Structural and dynamic properties of lithium silicate liquid: A view from molecular dynamics simulation

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Abstract. In this work, we have investigated the liquid lithium silicate by the method of molecular dynamics simulation (MD) using the Born-Mayer pairwise potentials under compression. The simulations have been carried out by systems including various pressure values from 5 to 30 GPa. The microstructure of lithium silicate was clarified through the thorough analysis of short-range order (SRO) and intermediate range order (IRO). The short-range order was investigated through factors such as pair radial distribution functions (PRDFs), coordination distributions, angular distributions. The results show that the structure of the system has a transformation from low-coordination to high-coordination under the influence of compression. Besides, the analysis of intermediate range order shows that the structure network in model consists of SiOx and LiOx units connected to others via an Oxygen atom. In the case for the intermediate range order, the fraction of OTy bond calculated under compression shows that their bonding angle and bond length are very little dependent on the pressure changes. Furthermore, the dynamics of liquid lithium silicates calculated through the diffusion coefficients of the atoms shows that there is a dependence of atomic mobility on pressure. The obtained results of simulations are in good agreement with previous experimental and simulated data.

1. Introduction

Lithium silicate materials have many applications in the fields of science, technology and life, including important applications such as using in solid-state electrolytes or using as a dental bio-ceramics, high-performance lithium ion batteries [1-7]. There are many authors who have studied their...
structure through both experiment and simulation, and several experimental methods have been used such as NRM, EXAFS, Raman spectroscopy, neutron and X-ray diffraction. [8-14]. Specifically, for the Lithium silicate system, the results obtained by X-ray diffraction method have shown that the average bonding distance of Si-O is 1.62 Å, and the average number of O atoms surrounding a Si atom is 4 [13-14]. In case of the Li-O bond, the average bonding distance is 1.97 Å, and the mean coordination number corresponding this distance is 3.2 Å. Whereas the O-O bond distance is 2.66 Å, and the corresponding average coordination number is 4.4 [13]. However, the study results in [14] showed that there is a small difference in the bonding distance of Li-O and O-O pairs with the results of 1.94 Å and 2.64 Å respectively. The Lithium silicate system structure is also characterized by the association between Si atoms through an O atom which was called the Q$n$ species with the change of density.

The SiO$_4$ tetrahedron plays a very important role not only in terms of structure but also has certain effects on the kinetic process of the systems. From the results of previous studies showed that the factors affecting the changes in the network structure of SiO$_4$ in the Lithium silicate system include temperature, pressure and chemical composition. When Li$_2$O is added to SiO$_2$, the Li atom acts as a change in the structure of the SiO$_4$ tetrahedron, and the phase transition temperature of glass also change with chemical compositions. The results show that the recorded glass phase transition temperature is 1000K reported in [16], while the glass transition temperature and melting temperature of the Li$_2$SiO$_3$ system are 940K and 1450K respectively.

In works [12, 17-19], the kinetic process of lithium system has been studied through the characteristic quantities of viscosity and diffusion coefficient. In their study, Lammert al et [18] suggested that there is the formation of mobile and less mobile regions in the Li$_2$SiO$_3$ model, these relate to the number of bridging oxygens (BOs) and non-bridging oxygen (NBO) in the model. Because of the difference of the motion properties in the models, the Li$_2$SiO$_3$ system has the diffusion coefficient of Li is bigger than the one in the Li$_2$SiO$_3$ system [17]. In this work, we analyze the structure as well as the kinetic process in the Lithium silicate model. In which the local structural order is carefully analyzed through the short-range and intermediate range order, while the kinetic factors are analyzed through the diffusion coefficient of the atoms.

2. Calculation method

Molecular dynamics simulation of the Li$_2$O SiO$_2$ system was performed with an initial configuration of 2250 atoms (375 Si, 750 Li and 1125 O atoms) contained in a cube shaped box with the periodic boundary conditions. We used the Born–Mayer interaction potential to perform the interactions of atoms in the system, which has been used extensively in the simulation of molecular dynamics,

$$\varphi_{ij} = \frac{q_i q_j}{r_{ij}} + A_{ij} \exp\left(-B_{ij} r_{ij}\right)$$

Where $r_{ij}$ is the distance between two ions of type i and type j in the model and $q_i$, $q_j$ is the charge of the atoms Si, Li or O. The potential coefficients A, B can be found in reference [22], including $A_{O}\text{0} = 1759$ eV, $A_{O:Si} = 10734$ eV, $A_{Si:Si} = 8.734 \times 10^3$ eV, $A_{O:Li} = 2391$ eV, $A_{Si:Li} = 239343$ eV, $A_{Li:Li} = 6720$ eV, $B_{O:O} = 2.8464$ Å$^{-1}$, $B_{O:Si} = 4.7959$ Å$^{-1}$, $B_{Si:Si} = 15.2207$ Å$^{-1}$, $B_{O:Li} = 4.0182$ Å$^{-1}$, $B_{Si:Li} = 9.4286$ Å$^{-1}$, $B_{Li:Li} = 6.82$ Å$^{-1}$.

To carry out the simulation, we have built the initial model by randomly inserting all the atoms into a cube simulation box. We then have used Verlet algorithm (with a time step of 0.5 fs) to perform molecular dynamics simulation steps. To avoid the non-physical features at extremely short distances, the initial sample was heated to a temperature of 6000 K through 50,000 MD simulation steps. After being cooled to the states of 3200 K and 0 GPa, this model was tested for reliability by comparing its PRDFs with that value in both the published experimental and simulation results. The next steps, by
compressing the sample obtained from a pressure of 0 GPa, six models were created with a pressure difference of 5 GPa, the model with the lowest and highest pressure being 5 GPa and 30 GPa, respectively. In which, creating each of the models experienced 10,000 simulation steps in NPT ensemble. Further, each parameter was calculated by taking the mean of 1000 configurations which was divided into 10 simulation steps. This is to increase the accuracy of the measurement.

3. Results and discussions

3.1. Short-range order

Figure 1 illustrates that the heights of the peaks of Si-Si, O-O, and Si-O pairs decrease and these peaks become broader with increasing pressure. This reveals that the order degree of the structure reduces when the pressure increases. On the contrary, the peak amplitude of O-Li pair decreases with rising pressure, in that the peak height of Si-O pair decreases the biggest from 10.34 to 6.09 Å. The position of peak of Si-Si, O-Li, and Si-O pairs almost unchanged with growing pressure, meanwhile the position of peak for O-O pair slight shifts to the left as the pressure increases. The peak positions of Si-Si, O-Li, and Si-O pairs are 3.03, 1.98, and 1.61 Å, respectively. These values are line with the experimental and simulated results [20-22].

![Figure 1](image-url)

**Figure 1.** Radial distribution of Li2O-SiO2 pairs at different pressure.

Figure 2 depicts the distribution of the basic structural units TOx as the pressure increases. It can be seen that the fraction of SiO4 unit at 0 GPa is dominant about 93.25%. This result is accordance with [20]. The fraction of SiO3 unit is not significant. Meanwhile, the one of SiO4 unit dramatically decreases by 84.68%. By contrast, the both of SiO3 and SiO4 units considerably go up in the fraction around 46% as the pressure rises to 30 GPa. Thus, there is a change in the coordination number of Si atoms from four-fold to five-fold and six-fold coordination with increasing pressure. For LiOx units, the LiO4 unit is the largest in the portion about 40% at laboratory pressure, meanwhile the fraction of LiO3 and LiO5 units are 16.86 and 31.89%, respectively and the smallest fraction is LiO6 unit. With an increment of the pressure, the fraction of LiO3 and LiO5 units rises, in which the fraction of LiO2 unit goes up to 43.28% at 10 GPa, however, the one decreases as the pressure gets over 10 GPa. The fraction of LiO6 unit increases steadily to 43.25%. Thus, in the model as the pressure increased, the Li atom has a transformation of the coordination number from three- and four-fold to five- and six-fold.
Figure 2. Distribution of coordination units in SiOx and LiOx.

The distribution of the bond length and bond angle of SiO₄, SiO₅ and SiO₆ units are shown in figure 3 at 0, 10, 20 and 30 GPa. The results show that the peak heights in the bond length distribution of the SiO₄, SiO₅ and SiO₆ units increase as the pressure rises, while the positions of them are not change. The peaks of the bond length distribution of SiO₄, SiO₅ and SiO₆ units are located at 1.61, 1.62 and 1.70 Å, respectively. These results are consistent with published data in [20-21]. The distribution of bond angle of SiOₓ (x=4,5,6) units shows that the peak height of distribution of bond angle of SiO₄ unit declines with increasing pressure, while the distribution of bond angle of SiO₅ and SiO₆ units is

Figure 3. Distribution of the bond length and bond angle in SiOₓ.
not dependent on pressure. The position of peak of the distribution of bond angle of SiO$_4$ unit slightly shifts to the left as the pressure raises. The distribution of bond angle of SiO$_4$ unit has a peak at 105°. This result is similar to the one reported in [20]. In addition, SiO$_5$ and SiO$_6$ units have first and second peaks at 89°, 88° and 157° and 160°, respectively. These results are in line with the results of [21].

The distribution of the bond length and the bond angle in LiO$\text{x}$ units is indicated in figure 4. It is clear that the bond length distribution in LiO$_{4}$, LiO$_{5}$ and LiO$_{6}$ units has a decrease of height as the pressure increases, while the one has a slight shifts to left in the position of the peak. This means that as the pressure goes up the bond length goes down. The bond length of LiO$_{4}$, LiO$_{5}$ and LiO$_{6}$ units is 1.86, 1.92 and 2.01 Å, respectively at 30 GPa. These results are accordance with [20-21].

There is a fluctuation in the peak height and the peak position of the distribution of bond angle in LiO$_{4}$, LiO$_{5}$ and LiO$_{6}$ units as the pressure changes in the 0-30 GPa range.

Figure 4. Distribution of the bond length and bond angle in LiO$\text{x}$.

3.2. Intermediate-range order

Figure 5. Bond angle and bond length distributions of OT$_{3}$ and OT$_{4}$ units.
The distribution of the T-O-T bond angle and the O-T bond length in OT\(_y\) (y=3,4) linkages in Lithium silicate liquid at the different pressures is shown in figure 5. The figure shows that the peak of T-O-T bond angle of OT\(_3\) and OT\(_4\) linkages is less dependent on pressure. They have the peaks at around 100\(^\circ\), 90\(^\circ\) and 85\(^\circ\), respectively. Yet the fractions of them slightly increase with increasing pressure (from 0.070\% to 0.085 in OT\(_3\) and from 0.077\% to 0.092\% in OT\(_4\)). On the other hand, the peak position of the O-T bond length distribution of OT\(_3\) and OT\(_4\) linkages slightly increase under compression. They range from 1.62 Å at 0 GPa to 1.64 Å at 30 GPa in OT\(_3\) and from 1.62 Å at 0 GPa to 1.66 Å at 30 GPa in OT\(_4\).

![Figure 5](image)

**Figure 5.** The distributions of bond angle and length of OT\(_3\) and OT\(_4\) linkages in Lithium silicate liquid.

In OSi\(_2\) linkage, the peak position of the Si-O-Si bond angle distribution slightly decreases from 135\(^\circ\) down to 130\(^\circ\), but the peak position of the O-Si bond length distribution slightly increases from 1.62 Å to 1.66 Å. The peak distribution of Li-O-Li angle of OLi\(_3\) and OLi\(_4\) linkages is slightly relying on compression. In case of the Li-O-Li angle distribution, the peak positions of OT\(_x\) linkages slightly decrease from 80\(^\circ\) to 70\(^\circ\) in OLi\(_3\) and from 75\(^\circ\) to 70\(^\circ\) in OLi\(_4\). However, the peak positions of O-Li bond length in OLi\(_3\) and OLi\(_4\) linkages are almost unchanged under compression with about 2.06 Å in OLi\(_3\) and 2.12 Å in OLi\(_4\). These results disclose that the shape and topological structure of OSi\(_2\), OLi\(_3\) and OLi\(_4\) linkages is deformed with increasing pressure.

3.3. Diffusion coefficients of atoms

The kinetic process of liquid Li\(_2\)O.2SiO\(_2\) system is also studied through the diffusion coefficient of Si, O, Li atoms. Figure 7 shows the change of diffusion coefficient of Si, O and Li atoms (D\(_{Si}\), D\(_{O}\) and D\(_{Li}\)) depending on the change of pressure. It can be seen that, as the pressure increases, the abnormal diffusion occurs for Si and Li atoms. Initially, when increasing pressure, the diffusion coefficient D\(_{Si}\), D\(_{Li}\) increases to maximum then decreases gradually. At the 0 GPa pressure, the diffusion coefficients...
Figure 7. Self-diffusion of atoms in Li$_2$O.2SiO$_2$ system as a function of pressure.

$D_{\text{Si}}$ is $6.532.10^{-11}$ m$^2$/s and that for $D_{\text{Li}}$ is $1.832.10^{-10}$ m$^2$/s, and the diffusion coefficient of Li reaches a peak at $3.182.10^{-10}$ m$^2$/s at the pressure of 5 GPa. For Si atoms, its diffusion coefficient reaches a maximum of $1.063.10^{-10}$ m$^2$/s at a pressure of 10 GPa. Meanwhile, the diffusion coefficient of O atom decreases steadily with increasing pressure. It is clear that the diffusion coefficients of the atoms are all significantly reduced in the pressure range 25 to 30 GPa. At 30 GPa, the diffusion coefficients of the atoms have the smallest value in the pressure range under investigation, this indicate that the atoms in the model are the least mobile at this pressure. During the compression process, the diffusion coefficient of the atoms decreases in the order $D_{\text{Li}} > D_{\text{Si}} > D_{\text{O}}$, which shows that the Li atom mobility is the largest and the O atom is worst mobile. Thus it can be seen that the atomic mobility is greatest in the range 5 to 10 GPa and becomes less mobile in the pressure range from 25 to 30 GPa.

4. Conclusion
The lithium-silicate system is constructed by molecular dynamics simulation including structural parameters good agreement with the experiment data. The simulation results demonstrate that structural units are mainly SiO$_4$, LiO$_3$ and LiO$_4$ at low pressure, and at high pressure most of the structural units are SiO$_5$, SiO$_6$, LiO$_5$ and LiO$_6$. Angular distribution of structural unit SiO$_4$ has a peak at 105°, while for SiO$_5$ and SiO$_6$ there are two peaks, around 89° and 157°, respectively. Under the influence of pressure, the structure of SiO$_4$ unit slightly changes, while the structural units of SiO$_5$ and SiO$_6$ are almost unchanged. As the pressure increases, however, the bond lengths of the LiO$_4$, LiO$_5$ and LiO$_6$ structural units decrease. The bonding angles of the OTx structure depend very little on the pressure change, but their bond length increases slightly with increasing pressure. In addition, the shape and topology of the OSi$_2$, OLi$_3$ and OLi$_4$ bonds are slightly deformed when the pressure increases. The results also show that the Li atom mobility is the largest while the O atom is worst mobile, with the order $D_{\text{Li}} > D_{\text{Si}} > D_{\text{O}}$. Furthermore, the diffusion coefficients of Li and Si have fluctuations with pressure while that for O is not. The atomic mobility is greatest between 5 and 10 GPa and becomes less mobile in the range of magnetic pressure from 25 to 30 GPa, this means the atoms are flexible at low pressure and less flexible at high pressures, in other words the atoms are high mobility at low density of the atoms.

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