



Original Article

The Microstructural Transformation and Dynamical Properties in Sodium-silicate: Molecular Dynamics Simulation

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Abstract: Molecular dynamics simulation of sodium-silicate has been carried out to investigate the microstructural transformation and diffusion mechanism. The microstructure of sodium silicate is studied by the pair radial distribution function, distribution of SiO_x ($x=4,5,6$), OSi_y ($y=2,3$) basic unit, bond angle distribution. The simulation results show that the structure of sodium silicate occurs the transformation from a tetrahedral structure to an octahedral structure under pressure. The additional network-modifying cation oxide breaking up this network by the generation of non-bridging O atoms and it has a slight effect on the topology of SiO_x and OSi_y units. Moreover, the diffusion of network-former atom in sodium-silicate melt is anomaly and diffusion coefficient for sodium atom is much larger than for oxygen or silicon atom. The simulation proves two diffusion mechanisms of the network-former atoms and modifier atoms.

Keywords: Molecular dynamics, microstructural transformation, mechanism diffusion, sodium-silicate.

1. Introduction

The structural transformation in multi-component oxide glasses has received special attention over the past decades [1-3]. The process of structural transformation effects mechanical-, physical- and chemical-properties. The structural transformation was observed by X-ray Raman scattering, infrared spectroscopy data, X-ray diffraction [4-6]. Namely, the influence of pressure on the structural transformation of silica materials (that is the typical network-forming oxide with corner-sharing SiO_4 tetrahedral at ambient condition) has been investigated in detail. Upon compression, silica transforms

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from tetrahedral structure to octahedral structure through intermediate phase structure which was SiO_5 [7, 8]. Due to the flexibility of the SiO_5 (intermediate phase), the dynamic characteristics strongly depended on the intermediate phase fraction. At a pressure of 10-12 GPa, SiO_5 concentration increased, resulting into the increase in diffusion coefficient and decrease in viscosity [9, 10]. The process of structural transformation under compression in multi-component oxide glass systems is similar to in silica system. However, due to the flexible network structure, this material has interesting structural change. For example, the addition of alkali oxides into pure silica (SiO_2) disrupts the basic silica network by breaking part of the Si-O bonds, generating non-bridging oxygen (NBO) [11-12]. But there is not this phenomenon at high pressure. The Na_2O concentration in sodium-silicate increases, it will result in increasing $[\text{NBO}]^-$ concentration, reducing melting temperature and viscosity... [13-14]. Research results in [15, 16] show that $[\text{NBO}]^-$ bonds and $[\text{BO}_4]^-$, $[\text{AlO}_4]^-$ units will be generated in the glass network structure as Na_2O is added into $\text{B}_2\text{O}_3\text{-SiO}_2$, $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$. At low Na_2O concentration, Na^+ cations tend to be close to the $[\text{BO}_4]^-$, $[\text{AlO}_4]^-$ units and they have role of charge-balance. Conversely, at higher Na_2O concentrations, the Na^+ cation tend to be closer to the $[\text{NBO}]^-$ and they act as the network-modifier. It can be seen that the structure as well as the structural transformation in the multi-component oxide glasses is an interesting issue. In addition, the dynamic change when adding alkali oxide was also reported [11,12,16]. In particular, several studies have shown that the mobility of alkali compare to network atoms (Si, O) and the existence of two different diffusion mechanisms of the network atoms and alkali atoms [17]. By experimental neutron scattering, the Raman spectrum shows that the structural factor of Na-Na has a peak at the wave vector $q = 0.95 \text{ \AA}^{-1}$ [18, 19]. This supports the study of the channel diffusion mechanism of alkali ion in many simulated studies. Accordingly, the preferential pathways are where the alkali atom moves easily [20, 21].

In this paper, we will investigate the influence of pressure on the process of structural transformation in Sodium-silicate ($\text{Na}_2\text{O-SiO}_2$). The structure properties are clarified through the pair radial distribution function (PRDF); distribution of SiO_x , OSi_y coordination units; the average coordination number for Silicon, Oxygen and Sodium; the partial bond angle distributions for structural units SiO_x , OSi_y ... The diffusion mechanism of sodium atom in the network will be studied clearly.

2. Calculation Method

Molecular dynamical simulations were performed for the $\text{Na}_2\text{O-9SiO}_2$ system. The simulated system is composed of $N = 3000$ atoms (900 Si, 1900 O and 200 Na atoms) at a temperature of 2500K and in the pressure range 0-60 GPa. We simulate sodium silicate with the short-range Buckingham potential that has the form:

$$V_{ij}(r) = A_{ij} \exp\left(-\frac{r}{Q_{ij}}\right) - \frac{C_{ij}}{r^6}$$

The Buckingham potential can induce spurious effects at high temperature. When r is close to zero, $V(r)$ can go to negative infinity which leads to a collapse of the interacting atoms. The potential equation consists of a long-range Coulomb potential, short distance in order for the potential energy and an additional repulsive term. This potential is applied with multicomponent silicate glasses. And it describes the glass at room density for various compositions very well. Detail about potential parameters can be found in Ref [22]. The Vervet algorithm is used to integrate the equation of motion with the simulation time step of 1.0 fs. The first model of the system is constructed by randomly generated atoms

in the simulated space. Then this model is heated to 5000K and kept at this temperature in 50.000 time-step simulations to break the initial memory of the model. Next the sample is cooled slowly to about 2500K and at the pressure of 0GPa. Next, a long relaxation (10^6 steps) has been done in NPT (the atomic number (N), the pressure (P) and the temperature (T) of the model are constant). We get the sample M1. The models at different pressures (5, 10, 15, 20, 30, 40, 60 GPa) were constructed by compressing the M1 model. To observe the dynamics of the models, the NVE (N-atomic number, volume V of total energy E constant) was used. In order to improve statistics, all quantities of considered structural data were calculated by averaging over the 5.000 configurations during the last simulation (10^6 MD steps).

The diffusion coefficient of atoms is determined via Einstein equation:

$$D = \lim_{t \rightarrow \infty} \frac{\langle R(t)^2 \rangle}{6t}$$

Where $\langle r(t)^2 \rangle$ is mean square displacement (MSD) over time t ; $t = N \cdot T_{MD}$; N is number of MD steps; T_{MD} is MD time step with value of 1.0 fs.

3. Result and Discussion

3.1. Structural Properties

The potential is used to reproduction the structure of silicate crystals and pressure dependence of transport properties of liquid silicate. Therefore, to assure the reliability of constructed models, the structure characteristic of sodium silicate under pressure is investigated via PRDF of all atomic pairs. The Figure 1 and Figure 2 display the PRDFs of Si-Si, Si-O, O-O and Si-Na, Na-O, Na-Na pairs at 3500K and 0 GPa. It can be seen that the position of first peak of $g_{Si-Si}(r)$, $g_{Si-O}(r)$, $g_{O-O}(r)$, $g_{Si-Na}(r)$, $g_{Na-O}(r)$ and $g_{Na-Na}(r)$ is 3.10 Å, 1.56 Å, 2.62 Å, 3.36 Å, 2.36 Å and 3.18 Å, respectively. The characteristic of PRDFs is in good agreement with previous data in refers [23, 24].

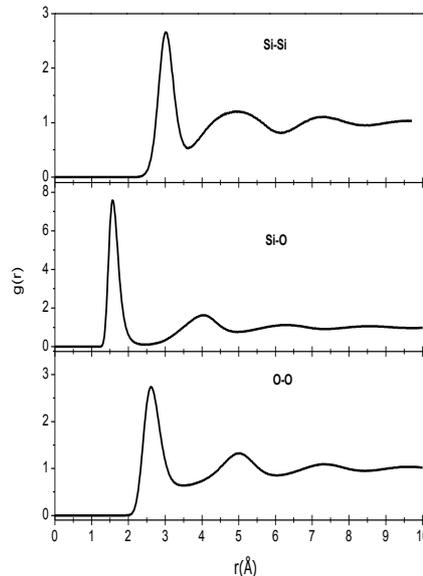


Figure 1. The pair radial distribution function of Si-Si, Si-O and O-O at 3500K and 0 GPa.

Moreover, the detail about PRDFs of all atoms at different pressure is presented in Table 1. The results reveal that the first peak of $g_{Si-O}(r)$ decrease in amplitude but its position is almost unchanged. Thus, the bond Si-O length is almost depended on compression. Under pressure, the position of the first peak of $g_{Si-Si}(r)$, $g_{Si-O}(r)$, $g_{O-O}(r)$, $g_{Si-Na}(r)$, $g_{Na-O}(r)$ and $g_{Na-Na}(r)$ decreases. Therefore, the short-range order of sodium-silicate liquid is not sensitive to the compression meanwhile intermediate- range order is very sensitive at pressures ranging from 0 to 60 GPa. Thus, liquid sodium silicate is well described by the short-range Buckingham potential.

Table 1. Structural characteristics of $Na_2O-9SiO_2$ liquid under pressure, r_{lk} is positions of first peak of PRDF, g_{lk} is high of first peak of PRDF

Model (GPa)	0	5	10	15	20	25	30	40	60	[23]	[24]
r_{Si-Si} , [Å]	3.10	3.08	3.08	3.08	3.06	3.04	3.02	3.02	2.98	3.12	3.05
r_{Si-O} , [Å]	1.56	1.56	1.56	1.56	1.56	1.58	1.56	1.56	1.58	1.65	1.62
r_{O-O} , [Å]	2.62	2.58	2.58	2.58	2.54	2.54	2.52	2.48	2.44	2.35	2.62
r_{Si-Na} , [Å]	3.36	3.26	3.14	3.06	3.08	3.02	2.98	2.88	2.86	-	3.5
r_{O-Na} , [Å]	2.36	2.30	2.26	2.24	2.20	2.18	2.16	2.10	2.08	-	2.29
r_{Na-Na} , [Å]	3.18	2.92	2.54	2.52	2.22	2.04	2.08	1.90	1.70	-	3.05
g_{Si-Si}	2.66	2.44	2.36	2.33	2.33	2.34	2.35	2.38	2.45	-	-
g_{Si-O}	7.57	6.68	6.11	5.74	5.45	5.21	5.08	4.74	4.41	-	-
g_{O-O}	2.74	2.57	2.53	2.53	2.54	2.55	2.56	2.60	2.70	-	-
g_{Si-Na}	1.62	1.77	1.85	1.91	1.91	1.94	1.93	1.95	1.95	-	-
g_{O-Na}	1.30	1.50	1.63	1.75	1.83	1.90	1.92	2.04	2.18	-	-
g_{Na-Na}	1.34	1.31	1.35	1.31	1.45	1.54	1.67	1.93	2.66	-	-

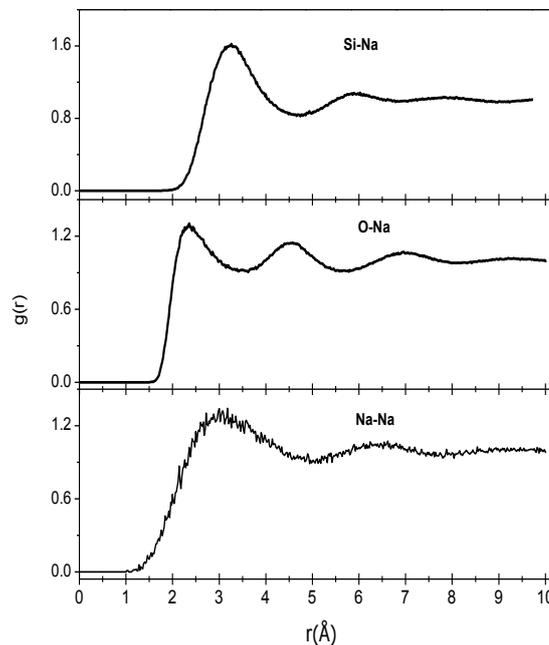


Figure 2. The pair radial distribution function of Si-Na, O-Na and Na-Na at 3500K and 0 GPa.

Figure 3 shows the coordination number distribution of network modifier atoms (Na). We can see that the average coordination of sodium is 5.8. As compressing the pressure, it increases sharply and almost unchanged at high pressure regions (40 GPa ÷ 60 GPa).

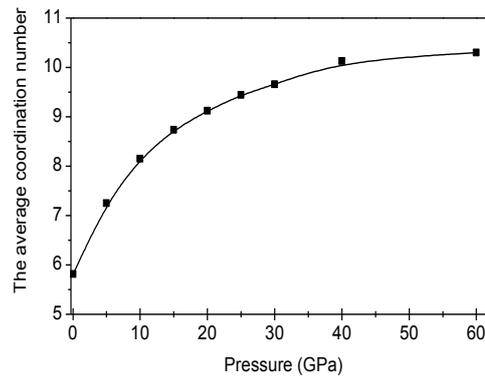


Figure 3. The average coordination number for Sodium as a function of pressure.

Moreover, it can be seen that, at ambient pressure, the average coordination of silicon is 4. Therefore, all Si atoms have fourfold-coordination forming SiO_4 tetrahedral and fraction of the structural units SiO_4 is equal to 89.35%. Under pressure, the average coordination of silicon increases. At high pressure (60 GPa), it is equal to 5.5. This means that the liquid transforms from a tetrahedral (SiO_4) to octahedral (SiO_6). Considering the distribution of structural units OSi_y , the fraction of OSi_2 is 85% at ambient pressure. It decreases meanwhile fraction of OSi_3 increases under pressure. At high pressure, the liquid has 43.97% OSi_2 and 49.36 % OSi_3 (Figure 4). The structure liquid sodium silicate consists of the structural units SiO_x and OSi_y . At ambient pressure, the structure consists of SiO_4 , OSi_2 and meanwhile the structure consists of SiO_5 , SiO_6 and OSi_3 at high pressure. Investigation results show that the local structural environment of silicon and sodium is strongly dependent on pressure. The densification mechanism in sodium-silicate system is due to the short-range order structure change of Si and Na atoms. There is the structural transformation in sodium-silicate under high pressure.

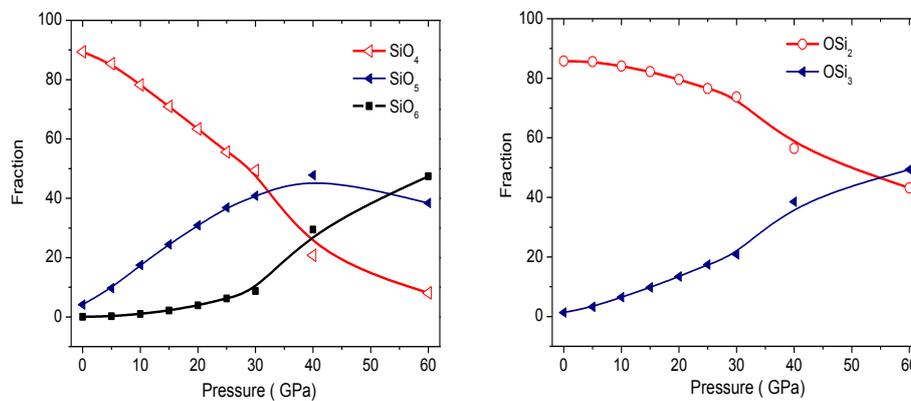


Fig 4. The distribution of structure unit SiO_x (right) OSi_y (left) as a function of pressure

The Figure 5 presents the O–Si–O bond angle distributions (BAD) in SiO_4 , SiO_5 and SiO_6 units, respectively, at different pressures. It can be seen that the partial O–Si–O BAD in each kind of coordination unit SiO_x is almost the same for different pressure. This means that the topology of SiO_4 , SiO_5 , and SiO_6 units is very stable and not dependent on compression. Here angle distribution in SiO_4 units has a form of Gauss function and a pronounced peak at 105° and 90° with SiO_5 unit. This result is

similar to experimental and other simulated data reported in [25] and indicates a slightly distorted tetrahedron with a Si atom at the centre and four O atoms at the vertices. In the case of angle distribution in SiO_6 , there are two peaks: a main peak locates at 90° and small one at 165° . The Si-O-Si BAD in OSi_y units is presented in Figure 6. The results show that the first peak of Si-O-Si BAD in OSi_2 is shifted left a little with compression pressure. It has the peak at around 145° at 0 GPa and 135° in the pressure of 25 GPa to 60 GPa; the Si-O-Si BAD in OSi_3 has a main peak at 115° and it is almost not dependent on pressure. This means that the topology of SiO_x units is very stable and only the topology of OSi_2 unit dependent on compression.

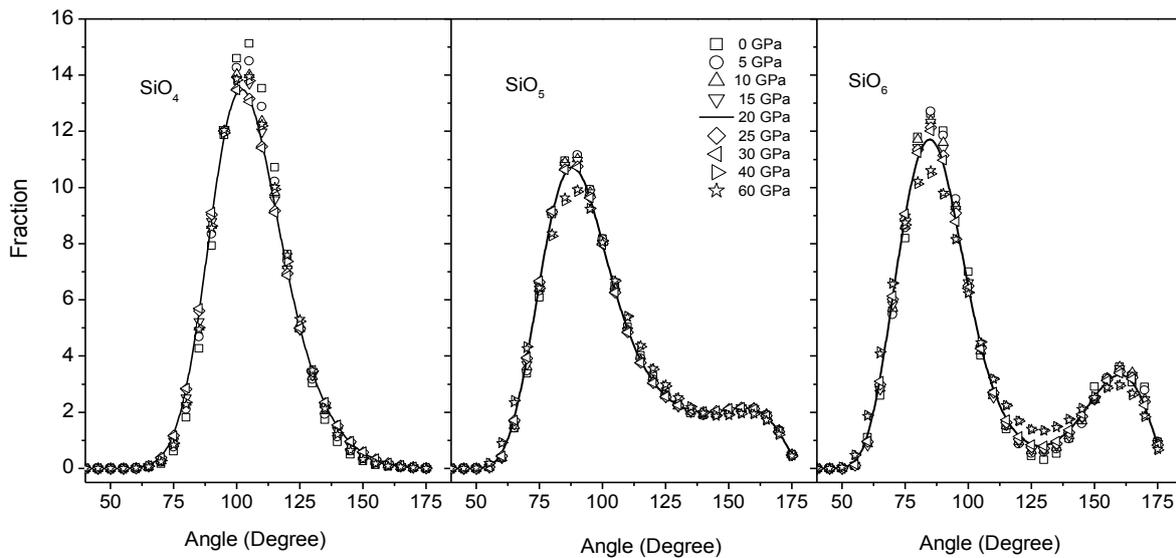


Fig 5. The distribution of O–Si–O bond angles in SiO_x ($x = 4 \div 6$) units at different pressures.

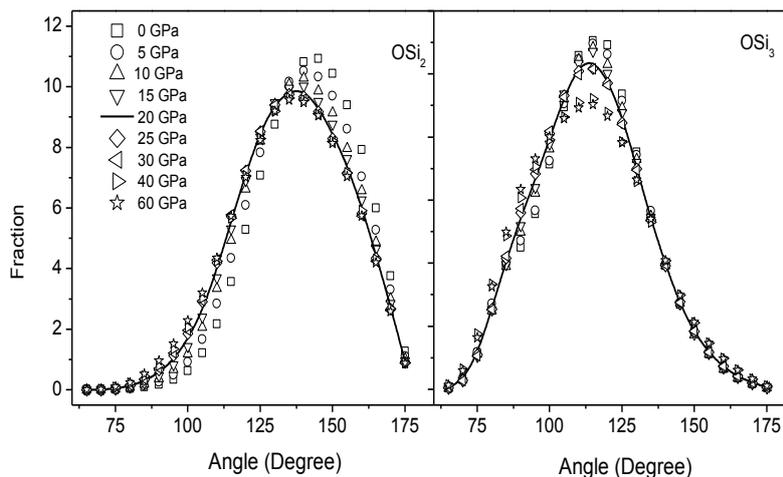


Fig 6. The distribution of Si–O–Si bond angles in OSi_y ($y=2,3$) units under pressures.

3.2. Dynamical Properties

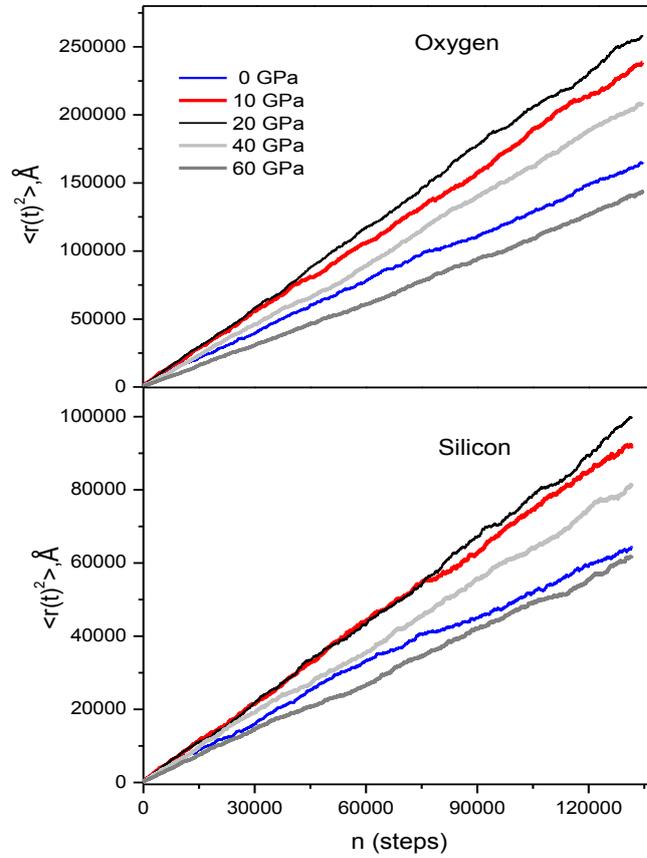


Figure 7. The dependence of mean square displacement on number of MD steps at different pressure.

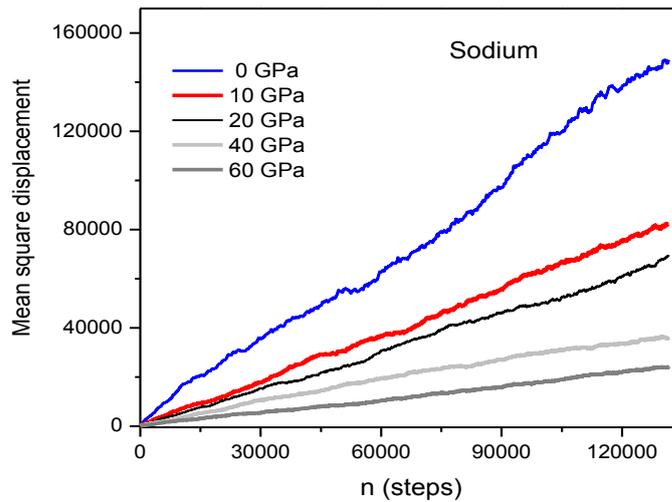


Figure 8. The mean square displacement for Sodium as a function of MD steps at different.

The Figure 7, 8 shows the dependence of MSD on number of MD steps. We can see that the dependence of MSD as a function of steps is also well described by straight line. Their slope is used to determine the diffusion coefficient of oxygen, silicon and sodium. The detail about the diffusion coefficient of oxygen, silicon and sodium atom is presented in Table 2.

Table 2. The diffusion coefficient of oxygen, silicon and sodium atom in Sodium- silicate

Model (GPa)	0	5	10	15	20	25	30	40	60
$D_{Si} \times 10^{-5}(cm^2/s)$	0.879	1.071	1.299	1.334	1.391	1.410	1.295	1.130	0.851
$D_O \times 10^{-5}(cm^2/s)$	0.417	0.507	0.615	0.632	0.659	0.668	0.613	0.535	0.403
$D_{Na} \times 10^{-5}(cm^2/s)$	39.58	48.19	58.45	60.04	62.60	63.47	58.25	50.87	38.30

From Table 2 following that there is the anomalous behaviour diffusion in sodium silicate. As pressure increases, the diffusion coefficient of silicon and oxygen atom increases and reaches a maximum at around 25GPa. The diffusion mechanism of atoms in liquid silica is occurred by the transition of the structural units $SiO_x \rightarrow SiO_{x\pm 1}$ and $OSi_y \rightarrow OSi_{y\pm 1}$. Under pressure, there is a phase transition from tetrahedral structure to octahedral structure through intermediate phase structure which was SiO_5 . Fraction of distribution of structural units SiO_5 increases and has a maximum at around 25GPa. Due to the flexibility of the intermediate phase (SiO_5), diffusion coefficient of silicon and oxygen increases. Thus, the instability of coordination units SiO_5 is the origin of anomalous diffusivity. An others hand, the diffusion coefficient for Na atom is about 44 times larger than for oxygen or silicon atom at 0 GPa. According this result, we predict that the diffusion mechanism of Na atom is quite different from the ones of network-former ions. The Na-O bonds is very weak in comparison with Si-O ones. So, the Na-O bond is easily broken, and na can displace easily in Si-O network as the consequence the diffusion coefficient of Na is much higher than O and Si.

5. Conclusion

Molecular dynamic simulation is employed to study the influence of pressure on the structural transformation and diffusion mechanism in sodium silicate. The simulation results reveal that the microstructure of sodium silicate has a phase transition under pressure. At ambient pressure, the structure consists of SiO_4 , OSi_2 and NaO_z ($z < 7$) meanwhile the structure consists of SiO_5 , SiO_6 , OSi_3 and NaO_z ($z > 8$). The topology of SiO_x and OSi_y units is investigated via the O-Si-O, O-Si-O bond angle distribution and Si-O bond distance distribution at different pressures. The results reveal that the Na^+ ions in Na_2O - SiO_2 system does not affect to the O-Si-O but and O-Si-O BAD is shifted left a little with compression pressure. Therefore, the additional network-modifying cation oxide breaking up this network by the generation of non-bridging O atoms and it has a slight effect on the topology of SiO_x and OSi_y units. The diffusion of Si, O in sodium silicate is the anomalous behavior. They have a maximum around 25 GPa. The diffusion coefficient for sodium atom is much larger than for oxygen or silicon atom. Thus, there is existence of two mechanism diffusion of network-former and modifier atom in sodium silicate.

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