Abstract

Microstructure and polyamorphism of amorphous SiO₂ at 500 K and 0–20 GPa were investigated by molecular dynamics simulation. The results indicate that in the studied pressure range, the network structure of amorphous SiO₂ includes SiO_x structure units ($x = 4, 5, 6$) and OSi_y ($y = 2, 3$). The two-state model (high density and low density) is used to describe the network structure of the amorphous SiO₂. High-density phase is formed by SiO₅ and SiO₆ linked via OSi₃, low-density phase is formed by SiO₄ linked via OSi₂. The proportion of high density phase and low density phase depend on pressure.

Keywords: simulations, molecular dynamics, polyamorphism

1. Introduction

The polyamorphism is the coexistence of many amorphous states (glass or liquid), which have the same composition but different local structure and density [1]. Microstructure and polyamorphism in amorphous SiO₂ are investigated by both simulations [2, 3] and experiments [4, 5]. The results show that the structure of amorphous SiO₂ is mainly the mixture of SiO_x polyhedra ($x = 4, 5, 6$) under compression. High pressure X-ray diffraction experiment on amorphous SiO₂ have insighted into the structure. Sato *et al.* have just observed the three-dimension network structure, comprising of coner-shared SiO₄ tetrahedra up to 8–10 GPa [4]. This was confirmed by using molecular dynamics (MD) simulation [3]. At higher pressure, the present of 5-fold coordination number (SiO₅) and 6-fold coordination number (SiO₆) correspond to the tranformation from tetrahedral network to octahedral network [5]. To clarify the changing structural process, two-state model has been developed [6]. Basing on this model, the structure of some amorphous materials such as SiO₂, H₂O, GeO₂, P, Si, etc. can be considered comprising two phases: low density phase and high density phase. The coexistence of these phases will lead to many states which have the same chemical composition and the different densities. However, the structural details are still a matter of debate. Our previous study, we used MD simulations and visulaziation to study polyamorphism and structural transition in liquid SiO₂ under pressure, the structural characteristic of low and high density phases. In this study, we

continue to use the same tool to investigate the strutral transition in amorphous SiO₂ under pressure. In addition, we also discuss further the relationship between structural and mechanical properties published by the other authors.

2. Caculation method

The SiO₂ models comprising 666 silicon and 1332 oxygen particles have been generated by MD simulations with BKS (Van Beest-Kramer-Van Santen) potential and periodic boundary condition [7]. It can be described as:

$$U(r_{ij}) = \frac{q_i q_j e^2}{r_{ij}} + A_{ij} \exp(-B_{ij} r_{ij}) - C_{ij} r_{ij}^{-6} \quad (1)$$

where u_{ij} is the interatomic potential; q_i or q_j is an effective charge of the ith atom; e is the electronic unit charge; r_{ij} is the interaction distance between atoms i and j ; a_{ij} , b_{ij} and c_{ij} are the interaction parameters (table 1). The Verlet algorithm is used to integrate the equation of motion, with the time step is 0.47 fs.

Table 1. Parameters of BKS potential used to model amorphous SiO₂ [8].

	A _{ij} (eV)	B _{ij} (Å ⁻¹)	C _{ij} (eV Å ⁶)	Charge (e)
O-O	1388.773	2.760	175.000	q _O = - 1.2
Si-O	18003.757	4.873	33.538	q _{Si} = + 2.4
Si-Si	0.0	0.0	0.0	

The SiO₂ models are constructed at 500 K and in the 0–20 GPa pressure ranges. Initial configuration is generated by placing all particles in simulation box.

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This configuration is heated to 5000 K and then cooled to 500 K. After that, the sample at 500 K and ambient pressure has been done in NPT ensemble (the constant pressure and temperature) until reaching equilibration. From this sample, we constructed samples at 500 K and different pressure. The obtained samples are relaxed in NVE ensemble (the constant volume and energy) for about 10^6 MD time steps. The coordination number and pair radial distribution function are calculated by averaging over 1000 last configurations separated by 10 MD time steps.

3. Results and discussion

At ambient pressure, the first peak of the Si-Si, Si-O and O-O pair radial distribution functions (PRDF) are 3.12, 1.60 and 2.60 Å, respectively. This result is in agreement with experiment in the position and height of first PRDF peaks [9].

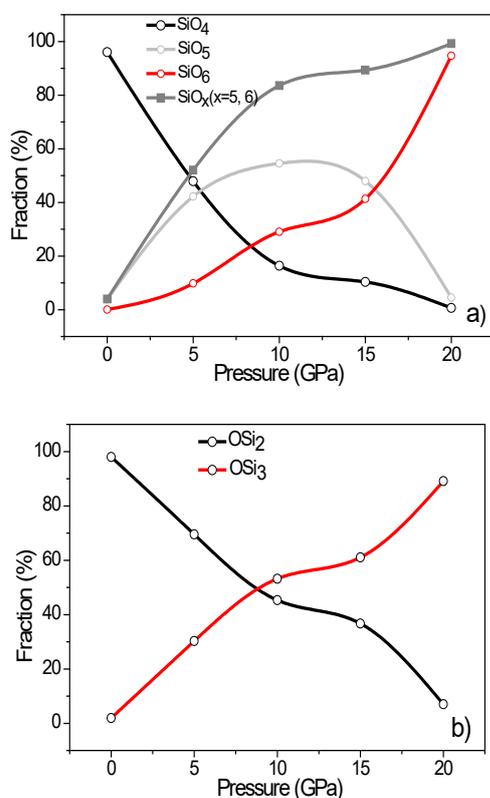


Fig.1. The fraction of SiO_x (A) và OSi_y (B) in amorphous SiO₂ under pressure.

The network structure of amorphous SiO₂ comprises of SiO_x units that relate to short range order and OSi_y units that relate to intermediate range order. The structure units consist of a centre atom that surrounded by neighbor atoms at the cut off distance. The cut off distance used equal 2.38Å. In the 0-20 range pressure, most of structure units are SiO_x with

$x=4, 5, 6$ and OSi_y with $y=2, 3$. Fig. 1a and 1b show how the fraction of structure units depend on pressure. At ambient pressure, the fraction of SiO₄ units and SiO₅ units are 96% and 4%, respectively; the fraction of SiO₆ units is very small (fig. 1a). As increased pressure, the fraction of SiO₄ units reduces to approximately 1% at 20 GPa, while the fraction of SiO₆ units tends to an increase, approximately 95% at 20 GPa. The fraction of SiO₅ units rises to maximum value in 10-15 GPa range before tending a decrease when pressure increases.

Fig. 1b shows that the fraction of OSi_y depends on pressure. As increased pressure, the fraction of OSi₂ units reduces from 96% at ambient pressure to 1% at 20 GPa. At 8-10 GPa, the fraction of OSi₂ and OSi₃ units approximately equal. Fig. 1a also shows that at threshold pressure, the fraction of SiO₄ units and the total fraction of SiO₅ and SiO₆ units have the same value. Therefore, as pressure increase, the decreasing fraction of SiO₄ units occurs simultaneously with the decreasing fraction of OSi₂ and the increasing total fraction of SiO₅ and SiO₆ units occurs simultaneously with the increasing fraction of OSi₃ units.

To clarify the geometry structure of structure units as pressure changes, we investigated the angle distribution and distance distribution in the SiO_x and OSi_y units at 0, 5 and 15 GPa (fig. 2 and 3). The results show that with each type of SiO_x structure units, the O-Si-O angle distribution and Si-O bonding distance distribution are independent on pressure. Thus, the network structure of amorphous SiO₂ only changes in the fraction of structure units without the geometry structure of each type of units under pressure.

Next, we investigated how SiO_x structure units linked together. At atmosphere pressure, the most linkages between SiO_x structure units via one bridging oxygen atom, the kind of linkage is called the corner-sharing linkage. As pressure increase, the number of OSi₃ increase, which leads to increase in the number of edge-sharing linkages (linkage between SiO_x structure units via two bridging oxygen atom or face-sharing linkages (linkage between SiO_x structure units via three bridging oxygen atom), see table 2. This result show that the amorphous SiO₂ structure becomes more tightly packed.

We visualized the SiO₂ network structure at 5 and 15 GPa (fig. 4). The yellow domain is formed by SiO₄ linked through OSi₂. The distribution of this domain is not uniform. The yellow domain dominates at low pressure (or low density) and called low density phase. The black domain is cluster of SiO₅ and SiO₆ linked together through OSi₃. At high

pressure, this domain expands and dominates. So, the structure of amorphous SiO_2 at high pressure (or high density) is mainly formed by the black domain, that called high density phase. The result indicates that the the structure of amorphous SiO_2 seem to be similar to the structure of liquid SiO_2 [10]. It was also shown in

previous experiments [11]. The compression mechanism in amorphous SiO_2 may be closely related to those in liquid SiO_2 . There is also transition from the low density phase to high density phase corresponding to the transition from OSi_2 to OSi_3 linkages, under pressure.

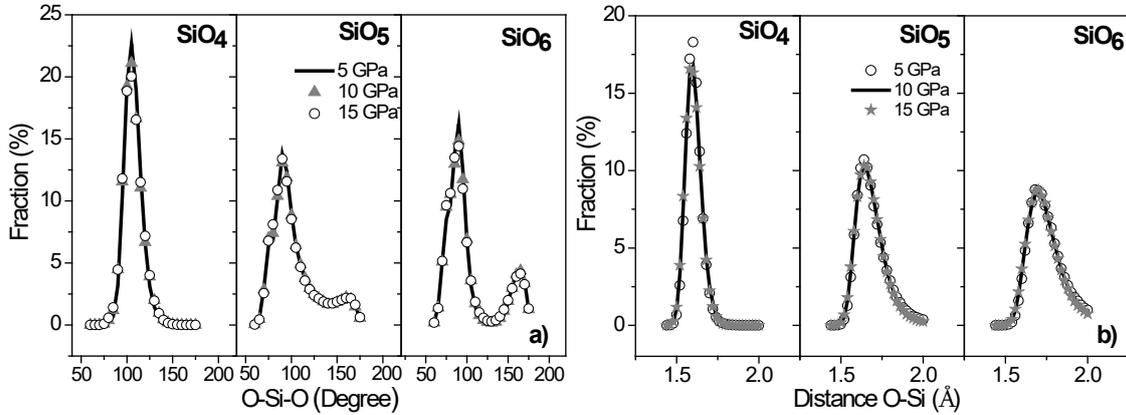


Fig. 2. The angle distribution O-Si-O (a) and the bonding distance distribution O-Si (b) of SiO_x .

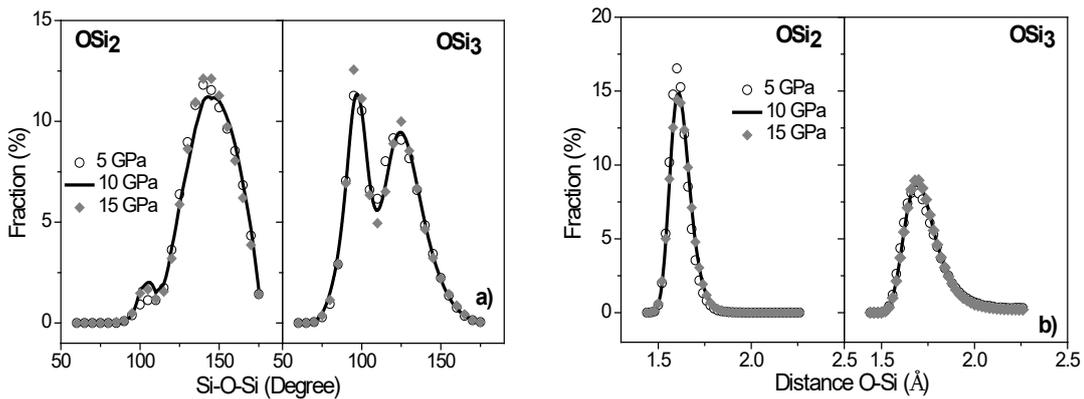


Fig. 3. The angle distribution Si-O-Si (a) and the bonding distance distribution O-Si (b) of OSi_y .

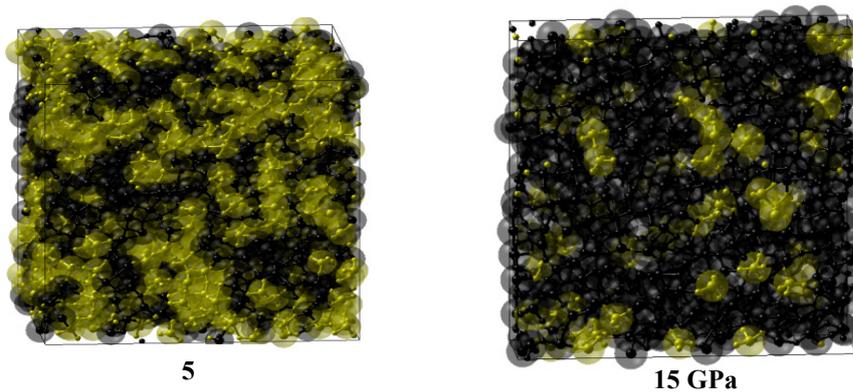


Fig. 4. The distribution of SiO_x and OSi_y at 5 and 15 GPa. The yellow domain is cluster of SiO_4 linked together through OSi_2 . The black domain is cluster of SiO_5 and SiO_6 linked together through OSi_3 .

Table 2. The number of OSi_3 , N_e and N_f in amorphous SiO_2 . N_e is the number of edge-sharing linkages, N_f is the number of face-sharing linkages.

P(GPa)	0	5	10	15
OSi_3	64	1007	1772	2034
N_e	21	560	1054	1229
N_f	1	17	69	72

Some studies using MD simulation showed that the relationship between structural and mechanical properties [12-14]. The strain at fracture increases from 10.5% to 24.1% when pressure increases from 0 to 15 GPa [12]. Other studies also indicated the transition from elastic to plastic behavior at 8÷10 GPa [13, 14]. Under pressure, the samples display more plastic before fracture. The appearance of 5-fold coordination during compression have been shown to be responsible for the enhanced ductility in amorphous SiO_2 [12, 14]. 5-fold Si atoms tend to stay closer together and the clusters of 5-fold Si atoms are not uniformly distributed throughout the sample. While, Davila et al. showed that the transition between elastic and plastic behavior is correlated to changes in the ring size distribution, which characterizes the intermediate range order of these amorphous materials [13].

In this study, 5-fold coordination plays an intermediate role in the conversion from 4-fold coordination into 6-fold coordination (Fig. 1b). The changing of intermediate range order leads to more and more tightly packed structure at high pressure. At 8÷10 GPa is an important pressure threshold. At this value, we observe the change in the correlation between the proportion of structure units. This leads to the domination of low density phase at below the pressure threshold and the domination of high density phase at above the pressure threshold. So, the structural origins of enhanced ductility and the transition between elastic and plastic behavior in amorphous SiO_2 can be attributed to the change of proportion of low density phase and high density phase in this material under compression.

4. Conclusion

Using MD simulation, we show that the network structure of amorphous SiO_2 is formed by five structure units, SiO_x units (with $x = 4, 5, 6$) and OSi_y units (with $y = 2, 3$). The network structure divides into two phases: low density phase and high density phase. The low density phase consists of SiO_4 linked through OSi_2 , high density phase consisting of SiO_5 and SiO_6 linked through OSi_3 . As pressure increases, there is a structure transition from the low density phase to the high density phase. The low density phase dominates at below 8÷10 GPa, and the high

density phase dominates above 8÷10 GPa. The structural transition is the structural origins which is responsible for the enhanced ductility in amorphous SiO_2 under pressure.

Acknowledgments

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