PAPER • OPEN ACCESS

Molecular dynamics simulation of amorphous silica under pressures

View the article online for updates and enhancements.

Molecular dynamics simulation of amorphous silica under pressures

G T T Trang[1,2]**, P H Kien**[2]**, P K Hung**[1] **and N V Hong**[1]

[1] Department of Computational Physics, Hanoi University of Science and Technology, 1 Dai Co Viet, Hanoi, Vietnam.
[2] Department of Physics, Thainguyen University of Education, 20 Luong Ngoc Quyen, Thainguyen, Vietnam.

E-mail: `giapthuytrang@dhsptn.edu.vn`

Abstract. Models of amorphous silica have been produced at 500 K, and in pressures range 0÷100 GPa by molecular dynamics simulation. Topological analysis is performed based on the basic units and transition to different a-types, where a is the O_{xx} and O_{xy} (x, y = 4, 5, 6). The simulation shows that the fraction of different types of basic units varies strongly and the mid-range structure modifies stronger than the short-range structure under pressure. In the 0÷100 GPa pressure range, structure of amorphous silica occurs the transformation from D4- to D6 domain which correspond to the intervals of 0÷ 5, 5÷15 and 15÷100 GPa. We also found a number of O_{456} connected with three different Si atoms. Upon compression, the structural change is accompanied with the $O_{xx} \rightarrow O_{xy}$ transition and two parallel processes: merging and splitting of domains which relate to the change of domain-boundary atoms.

1. Introduction

Silica glass has received great interest from both experimental and theoretical studies. It is the typical network-forming oxide with cornersharing tetrahedral (SiO_4) at ambient condition. The relatively-rigid SiO_4 tetrahedron is the basic structural unit in silica glasses: each Si connects to four nearest neighbor O atoms, with Si–O bond length of approximately 1.62 Å, and each O links to two nearest neighbor Si atoms [1-3]. The Si–O–Si bond angle is very flexible and distributes in a 120°-180° wide range with the peak at around 144° which shows the structural differences of amorphous silica in comparison to crystalline forms. Besides, the O–Si–O angles distribution in relatively-rigid SiO_4 tetrahedra has the peak at around 105°–109° and these SiO_4 tetrahedra a link to each other forming a continuous random network in 3D space [4-6]. As having revealed in works [7-8], the topology of SiO_x tetrahedra is identical and as initial study of α-SiO_2 compacted by applying the pressure of the order of 10^4 to10^5 atm, Bridgman et al. [8] showed that the shortrange order of the basic structural units unchanged. By using infrared spectroscopy data, Williams et al. [9] suggested that the change in the coordination number occurs starting around 17 to 25 GPa. X-ray Raman scattering indicated that the transformation occurs from a tetrahedral quartzlike to an octahedral stishovitelike in α-SiO_2 between 10 and 20 GPa [10]. Sato [7,11] also confirmed that upon compression α-SiO_2 behaves as a single amorphous polymorph having a tetrahedral structure below 10 GPa and, α-SiO_2 transforms from SiO_4 to SiO_6 unit structure at the pressure from 20 to 35 GPa, and then behaves as a single amorphous polymorph having an octahedral (SiO_6) structure at the pressure from 35 GPa

to at least 100 GPa. Although xray diffraction [11] elucidated some effects of high pressures on the structure of α-SiO_2, it was not possible to solve the structure using this technique alone [12]. A combination of experimental diffractions and molecular dynamics simulations has shed light on the analysis of the structural transformation of α-SiO_2 upon compression [13,14]. The transformation in the short-and intermediate-range order of α-SiO_2 has been studied by many molecular dynamics simulations [15-18]. Amorphous silica has been study for a long time. However, structural characteristics are still open questions. The experimental evidence of phase boundaries is still in debate and many results were contradictory among different publications on structural phase transition at high pressures [19-21]. In this work, the structure and structural transformation of silica glass under densification will be investigated via analyzing the geometric units and transition to different a-types, where a is the O_{xx} and O_{xy} (x, y = 4, 5, 6).

2. Calculation method

Molecular dynamics simulation was carried out for amorphous silica at temperature of 500 K and pressures of 0÷100 GPa. The model contained 1666 Si and 3332 O atoms. The van Beest Kramer van Santen potential [22] was applied. Structural analysis of the model are well suited to other experimental and other calculated results [23]. In this simulation, to integrate the equation of motion, the Verlet algorithm is used with time step of 0.48 fs.
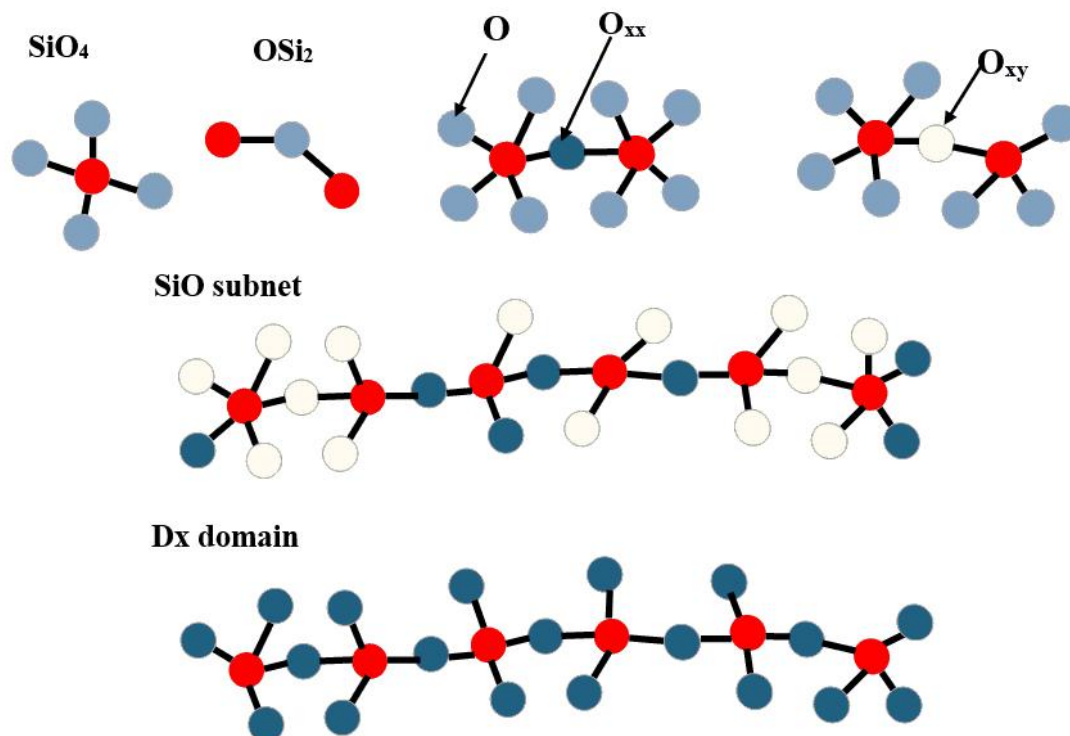

Figure 1. Basic unit, SiO subnet and Dx domain. The basic unit consists of central atom and coordinated atoms connected with the central atom by Si-O bond (SiO_4, SiO_5, SiO_6, OSi_2 and OSi_3); O_{xx}, O_{xy} is connected with Si having the same and different number x, respectively; SiO subnet consists of atoms connected with each other by Si-O bonds; Dx domain is a SiO subnet which comprises Si having the same coordination number and O_{xx}.

The initial configuration is generated by placing all atoms randomly in a simulation box and heating it up to 5000 K to remove initial configuration. After that the sample is cooled down to 5000, 4000, 3000, 2000, 1000 and 500K. Next, a long relaxation (10^7 time steps) has been done to get equilibrium state using isothermal-isobaric (NPT) ensemble (in the isothermalisobaric ensemble, the number of atoms (N), pressure (P) and temperature (T) are constant).

The Si-O bond is formed by Si and O of which the distance is smaller than r_{cut}. Here r_{cut} = 2.3 Åis determined from the first minimum of pair radial distribution function (PRDF). The basic unit such as SiO_x and OSi_y consists of a central atom and coordinated atoms, where x, y is the number of coordinated atoms for SiO_x and OSi_y, respectively. Si atoms can be assorted into Si_4, Si_5, Si_6 and Si_{oth} where Si_4, Si_5 and Si_6 have the coordination number of 4, 5 and 6, respectively; the coordination number of Si_{oth} is less than 4 or larger than 6. O is classified into two types: O_{xx} and O_{xy}. The first type is connected only with Si having the same coordination number. In contrast, the second type is connected with Si atoms which possess different coordination number. For instance, O is connected with two Si_4 and one Si_5. We also assort O by s index which denote Si_x connected with the given O. For instance, O_{44} links with two Si_4; O_{456} is connected to Si_4, Si_5 and Si_6. SiO subnet comprises Si and O atoms which are connected with each other by bridging oxygen as schematically illustrated in Fig. 1. Dx domain is the SiO subnet comprising Si and O_{xx} as shown in Fig. 1. Here all Si atoms have the same coordination number. The atoms are divided into four groups: D4, D5, D6 and domain-boundary (DB). Dx includes atoms belonging to Dx domains, while DB comprises O_{xy}, non bridging oxygen and Si_{oth}. Because most of SiO_x are either of SiO_4, SiO_5 or SiO_6, the majority of Si belong to D4, D5 and D6. In contrast, most DB atoms are O_{xy}. From such definition follows that the atoms of Dx domains are located nearby in separate space regions of network structure. Meanwhile DB atoms reside in the boundary between those regions. The size of Dx domain as well as SiO_x subnet is defined as the number of atoms in it. The fraction of basic units is given as $C_{SiO_x} = n_{SiO_x}/n_{Si}$; $C_{OSi_y} = n_{OSi_y}/n_O$; where n_{SiO_x}, n_{OSi_y}, n_{Si}, n_O is the number of SiO_x, OSi_y units, Si and O atoms, respectively; x = 4, 5, 6 and y = 2, 3. The fraction of DB and Dx atoms is equal to $C_{DB} = n_{DB}/n$; $C_{Dx} = n_{Dx}/n$, where n_{DB}, n_{Dx}, n is the number of DB, Dx atoms and total number of atoms, respectively.

3. Results and discussion

Fig. 2 shows the fraction of basic units as a function of pressure. As can be seen, the fraction C_{SiO_4} monotonously decreases with increasing pressure, while C_{SiO_6} increases which indicates the transformation from tetrahedral to octahedral structure. Such transformation results in the variation of C_{D4} and C_{D6} in opposite directions (see Fig. 3). We note that the curve for C_{D5} intersects with the one for C_{D4} and C_{D6} at 5 and 15 GPa, respectively and has a maximum at 10 GPa. That is similar to the results in references [7, 11, 12, 24, 25]. The transformation O_{xx} $\rightarrow O_{xy}$ is accompanied with splitting of large domains into small ones. For instance, O_{44} O_{45} results in that O_{44}, Si_4 of a D4 domain transform to O_{xy} and Si_5. In contrast, $O_{xy} \rightarrow O_{xx}$ leads to merging of small domains into large ones.

As shown in Fig. 3, C_{DB} rapidly increases up to 0.47 and then decreases, which indicates the intensive splitting of D4 domains within 0÷10 GPa. At pressures larger than 10 GPa, the splitting of D5 and merging of D6 domains occurs parallel so that C_{DB} varies.

Unlike C_{SiO_4} and C_{SiO_6} the graph for C_{SiO_5} possesses a maximum around 10 GPa. The fraction of DB and D5 atoms shows a pronounced peak around 10 GPa demonstrating that the number of domains increase fast upon small pressures, and then decreases at large pressures. This trend can be seen from Table 1 showing the size distribution of domains obtained from a configuration of simulated models. It is clearly that the number of domains having fewer atoms largely increases and then decreases. We also found a small amount of domains with size about 50 atoms (about 1 % of total atoms). Moreover, all models contain one domain with size bigger
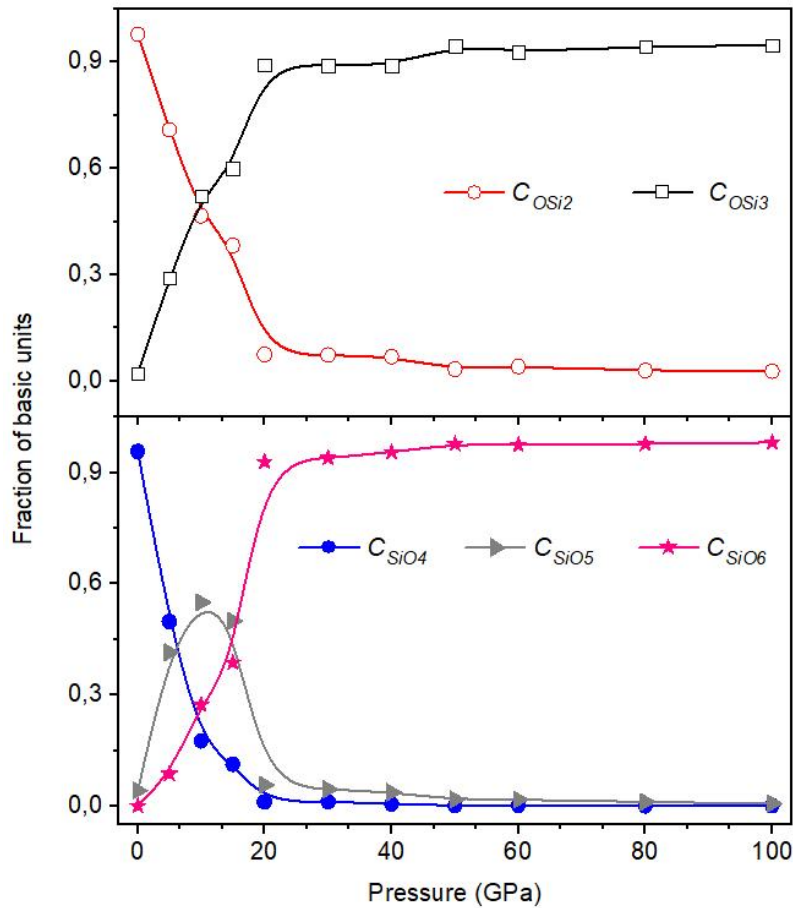
Figure 2. Pressure dependence of fraction of basic units OSi_y (upper) and SiO_x (lower).

200 (about 4% of total atoms).

The structure of glass silica under compression can be described by the three-phases: D4, D5 and D6 phase. The D4, D5 and D6 phase is formed by D4, D5 and D6 domain, respectively. We note that the curve for C_{D5} intersects with the one for C_{D4} and C_{D6} at 5 and 15 GPa, respectively. This shows that, when the pressure is less than 5 GPa, the system exists at D4 phase; at 5 GPa system consists of D4 and D5 phases, in the pressure range 5÷15 GPa system exists at D5 phase; at 15 GPa system consists of D5 and D6 phases, greater than 15 GPa system exists in D6 phase.

According to Fig. 4, the pressure dependence of number of D4, D5 and D6 domains has a maximum. At pressures less than 10 GPa the number of D4 domains increases due to splitting of large domains into small ones. Upon larger pressures the decreasing number of D4 domains is caused by decreasing number of SiO_4. In the case of D6 domains the increase and decrease of domain's number is due to increasing number of SiO_6 and merging of small domains into large ones. Unlike D4 and D6 the graph for D5 possesses a minimum around 10 GPa. This probably
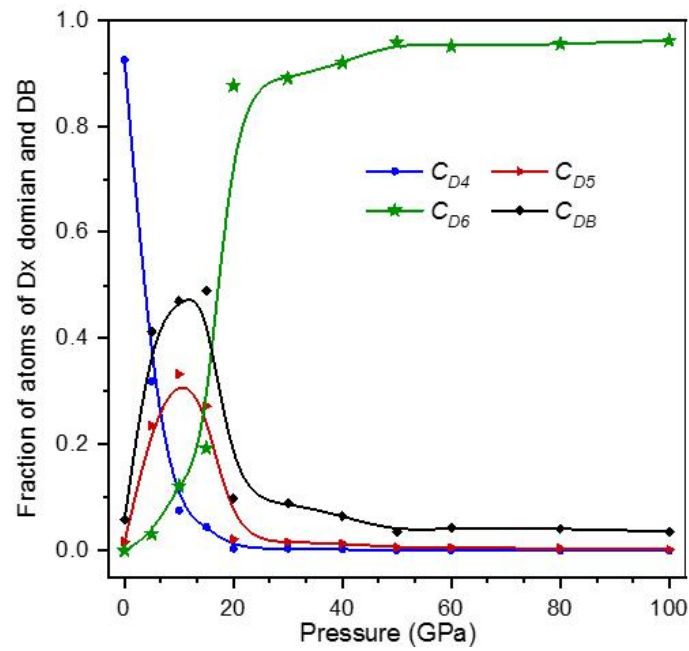
Figure 3. . Pressure dependence of fraction of DB and Dx atoms. Here DB atoms are located in the boundary region between domains. Dx domain comprises Si having the same coordination number and O_{xx} which are connected with each other by Si-O bonds.
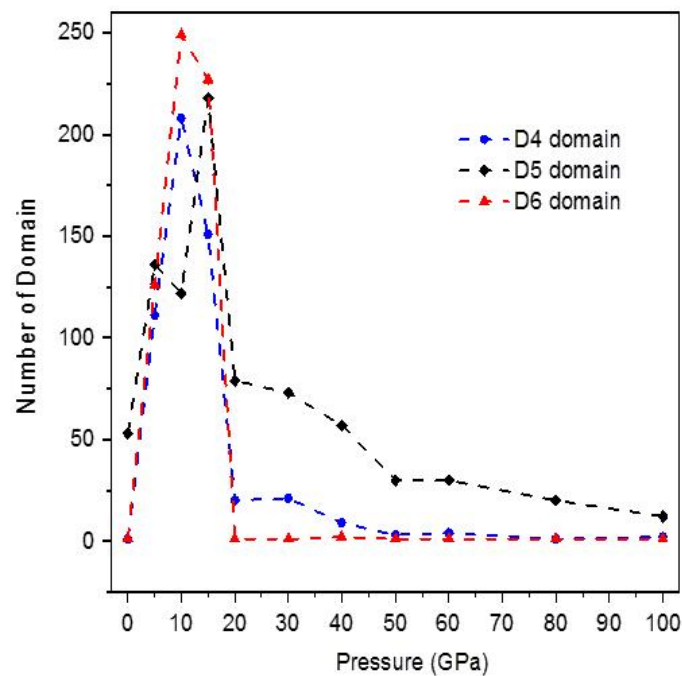

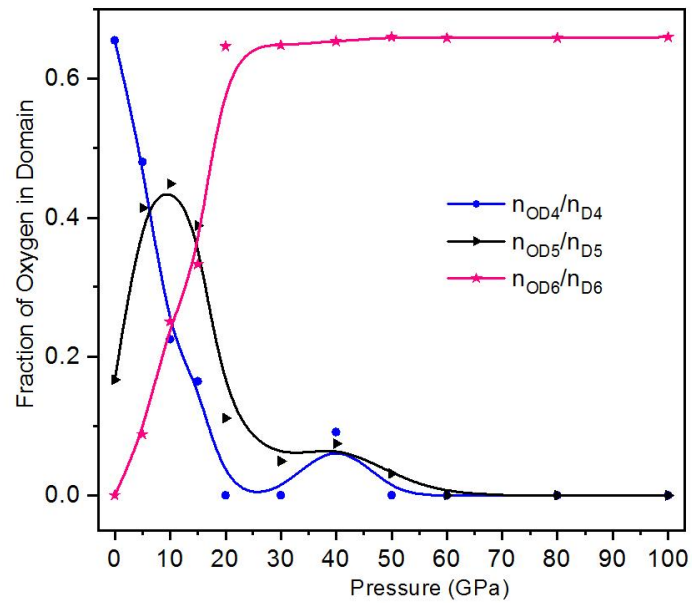**Figure 4.** Pressure dependence of number of domains.

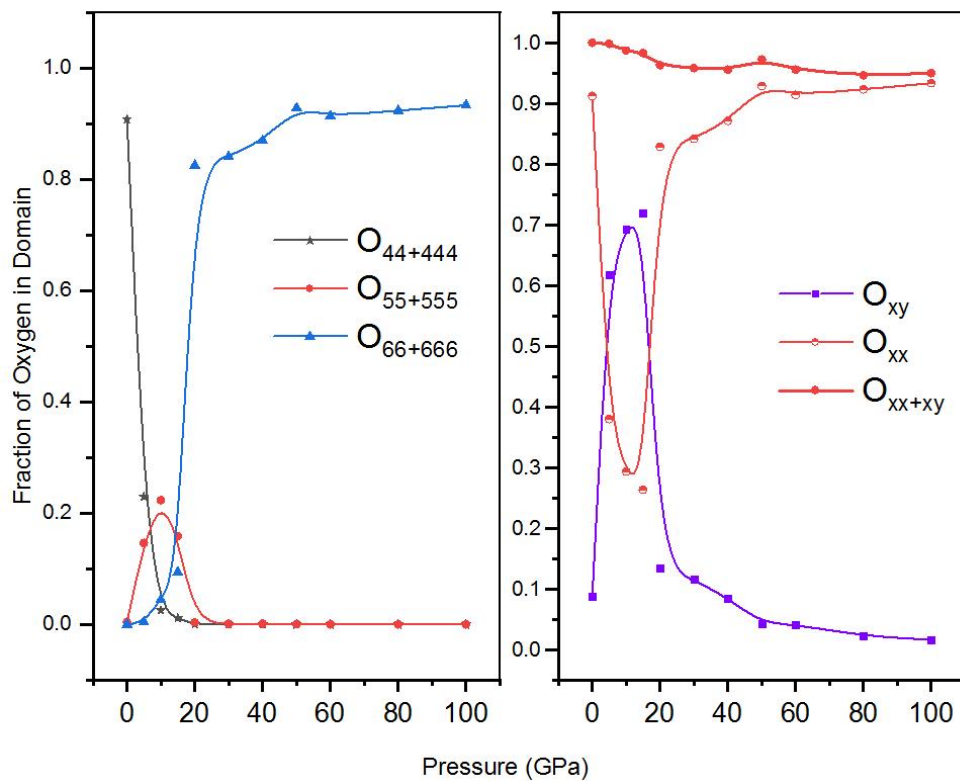**Figure 5.** Pressure dependence of fraction of oxygen in Domain.

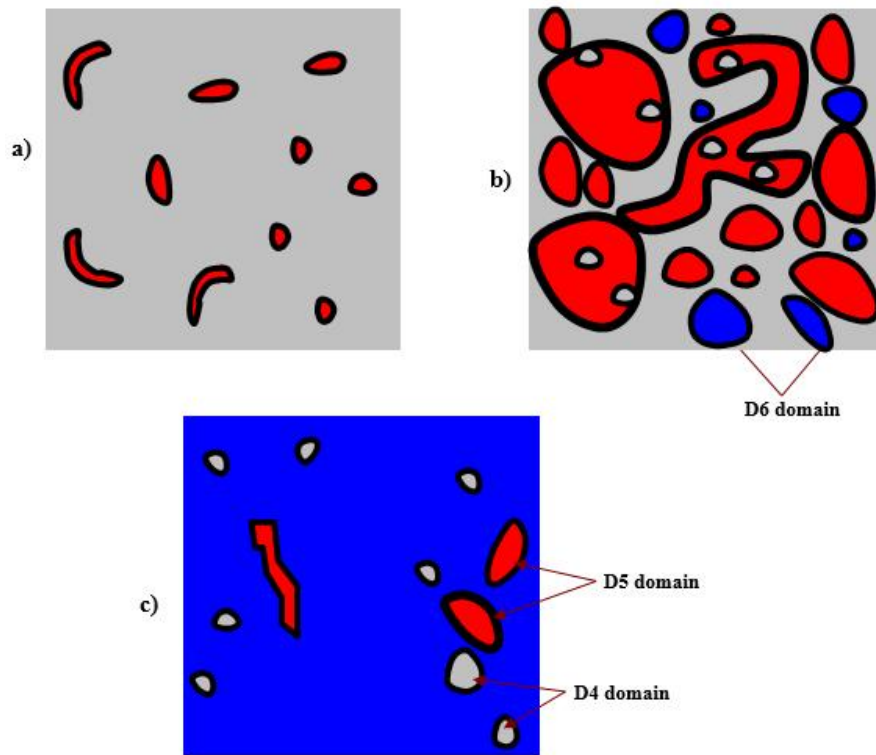**Figure 6.** Pressure dependence of fraction of type of oxy in domain.

Figure 7. a) Domain structure at ambient pressure, b) three-domain region and c) high pressure. The BD atoms are located in the black area.

Table 1. Size and number distribution of domains under pressure.

Size range	0 GPa	5 GPa	10 GPa	15 GPa	20 GPa	40 GPa	60 GPa	80 GPa	100 GPa
1-4	51	317	520	530	97	67	34	21	14
5-19	3	46	54	50	2	0	0	0	0
20-49	0	3	4	11	0	0	0	0	0
50-99	0	4	0	3	0	0	0	0	0
100-199	0	1	0	1	0	0	0	0	0
> 200	1	2	1	1	1	1	1	1	1

corresponds to that the fraction of SiO_5 reaches a maximum at this point. At pressures $0 \div 5$ GPa and $10 \div 15$ GPa the number of D5 domains increases due to increasing number of SiO_5 and splitting of large domains into small ones, respectively. At pressures $5 \div 10$ GPa and $15 \div 20$ GPa the number of D5 domains decreases due to decreasing number of SiO_5 and splitting of large domains into small ones, respectively.

As shown in Fig. 5, n_{OD4}/n_{D4} monotonously decreases in opposite with increasing n_{OD6}/n_{D6}. This is caused by that the D4 and D6 domain have respectively large and small size at low pressures. In contrast at high pressures the size of D6 domain is larger than that of D4 domain.
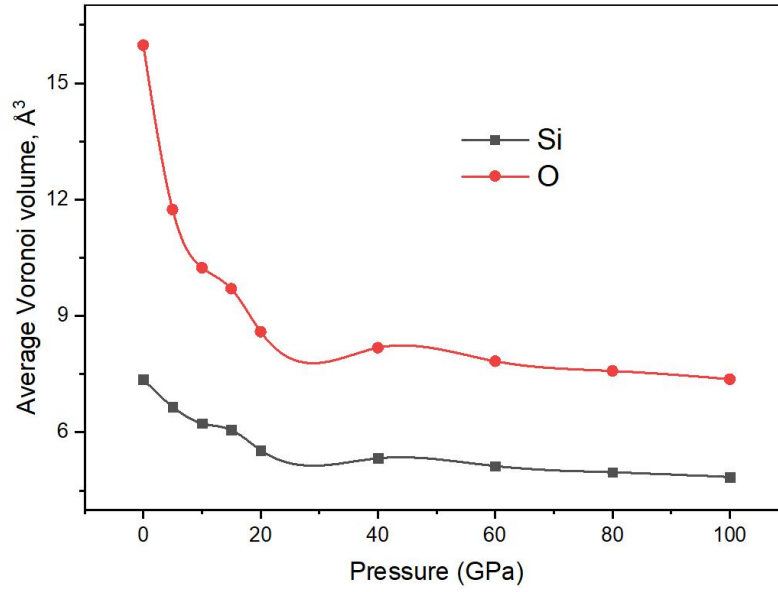
Figure 8. Pressue dependence of average Voronoi volume of Si-, O-atoms and DB-, Dx- atoms.
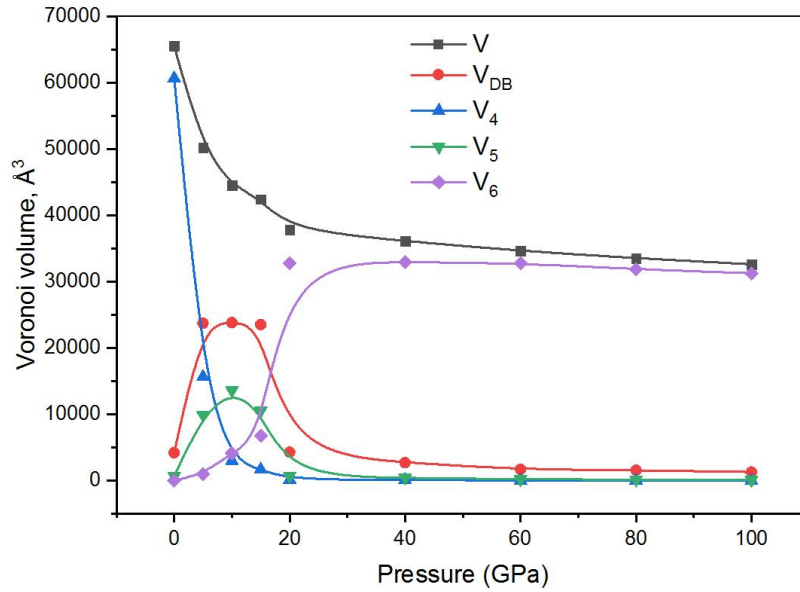

Figure 9. Pressue dependence of Voronoi volume of DB and Dx atoms.

D5 domain possesses large size in the interval of 10÷15 GPa. Therefore the fraction n_{ODi}/n_{Di} (i=4, 5, 6) is correlated with size of domains.

Table 2 displays the fraction of different type O_s. We note that O_{44}, O_{444}, O_{55}, O_{555}, O_{66} and O_{666} belong to D4, D5 and D6 domains. 90 % of total O are O_{44} at ambient pressure and O_{66}, O_{566} and O_{666} are dominant at 100 GPa. The fraction O_{xy} possesses a maximum at 10 GPa, where the number of O_{xy} is about 7% of total O (see Fig. 6), which corresponds to the

Table 2. Fraction of different type O_s, $O_s = n_{O_s}/n_O$. Here n_{O_s} is the number of O_s.

s	0 GPa	5 GPa	10 GPa	15 GPa	20 GPa	40 GPa	60 GPa	80 GPa	100 GPa
44	0.9043	0.2268	0.0252	0.0111	0	0.0003	0	0	0
45	0.0702	0.3066	0.1158	0.0570	0.0009	0	0	0	0
46	0.0003	0.0516	0.0549	0.0459	0.0027	0.0009	0.0015	0.0003	0.0006
55	0.0030	0.0864	0.1377	0.1017	0.0021	0.0015	0	0	0
56	0.0006	0.0351	0.1107	0.01290	0.0138	0.0132	0.0045	0.0024	0.0006
66	0	0.0021	0.0216	0.0375	0.0558	0.0522	0.0354	0.0249	0.0243
444	0.0039	0.0027	0.0003	0	0	0	0	0	0
445	0.0063	0.0147	0.0033	0.0006	0	0	0	0	0
446	0	0.0045	0.0018	0.0021	0	0	0	0	0
455	0.0084	0.0765	0.0375	0.0219	0	0	0	0	0
456	0.0006	0.0513	0.0576	0.0444	0.0015	0.0003	0.0003	0	0
466	0.0012	0.0084	0.0240	0.0285	0.0177	0.0090	0.0027	0.0009	0.0012
555	0.9043	0.0600	0.0858	0.0570	0.0015	0	0	0	0
556	0.0003	0.0504	0.1710	0.1890	0.0087	0.0048	0.0015	0	0
566	0	0.0195	0.1170	0.2010	0.0891	0.0561	0.0312	0.0192	0.0141
666	0	0.0021	0.0231	0.0564	0.7696	0.8176	0.8788	0.8989	0.9094

pressure interval where the total number of domains is maximal. The curve for O5 intersects the one for O_4 and O_6 at 5 and 15 GPa, respectively where $O_4 = O_{44} + O_{444}$, $O_5 = O_{55} + O_{555}$, $O_6 = O_{66} + O_{666}$. As we already mention, O_{xx} play a role to merging of domains. So the formation of large Dx domains depends on the relative value O_x. According to Fig. 6, largest O_x for 0÷5, 5÷15, 15÷100 GPa intervals is O_4, O_5 and O_6, respectively; O_{xx+xy} (x, $y = 4, 5, 6$) decreases and becomes smaller one the pressure increases indicating the appearance of SiO_m structure units ($m > 6$).

At pressures less than 5 GPa, the model contains a large D4 domain and other domains has the sizes less than. Similarly, at pressures larger 15 GPa the model possesses only one large D6 domain. In the interval of 5÷15 GPa, the largest domain is D5 type. We note that the fraction O_x ($x=4, 5, 6$) at intersected points is larger than 0.1 for two types of domains. This means that at those pressures the model contains different type domains. The domain structure at ambient pressure can be described as shown in Fig. 7a. Here a number of D5 domains separated at large distances from each other are uniformly distributed in the model. The D4 domain spreads over whole model which comprises about 90 % of total atoms. With increasing pressure a number of large D4, D5 and D6 appear and the total number of domains increases. At high pressures only large D6 and D5 domains coexist. The D4 domain consists of fewer atoms (see Fig. 7b and 7c). Fig. 8 shows average Voronoi volumes of Si- and O-atom. As expected, $< v_{Si} >$, $< v_O >$ monotonously decreases. Moreover, $< v_O >$ decreases faster than $< v_{Si} >$ indicating that the mid-range structure modifies stronger than the short-range structure upon compression. The volume occupied by DB and Dx atoms is also presented in Fig. 9. From these graphs we can make following remarks: (i) The volume occupied by DB increases and then decreases with increasing pressure. This is due to increasing number of DB for the interval of low pressures and the compensation effect between the increasing DB atoms and decreasing Voronoi atomic volume at large pressures. For the interval of 5÷15 GPa, the volume occupied by DB is larger than that occupied by D4, D5 and D6 atoms. (ii) The volume occupied by D4 atoms, monotonously

decreases due to the decreasing D4 atoms and Voronoi atomic volume. The D5 atoms show a pronounced maximum at 10 GPa is mainly related to strong variation of number of D5 atoms. (iii) The volume for D6 atoms increases fast for the interval of $0 \div 20$ GPa and then slightly varies at higher pressures. The increasing volume for $0 \div 20$ GPa is caused by increasing number of D6 atoms.

Under compression, Voronoi volumes of O atoms decreases faster than Voronoi volumes of Si indicating that the mid-range structure modifies stronger than the short-range structure upon compression. Therefore, this study can explain the densification is caused by (i) decrease in Voronoi volume; (ii) transformation D4 $\rightarrow$ D5 domain and D5 $\rightarrow$ D6 domain. The results are in agreement with previous studies [26-28].

4. Conclusion

Molecular dynamics simulation is carried out for models of amorphous silica consisting of about 4998 atoms at 500 K under pressure from 0 to 100 GPa. We found that the fraction of different types of basic units varies significantly and the mid-range structure modifies stronger than the short-range structure upon compression. The heterogeneity about structure consists of separate space regions where Dx atoms reside ($x = 4$, 5 and 6). In the interval of $0 \div 5$, $5 \div 15$ or $15 \div 100$ GPa the dominant structure of amorphous silica is D4, D5 or D6 phase, respectively. Furthermore, oxy atoms bonded with different types Si are located in boundaries between domains. Each model comprises a large amount of small domains and fewer ones with size bigger than 1% of total atoms. The size of largest domain in all models exceeds 4% of total atoms. We also found that in amorphous silica, a number of oxy connected with three Si types; they can reaches up to 7% O atoms in the model which has 3332 O atoms. Upon compression, the structural change is accompanied with the $O_{xx} \rightarrow O_{xy}$ transition and two parallel processes: merging and splitting of domains.

References

[1] Prescher C et al. 2017 *Proc. Nat. Acad. Sci.* **83** 10041
[2] San L T, Hong N V and Hung P K 2016 *High Pressure Res.* **36** 187
[3] Hung P K, Hong N V and Vinh L T 2007 *J. Phys.: Condens.Matter* **19** 466103
[4] Mei Q, Benmore C J, Weber J K R 2007 *Phys. Rev. Lett.* **98** 057802
[5] Mozzi R L and Warren B E 1969 *A* **2** 164
[6] Wright A C 1994 *J. Non-Cryst. Solids* **84** 352
[7] Sato T, Funamori N 2010 *Phys. Rev. B* **82** 184102
[8] Bridgman P W, Simon I 1953 *A* **24** 405
[9] Williams Q, Jeanloz R 1988 *Science* **239** 902
[10] Lin J F, Fukui H, Prendergast D, Okuchi T, Cai Y Q, Hiraoka N, Yoo C S, Trave A, Eng P, Hu M Y, Chow P 2007 *Phys. Rev. B* **75** 012201
[11] Sato T, Funamori N 2008 *Phys. Rev. Lett.* **101** 255502
[12] Benmore C J, Soignard E, Amin S A, Guthrie M, Shastri S D, Lee P L and Yarger J L 2010 *Phys. Rev. B* **81** 054105
[13] Keen D A, McGreevy R L 1990 *Nature* **344** 423
[14] Zeidler A, Wezka K, Rowlands R F, Whittaker D A J, Salmon P S, Polidori A, Drewitt J W E, Klotz S, Fischer H E, Wilding M C, Bull C L, Tucker M G and Wilson M 2014 *Phys. Rev. Lett.* **113** 135501
[15] Guerette M, Ackerson M R, Thomas J, Yuan F, Watson E B, Walker D and Huang L 2015 *Sci. Rep.* **5** 15343
[16] Tse J S, Klug D D and Page Y L 1992 *Phys. Rev. B* **46** 5933
[17] Yuan F and Huang L 2014 *Sci. Rep.* **4** 5035
[18] Koziatek P, Barrat J L and Rodney D 2015 *J. Non-Crystal. Solids* **414**
[19] Andrault D, Fiquet G, Guyot F and Hanfland M 1998 *Science* **282** 720

[20] Andrault D, Angel R J, Mosenfelder J L and Bihan T L 2003 *Am. Miner.* **88** 301
[21] Saika-Voivod I, Sciortino F, Grande T and Poole P H 2004 *Phys. Rev. E* **70** 061507
[22] Beest B V, Kramer G and Santen R V 1990 *Phys. Rev. Lett.* **64** 1955
[23] Nhan N T, Trang G T T, Iitaka T and Hong N V 2019 *Canadian Journal of Physics* **97**1133
[24] Liang Y, Miranda C R and Scandolo S 2007 *Physical review B* **75** 024205
[25] Wu M, Liang Y, Jiang J Z and John S T 2012 *Scientific reports* **2** 398
[26] Hung P K, Hong N V, Trang G T T and Iitaka T 2019 *Materials Research Express* **6** 085201
[27] Mitra S K 1982 *Philos. Mag. B* **45** 529
[28] Hung P K, Vinh L T, Hong N V, Trang G T and Nhan N T 2019 *The European Physical Journal B* **92** 166