THE ROLE-CHANGE OF Na$^+$ IONS IN SODIUM SILICATE SYSTEM UNDER COMPRESSION

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Abstract. Structural properties of Na_2O-$9SiO_2$ liquid under compression are studied by computer simulation. The local structure characteristics as well as topology of SiO_x are investigated via pair radial distribution function, coordination number, Si-O bond distance and O-Si-O bond angle distribution. The incorporation mechanism of Na$^+$ ions in Si-O network as well as their role in network structure will be clarified. Specially, influence of Na$^+$ ions to the topology of SiO_x units will be explained in detail.
Keywords: High pressure, structural dynamics, transition.

1. Introduction

Alkali-silicate systems are the typical group of multicomponent oxide glasses with tetrahedral network structure (SiO_4). The structure of Alkali-silicate glasses and melts is more than often centered on their cationic constituents and oxygen ions determine their connectivity, directly impacting the physical properties of the material system. Therefore, their structural properties have been extensively studied for a long time by both experimental measure and computer simulation [1-7]. Namely, in works [5, 6], by the X-ray diffraction, Warren and co-workers have shown the evidence of the continuous random network (CRN) of Zacharaisen [7], which has been accepted as the structural model of these glasses for many decades. X-ray and neutron diffraction studies in works [8-10] provided more detailed structure features of sodium silicate glasses. By neutron diffraction, it shown that Si-O bond distance increases with sodium content. In work [11-14], it showed that the O-Si-O and Si-O-Si bond angle distributions have the peak at around 109 and 144° respectively. An addition of sodium into silica glass causes breaking the Si-O-Si linkage in CRN of silica forming non-bridging oxygen (NBO) and the sodium atoms tend to incorporate in silica network via NBO. By X-ray absorption fine-structure spectroscopy (XAFS) [15-18], authors have

shown more detailed structural information around sodium ions. Namely, the Na-O and Na-Si bond distance are around 2.30 and 3.80 Å respectively and it is almost not dependent on the sodium content. However, the Na-O and Na-Si coordination number are significantly dependent on the sodium content. Specially, the local environment of sodium is very similar to those of their crystalline counterparts [15, 16]. Based on the experimental data in works [15-17], Greaves and co-workers proposed the modified random network model (MRN), they also suggested that sodium and NBO segregate rather than being randomly distributed in the Si-O network. So, it formed sodium-rich regions and silica-rich regions [16]. Besides, Q_n distribution (SiO_4 with n BO) were investigated by NMR experiment [19-22]. It has been shown that Q_3 species is dominant for the sodium disilicate systems, and similar results were shown by Raman spectroscopy [21, 23]. Although the structure of sodium silicate systems has been studied extensively for a long time, their medium range structure is still an open question. Besides, distribution of modifier in these glasses is also not be clarified. So, it is necessary to have more experiment and simulation studies to clarify the above problems.

With the development of technology information both hardware and software, the computer simulation becomes a useful tool to clarify the structure of glassy system (disordered materials). Molecular dynamics (MD) simulation are the most common and widely used computer simulations techniques to study structural and dynamical properties of disordered materials systems.

By MD simulation [24-31], authors have shown the clustered modifier regions. In works [32, 33], the distribution of ring size in both silica and sodium silicates systems has also been reported. However, detailed medium structure information of sodium silicate glasses under compression is still in debate.

In this work, the structural characteristics and network structure of sodium silicate (Na_2O-$9SiO_2$, denote as NS9) under a wide pressure range will be presented in detail. The incorporation mechanism of Na+ ions in Si-O network as well as their role in network structure will be investigated. Specially, influence of Na+ ions on the topology of SiO_x units will be discussed in detail.

2. Content

2.1. Calculation method

Molecular Dynamics simulation is conducted for sodium silicates system (Na_2O-$9SiO_2$, 3000 atoms) at temperatures of 3500 K and 0-60 GPa pressure range. The Morse potentials are applied in this work. This is empirical potential model developed for application with multicomponent silicate glasses. The potential equation consists of a long-range Coulomb potential, a short-range Morse potential and an additional repulsive term. The detail of potential parameters can be referred in the work [2]. The size of model is very small in comparison to real sample. Thus, its surface effect is very significant. To eliminate the surface effect, the periodic boundary condition is applied for all three dimensions.

The simulation program was written in C language that can be applied for simulation of silicate glasses and melts. In this study, the program is applied for simulation of NS9. Calculation is performed on High performance computing system at RIKEN institute in Japan with MD step of 0.5 fs. This value assures the requirement to accurately integrate the Newtonian equations of motion in order to track atomic trajectories and the computational cost is reasonable. Initial configuration is generated by randomly placing all atoms in a simulation cell. To eliminate the memory effect of initial configuration, the model is equilibrated at temperature of 6000 K for a long time (about 10^5 time-steps). Next, this model is compressed to different pressure (from 0 to 60 GPa) and relaxed for about 10^6 MD steps. After that the models at different pressures are cooled down to the desired temperature of 3500K with the rate of about 10^{12} K/s. A consequent long relaxation (about 10^6 MD steps) has been done in the NPT ensemble (constant temperature and pressure) to obtain equilibrium state.

In order to improve the statistics, the measured quantities such as the coordination number, partial radial distribution function as well as distribution of bond angle, bond length, NBOs, BOs are computed by averaging over 500 configurations separated by 20 MD steps.

2.2. Results and discussion

Firstly, to assure the reliability, the basic structural characteristic is investigated and compared with experimental data. Figure 1 shows the radial distribution function of Si-O, Na-O, O-O, Si-Si, Na-Na atomic pairs. Result in figure 1 reveals that the bond distances of Si-O, Na-O, O-O and Si-Si pairs are 1.62, 2.34, 2.62, and 3.10 Å respectively, which is in good agreement with experimental values as well as simulation result in works [1-4, 6, 8, 10]. It also shows that, under 0-60GPa pressure range, the Si-O bond distance is almost not dependent on pressure. However, the Si-Si and O-O bond distance is significantly dependent on pressure. The Na-O, Na-Si and Na-Na bond distance is strongly dependent on pressure. Figure 2 displays the Si-O coordination number distribution. It can be seen that, at ambient pressure, most of Si atoms are fourfold coordinated (around 90%), forming SiO_4 units. The number of Si atoms with five-fold coordination is about 5%. It also exists about 5% SiO_3 units (because the fraction SiO_3 only exits at ambient pressure, so it is not presented in figure 2). There is no SiO_6 unit at ambient pressure. The average Si-O coordination number is around 4.0 at ambient pressure, see the figure 2 (left). This result is in good agreement with the experiments and simulation in [1-4, 6, 8, 19].

As pressure increases, the fraction of SiO_4 decrease strongly meanwhile the fraction of SiO_5 and SiO_6 increases. The fraction of SiO_5 get maximum value at around 40 GPa and then decreased slightly with pressure. At pressure 60 GPa, the fraction of SiO_4, SiO_5 and SiO_6 is around 10%, 40% and 50% respectively.
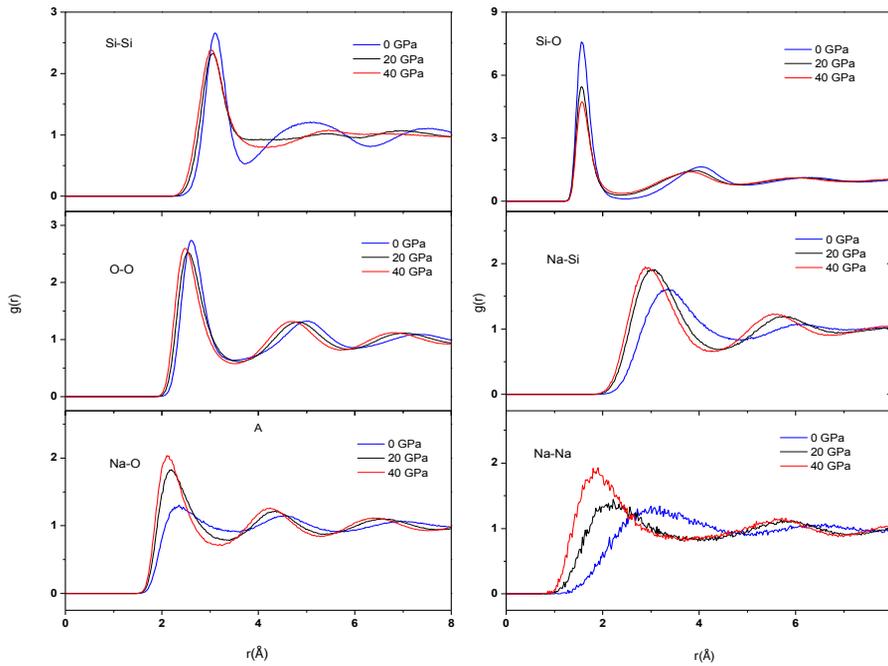
***Figure 1. The radial distribution function of atomic pairs in NS9 systems
at different pressure and at 3500K***
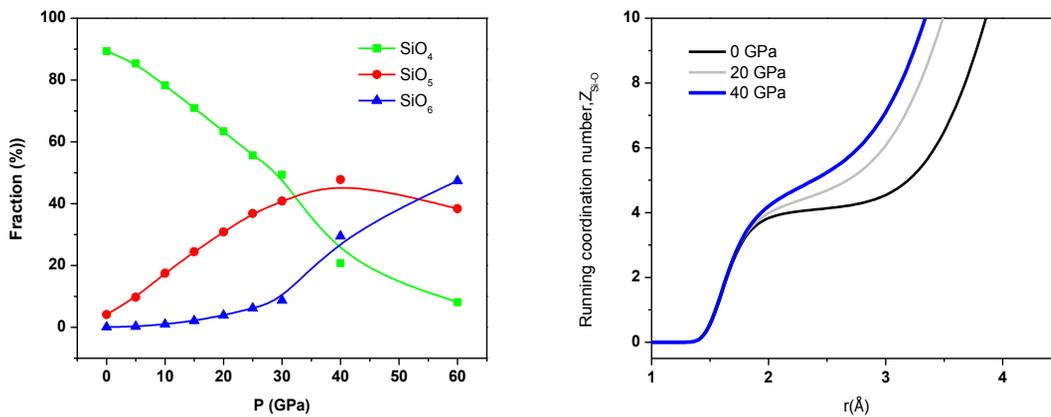
***Figure 2. The Si-O coordination number distribution as a function of pressure (left);
running coordination number (right)***
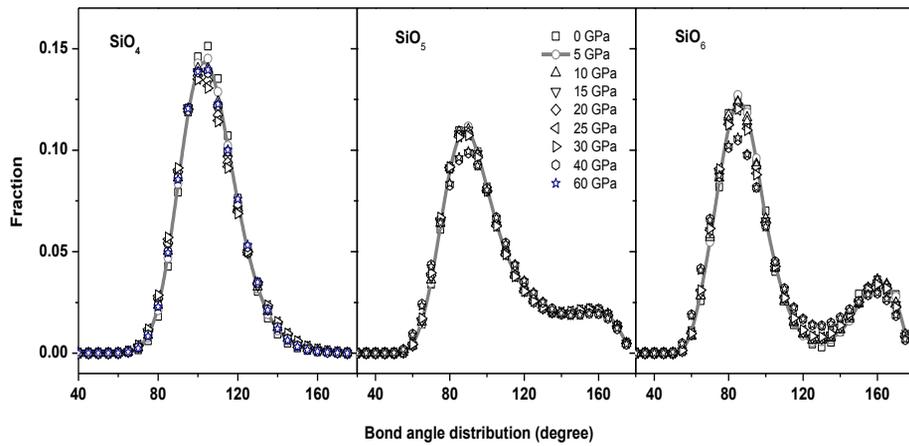
Figure 3. The O-Si-O bond angle distribution in SiO$_x$ (x = 4, 5, 6) of NS9 systems at different pressures
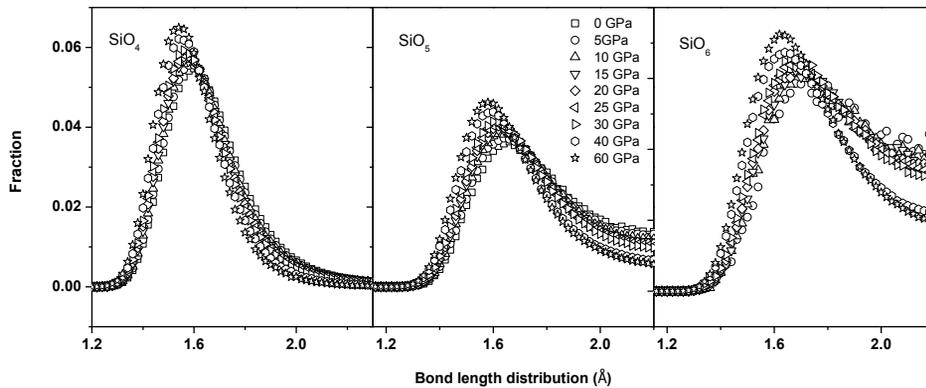
Figure 4. The Si-O bond distance distribution in SiO$_x$ (x = 4, 5, 6) of NS9 systems at different pressures

Now we will focus on investigating the topology of SiO$_x$ units and clarifying the influence of Na$^+$ ions to the network structure as well as topology of SiO$_x$ units. Figure 3 shows the O-Si-O bond angle distribution (BAD) in SiO$_x$ units. It can be seen that in the considered pressure range, O-Si-O BAD is almost not dependent on pressure. The O-Si-O BAD in SiO$_4$ has the peak at around 105-108°; the O-Si-O BAD in SiO$_5$ has a main peak at around 85-90° and a shoulder at around 160°; meanwhile the O-Si-O BAD in SiO$_6$ has one main peak and a small one at around 85-90° and 160-165° respectively. It can be seen that O-Si-O BAD in SiO$_x$ of NS9 system is similar the ones in SiO$_x$ units of silica system. This reveals that the Na$^+$ ions in NS9 system does not affect to the O-Si-O BAD in SiO$_x$. Figure 4 shows the Si-O bond distance distribution (BDD) in SiO$_x$ at different pressures. It can be seen that, the Si-O BDD in SiO$_4$ is almost not dependent on pressure. However, the Si-O BDD in SiO$_5$ and SiO$_6$ is slightly dependent on pressure. The peak of Si-O BDD in SiO$_5$ and SiO$_6$ tend to shift to the left with the increase of pressure. It reveals that average Si-O bond distance in SiO$_5$ and SiO$_6$

decreases slightly with pressure. The above analysis demonstrates the topology of SiO_4 is almost not dependent on pressure and is not affected by Na^+ ions. Meanwhile the topology of SiO_5 and SiO_6 is changed slightly with pressure. In the previous works [34, 35], it has shown that the topology of SiO_x (x = 4, 5, 6) in silica system is not dependent on pressure. This reveals that, the Si-O BBD or in other word the topology of SiO_5 and SiO_6 changed under compression is due to the present of Na^+ ions. Therefore, topology of SiO_4 units is not affected by Na^+ ions. This can be explained as follows:

At ambient pressure, most of SiO_x units are SiO_4 (90%) and the number of non-bridging oxygen (NBO) and bridging oxygen (BO) is about 13% and 87% respectively, see Figure 5. One part of Na^+ ions tends to be close to NBO, in this case they have the role of network modifier ions; the remain part of Na^+ ions tends to be close to SiO_5, in this case they have role of charge balance (at ambient pressure, the fraction of SiO_5 is about 5%). Besides, because the number of Na^+ in NS9 system is very small in comparison to the number SiO_4, the topology of SiO_4 is not affected by the present of Na^+ ions. (Note: Na^+ ions have positive charge, meanwhile NBO, SiO_5 and SiO_6 units have negative charge, from now denote as $[NBO]^-$, $[SiO_5]^-$, $[SiO_6]^-$).
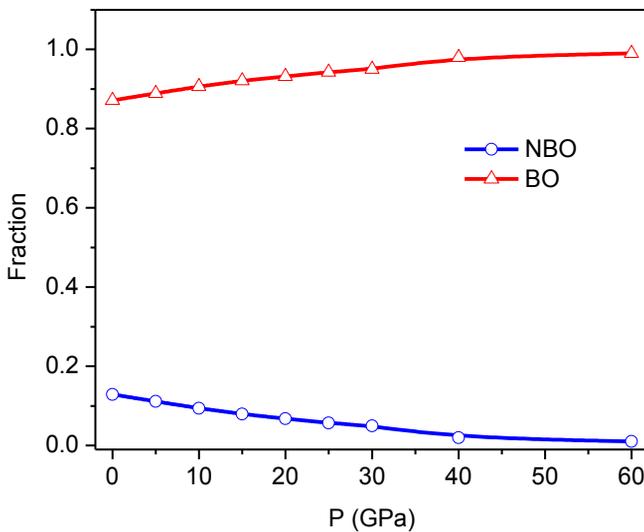
Figure 5. Distribution of BO and NBO in NS9 systems as a function of pressure

At high pressure, most of SiO_x units are $[SiO_5]^-$ and $[SiO_6]^-$ and there is no $[NBO]^-$. Therefore, the Na^+ ions tend to be close to $[SiO_5]^-$ and $[SiO_6]^-$ and they cause the decrease of Si-O bond distance in SiO_5 and SiO_6 units. This can be explained as following: the O-Si-O bond angle in the $[SiO_5]^-$ and $[SiO_6]^-$ units is smaller than the one in SiO_4. So, the distance between O^{2-} and O^{2-} ions decreases and the repulsion coulomb force between them increases. It results in increasing the Si-O bond length in comparison to the one in SiO_4. When Na^+ ions locate near $[SiO_5]^-$ and $[SiO_6]^-$, the repulsion coulomb force between O^{2-} and O^{2-} ions decreases leading to decrease of some Si-O bond distances in $[SiO_5]^-$ and $[SiO_6]^-$. This leads to the change of topology of $[SiO_5]^-$ and $[SiO_6]^-$ units. In this case, all Na^+ ions have the role of charge balance.

In previous works [36, 37], it showed that, the SiO$_4$, SiO$_5$ and SiO$_6$ were not distributed uniform but forming separated clusters (SiO$_5$-clusters, SiO$_5$-clusters, SiO$_6$-clusters). Therefore, the Na$^+$ ions incorporate in Si-O network via [SiO$_5$]$^-$ and [SiO$_6$]$^-$ will form the Na-rich regions.

3. Conclusions

The structure of sodium silicate systems in the 0-60 GPa pressure range has been investigated by MD method. Results show that their structure consists of SiO$_x$ units linking to each other via BO and forming CRN. The Na$^+$ ions incorporate in Si-O network via negative charge species as [NBO]$^-$ and [SiO$_5$]$^-$ and [SiO$_6$]$^-$. At ambient pressure, the fraction of [NBO]$^-$ is rather high and most of Na$^+$ ions locate near [NBO]$^-$. In this case, Na$^+$ ions have the role of network modifier. As pressure increases, the number of NBO decreases while the [SiO$_5$]$^-$ and [SiO$_6$]$^-$ increases and one part of Na$^+$ ions incorporate in Si-O network via [NBO]$^-$, the remain part incorporate in Si-O network via [SiO$_5$]$^-$ and [SiO$_6$]$^-$. In this case, one part of Na$^+$ ions has the role of network modifier and the other part with the role of charge balance. At high pressure, there are no [NBO]$^-$ in Si-O network and all Na$^+$ ions incorporate to Si-O network via [SiO$_5$]$^-$ and [SiO$_6$]$^-$ and in this case they have the only role of charge balance. The Na$^+$ ions locate near [SiO$_5$]$^-$ and [SiO$_6$]$^-$ as pressure increases leading to the topology change of [SiO$_5$]$^-$ and [SiO$_6$]$^-$. The Na$^+$ ions tend to form the Na-rich regions in sodium silicate.

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