



Original Article

Distribution of Sodium and Diffusion Mechanism in Sodium Silicate Liquid

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Abstract: In this study, molecular dynamic simulation is employed to study the structural properties and diffusion mechanism in sodium silicate ($\text{Na}_2\text{O} \cdot 4\text{SiO}_4$). Structural characteristics are clarified through the pair radial distribution function, distribution of SiO_x coordination units and network structure. The simulation results reveal that the structure of $\text{Na}_2\text{O} \cdot 4\text{SiO}_4$ liquid consists of one Si-O network that is mainly formed by SiO_4 units. The spatial distribution of sodium is non-uniform; sodium tends to be in the non-bridging oxygen-simplexes and in larger-radius simplex. Moreover, the sodium density for non-bridging oxygen region is significantly higher than the one for other regions. The study results also show that Si and O diffuse by bond break-reformation mechanism, while the motion of Na consists of two parallel processes. Firstly, Na atoms hop from one to another O within a disordered network where each bridging oxygen (BO) has one site, while a non-bridging oxygen (NBO) possesses two sites. The average resident time for Na staying near NBO is much longer than that near BO.

Keywords: Simulation, structure, mechanism diffusion, sodium-silicate.

1. Introduction

Glass-forming mixtures of SiO_2 with an alkali oxide are the important materials group that has been widely applied in many fields such as: microelectronics, medicine (bio-material), high technology materials. Therefore, understanding their structure and dynamical properties is fundamentally necessary [1-3]. By using the neutron, X-ray diffraction (XRD) techniques, magic-angle spinning (MAS) nuclear magnetic resonance (NMR) [4, 5] and simulation methods [6, 7] observed the change in structure of alkali silicate. Namely, the addition of alkali oxides into pure silica (SiO_2) disrupts the basic silica network by breaking part of the Si-O bonds, creating non bridging oxygen (NBO). The percentage of NBOs in the system increases with the alkali oxide concentration [8, 9]. In the multicomponent alkali

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silicates, the “mixed alkali effect” refers to a drastic change of the relaxation dynamics. The ionic diffusivity of both alkali ions decreases in the mixed alkali composition; compared to the corresponding single-alkali silicate [10]. The effect is caused by mutual interception of jump paths of both kinds of mobile alkali ions. So the cooperative forward-correlated jumps are blocked and the immobilization of faster ions is responsible for the mixed alkali effect [11]. Moreover, alkali atom is found to migrate predominantly within NBO rich region in the system [8] and the diffusion of the alkali atoms mobility that is much higher than that of the silicon and oxygen atoms forming a tetrahedral network structure [12]. According to studies, the alkali atoms can easily move in preferential pathways, also called “channels”. Thus, the fast transport of the alkali ions in silicate melt was explained [13, 14]. The partial Na–Na structure factor has a pre-peak at a wave vector $q = 0.95 \text{ \AA}^{-1}$. These experimental results support a mechanism of ionic transport channel in alkali silicate [15, 16]. The preferential pathways have been found via simulation method. The simulation box is divided into cubes and then they calculated the number density of the sodium atoms in each of these small boxes. The research results show that 50% of the cubes have been visited by sodium ions [17] and most of the Na motion occurs in 6% subsets of the total available space. However, the boxes are fixed and placed in the space simulation box.

In this paper, we have calculated the statistical and dynamical distribution of sodium through the Si–O network of $\text{Na}_2\text{O} \cdot 4\text{SiO}_4$ (NS_4) liquid via simplex method. Furthermore, we focus on two diffusion mechanisms of network former and modifier atoms.

2. Computational method

MD simulation is carried out for $\text{Na}_2\text{O} \cdot 4\text{SiO}_2$ (NS_4) melts at pressure of 0.1 MPa and temperature of 1873 K. The model contains 1066 Sodium, 2132 Silicon and 4797 Oxygen atoms. We apply the inter-atomic potential including two-body and three-body terms. This potential provided the reproduction of structure of silicate crystals and pressure dependence of transport properties of silicate liquid. More details about the applied potential can be found elsewhere [18, 19]. The constructed models have been relaxed for long times until reach the equilibrium. Afterward, we perform additional runs of 150 ps to produce a series of configurations separated by 10 ps. The dynamical and structural data are collected from these configurations.

The simplex is a sphere passing center of four oxygen atoms (NBO or BO) without Si or O atom inside. The simplex has no fixed radius. The radius of simplex depends only on position of four atoms. The simplexes consist of two main types: void-simplex (the sphere passing four atoms without any atom inside) and Na-simplex (the sphere passing four atoms and containing one or many sodium atoms). The Fig. 1a, b presents void-simplex. The Fig. 1c presents the Na-simplex. The characteristic of simplexes is determined by radius and type (BO, NBO) atom that sphere passing and the number of sodium inside.

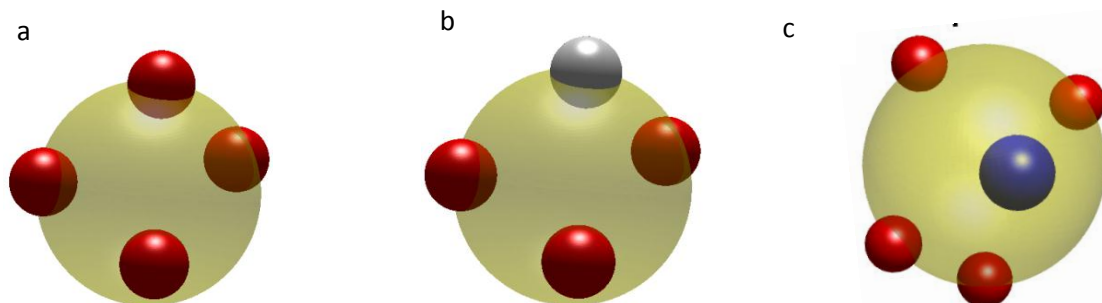


Fig 1. The schematic illustration of the simplex: void-simplex (a,b); and Na-simplex (c). Here the red, gray and blue spheres represent the NBO, BO and Na atoms, respectively; the circle represents the simplex sphere.

3. Results and discussion

Table 1. the inter-atomic distances (r_{AB} Å) calculated from PRDF of sodium silicate

Reference	r_{OO}	r_{SiO}	r_{ONa}	r_{SiSi}	r_{SiNa}	r_{NaNa}
NS ₄	2.62	1.62	2.15	3.12	3.20	3.32
[20, 21]	2.62	1.62	2.29	3.05	3.5	2.6, 3.05
[2]	2.35	1.65		3.12		

Firstly, we examine the structural and dynamical characteristics in NS₄ liquid. Table 1 lists the inter-atomic distances calculated from PRDF and these results are compared with experimental data [2, 20-21] for comparison. As seen, although r_{SiNa} and r_{NaNa} show some discrepancies, the constructed models are well consistent with experiments. In particular, the simulation reproduces the experimental data for r_{OO} , r_{SiO} , r_{SiSi} and r_{NaO} . The fraction of SiO_x and different oxygen types is shown in Table 2. The structure comprises SiO₄ tetrahedrons and a small amount of SiO₃. Close values of D_O and D_{Si} evidence the bond break-reformation mechanism for network atom [22]. Accordingly, the collective movement of network atoms occurs when a Si-O bond is broken and then a new bond is formed. This leads to rearrangement in the Si-O network and that Si moves cooperatively with its coordinated O. From Table 2 follows that fast Na move inside a network of slow atoms.

Table 2. Fraction of SiO_x units and different oxygen types.

Units SiO _x	Fraction of SiO _x	Oxygen	Fraction of type Oxygen	Diffusion coefficient, [cm ² /s]
SiO ₃	0.0041	FO	0.0007	D_O 8.50 x 10 ⁻⁸
SiO ₄	0.9958	NBO	0.2225	D_{Si} 6.50 x 10 ⁻⁸
SiO ₅	0.0001	BO	0.7767	D_{Na} 4.74 x 10 ⁻⁵

To determine the temporal locations of Na we calculate the distances between every Na and network atoms. Then we determine a network atom that is separated from the given Na at a shortest distance. We assume that this Na is located in a site near the finding network atom. The calculation result is shown in Table 3. We observe that all Na are located in sites near O atoms and no one is present near Si atoms. This is due to both Si and Na are positively charged ions. For the convenience of discussion, we refer the phrase 'sites near O atoms' as 'near O atoms' for short. Although the number of BO more than three times exceeds that of NBO, about 75% of Na is near NBO. This can be interpreted by the fact that Na is bonded to NBO much stronger than to BO because of NBO is connected only with one Si. From this follows that t_{NBO} is much longer than t_{BO} , where t_{BO} , t_{NBO} is the average resident time for Na being near BO and NBO, respectively. Furthermore, we observe that the number of Na located near an O varies from 0 to 1 when this O is BO and from 0 to 2 if it is NBO. There are some exceptions, for instance, three Na are present near NBO. However such cases occur very rarely. From this follows that each NBO has two sites, while a BO possesses one site. The total number of sites is calculated from the number of NBO and BO. For the configuration at $t = 0$ it equals to 5870 which is more than five times larger total number of Na. This fact indicates that the simple vacancy mechanism is not appropriate for diffusion of sodium in NS₄ liquid.

Using simplex method to identify the distribution of sodium in network Si-O, the results present Table 4. The most of NBO⁴-simplexes (four atoms are NBO) and BONBO³- simplexes (three NBO and one BO) have the existence of Na atoms inside. The fraction of Na decreases with increasing number of BO. The result is consistent with the data in Table 3.

Table 3. Spatial distribution of Na in Si-O network. m_{Na} is the number of Na which are located near NBO or BO; m_{BO} , m_{NBO} is the number of BO and NBO, respectively.

m_{Na}	t = 0 ps		t = 100 ps		t = 140 ps	
	m_{BO}	m_{NBO}	m_{BO}	m_{NBO}	m_{BO}	m_{NBO}
0	3485	373	3468	394	3477	391
1	243	570	252	555	243	549
2	0	125	1	124	1	133
3	0	1	0	3	0	2

Table 4. Characteristic of simplex in sodium silicate.

Type of simplex	$m_{\text{simplexes}}$	Fraction of simplexes	Simplexes with Na	Fraction of simplexes with Na
NBO ⁴	338	0.0179	327	0.9675
BONBO ³	1454	0.0770	1339	0.9209
BO ² NBO ²	4011	0.2124	3396	0.8467
BO ³ NBO	6940	0.3675	4768	0.6870

Moreover, the characteristic of simplex is determined by radius of simplex and the radius distribution of void simplex, 1Na-simplex and 2Na-simplex is illustrated in Fig 2. It reveals that the radius distributions have the Gaussian form and the position of the peak systematically shifts to right (larger radius) as a number of sodium inside simplex increases. So, we conclude that Na atoms tend to be in the NBO-simplex and simplex has larger radius. The motion of Na relates strongly to simplex-type (BO or NBO).

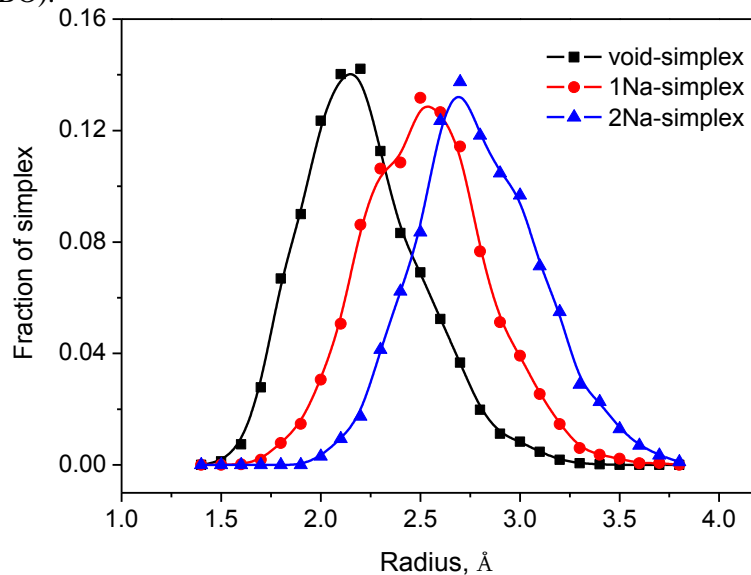


Fig 2. The radius distribution of void simplex, 1Na-simplex and 2Na-simplex.

We also calculate the time dependence of fraction X^n/X , where X is the total number of BO (or NBO); X^n is the number of BO (or NBO) near which n sodium atoms are present. The result is presented in Fig.3. As expected, BO^1/BO is significantly smaller than NBO^1/NBO and NBO^2/NBO . Very small fraction BO^1/BO confirms the fact that Na atoms stay near NBO in average for much longer time than that near BO. Thus we can conclude that Na atoms move from sites to sites located near O atoms and the resident time for Na near NBO is much longer than that near BO.

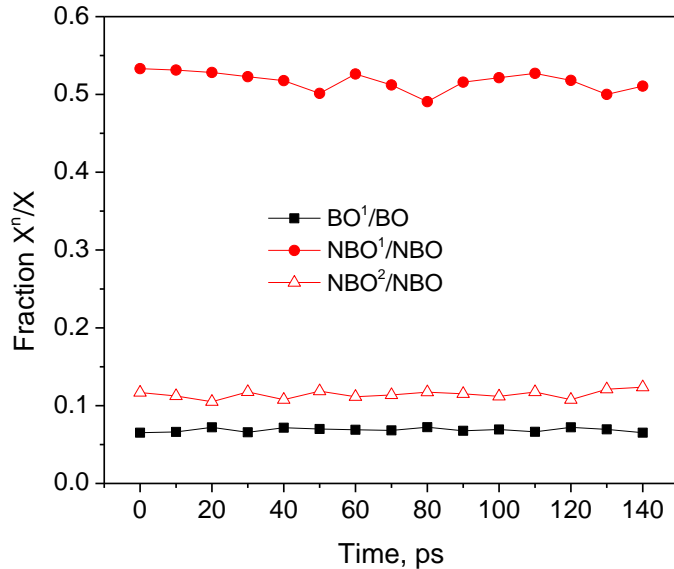


Fig.3. Fractions X^n/X as a function of time.

Next, we examine the status (BO or NBO) and occupancy for O. The occupancy for O is busy if Na is present near this O, otherwise it is free. We consider 15 configurations separated by 10 ps. For every O we count how many times when its status is BO (M_{BO}) and the occupancy for O is busy (M_{Na}). Obviously, M_{Na} and M_{BO} vary from 0 to 15. The plots of number of O versus M_{Na} and M_{BO} are shown in Fig 4. We observe that about 14% of O atoms have M_{BO} from 1 to 14. These O undergo transformations from NBO to BO and vice versa during the time t_{obs} . When the transformations of O status occur, Na atoms will be redistributed between different O atoms. In particular, as NBO transforms to BO, the Na atoms located near this NBO move to other O atoms. In the case when BO transforms to NBO, many Na atoms replace to the transformed BO. Thus, the motions of Na is strongly correlated with the one of network atom. We also mention that 86% of O atoms have M_{BO} equal to 0 or 15. This means that during the time t_{obs} the redistribution of Na happens with a small number of O atoms.

As shown in Fig.4, most of O atoms possess M_{Na} varied from 1 to 12 indicating a high rate of Na jumping. However there are 27% of O atoms having $M_{Na} = 0$, i.e. Na atoms do not enter sites near these O. This indicates the non-uniform spatial distribution of Na. Note that two O atoms connected to a common Si also form a linkage with $r_{lk} = 3.6 \text{ \AA}$. Further, we observe that Na located near a before-hoping O can jump to one among neighbors of the before-hoping O. From this follows that Na atoms hop from O atom to its neighbors within the O network. The hoping may be blockaded when neighboring atoms are completely occupied by other Na atoms.

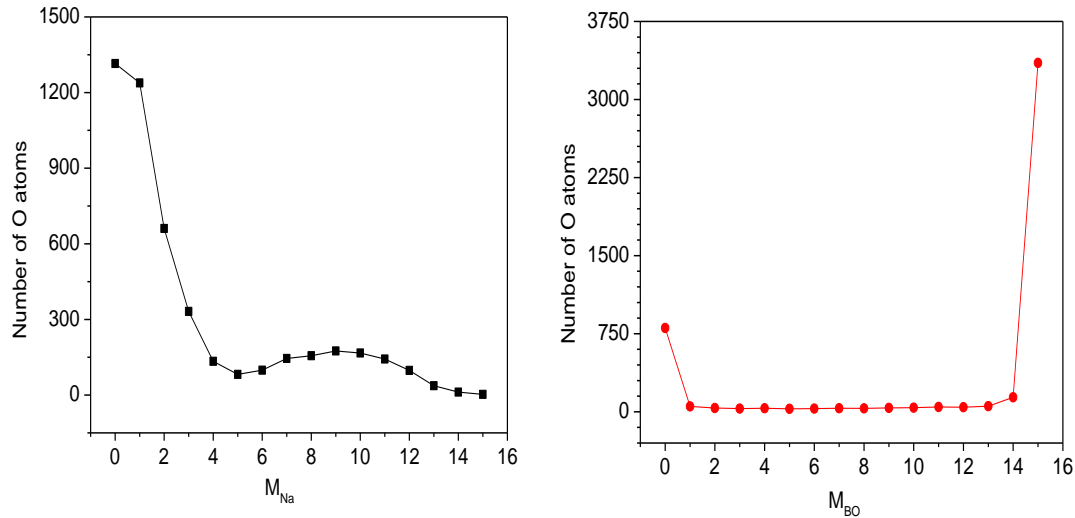


Fig.4. Plots of number of O versus M_{Na} and M_{BO} . Here M_{BO} , M_{Na} respectively is the number of times when the status is BO and the occupancy is busy.

4. Conclusion

The NS_4 liquid is systematically analyzed on dynamics and structure by MD simulation. The results show that the structure of liquid consists of a network of SiO_4 connected with each other via BO. There is also a large amount of NBO, up to 22 % of total Oxygen atoms. Furthermore, the distribution of sodium is determined via the simplex and the average resident time for Na staying near NBO or BO. It reveals that the density of Na for NBO- region is significantly larger than that for other region and sodium atoms can easily move in NBO regions. Two diffusion mechanisms of network former and modifier are discussed. : the network atoms diffuse by the bond break-reformation, while diffusion of Na consists of two parallel processes. First, Na atoms move from one to another O atom within a disordered O network where the majority of atoms have from 5 to 8 neighbors. The jump of Na is realized between two O atoms forming a linkage with $r_{lk} = 3.6 \text{ \AA}$. Second, Na atoms are redistributed between O atoms as the transformation of O status happens. Furthermore, we found that the O network comprises a number of sites where each BO has one site, while NBO possesses two sites.

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