

THE STUDY IN DIFFUSION MECHANISM BY VORONOI POLYHEDRON IN SODIUM TETRA-SILICATE MELT

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Abstract. Molecular dynamic simulation is carried out for Sodium tetra-silicate (NS4) melt at 1873 K and pressure of 0.1 MPa. The diffusion mechanism of Na atoms is investigated in terms of Voronoi polyhedron around network former and displacement of Na atoms between them. The simulation shows that Na atoms are not uniformly distributed through polyhedrons, but they mainly gather in non-bridging oxygen (NBO) and free oxygen (FO) polyhedrons. More than 75.22% of total Na atoms are place in NBO polyhedrons, although the number of NBO polyhedrons is only 22.27%. The two motion types give mainly contribution to Na diffusion: hopping of isolated Na atom or collective displacement. During 150 ps, the system comprises two separate regions: Na-poor regions formed by Si-O subnets and Na-rich regions formed by O2 clusters. The two regions have strongly different chemical composition, the density of Na atoms as well as motion type of Na atoms.

Keywords: voronoi polyhedron, molecular dynamics, diffusion, sodium tetra-silicate.

1. Introduction

Alkali silicate of various compositions is among the most widely used materials in optical technology. This material exhibits peculiar behaviors that come from their network structures, which comprise a corner sharing SiO₄ tetrahedra. The structure of alkali silicate is often focused on their ionic constituents, distribution of alkali ions as well as the influence of alkali ions on the structure network. Until now, a number of experimental and simulational studies concentrating on the structural analyses of alkali silicate have been conducted. The result of recent works [1, 2] shows that Si-O bond distance increases with sodium content, which corresponds to the formation of non-silica groups with a large bond angle. The O-Si-O and Si-O-Si bond angles very little with composition and are always close to 109⁰ and 144⁰, respectively. The local environment of sodium ions is viewed by X-ray photoemission spectroscopy and X-ray

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absorption fine structure spectroscopy [3]. The average bond distance Na-O and Na-Si locate at 2.3 Å and 3.8 Å, respectively. However, the coordination number Na-O and Na-Si significantly depends on sodium concentration. The alkali modifiers (such as sodium, lithium, and potassium ions) behave as bond breakers in the silica network, transforming part of bridging oxygen (BO) into NBO, leading to a decrease in the degree of polymerization [4]. The study [5] demonstrated that there are two types of BO: BO coordinate to two Si atoms and BO coordinates to two Si atoms and a Na atom (BO-Na). Then, there are three distinct zones of oxygen atoms, NBO zone at the interface between the channels and network, BO-Na zone located within the covalent network but close to the channels, and BO zone locates deep within the covalent network.

Using molecular dynamics simulation, Jun *et al.* [6] showed that the sodium trajectories form a well-connected network of pockets and channels. Inside these channels, the motion of the atoms is not cooperative, but rather is given by the hopping of individual atoms between the pockets. Most sodium motion occurs in a relatively small subset of the total available space, and their trajectories do not fill uniformly the space. It is also suggested by Meyer *et al.* [7, 8] that the mobility of sodium ions is originated from the formation of sodium rich channels. The sodium ions diffuse along these channels in a Si-O matrix, through which the sodium ions can easily move.

In this work, we clarify the distribution of Na ions in Si-O network and its effect on the diffusion dynamics in NS4 by using Voronoi polyhedron. The method is widely used to study the structure of ordered and disordered systems [9, 10]. The dynamics are specified by the number of Na atoms in the polyhedron and the number of visiting Na atoms for the polyhedron.

2. Content

2.1. Calculation method

Molecular dynamics simulation is done for NS4 at ambient pressure and temperature of 1873 K. This model comprises approximately 8000 atoms. The run was performed using the inter-atomic potential including two-body and three-body terms. The potential parameters can be searched at reference [11]. This model was relaxed for a long time to reach equilibrium. After that, additional runs of 150 ps are carried out to produce 15 configurations separated by 10 ps. The structural and dynamical data of the considered model is determined from these configurations. We describe the structure in terms of pair radial distribution functions (PRDF), network connectivity, and Voronoi polyhedron. We also employ voronoi analysis to view the diffusion mechanism in NS4.

This study focuses on both Si-centered polyhedrons and O-centered polyhedrons. The O atoms can be one of three types: BO, NBO, and FO. We identify the each polyhedron by a list of polyhedral faces as reference [12]. The Voronoi polyhedron determined for G atom is denoted as PG $_x$, where G is either of Si, O, BO, NBO, or FO; x is the number of Na atoms in PG. Every Na atom is located in one of these polyhedrons. The polyhedron around a network former varies in volume and form with time. The number of Na atoms in the polyhedron also changes. With each O atom, we calculated the list of available Na atoms and the average number of Na atoms in PO

overall configurations. We also determined the list of Na atoms visiting the polyhedron and an average number of visiting Na atoms for the polyhedron.

2.2. Results and discussions

Table 1. The mean inter-atomic distance determined from pair radial distribution functions and diffusion constant

System	$r_{Si-O}, \text{\AA}$	$r_{O-O}, \text{\AA}$	$r_{Si-Si}, \text{\AA}$	$r_{Na-O}, \text{\AA}$	$r_{Na-Si}, \text{\AA}$
This work	1.62	2.62	3.12	2.15	3.20
[13]	1.63	2.69	3.12	2.3	3.3
[1]	1.65	2.35	3.12	-	-
[3]	-	-	-	2.30	3.8
Diffusion constant, cm^2/s					
		D_{Si}	6.50×10^{-8}		
		D_O	8.50×10^{-8}		
		D_{Na}	4.74×10^{-5}		

Firstly, to assure the reliability of the constructed model, we determine the structural and dynamical properties in NS4. Table 1 lists the mean inter-atomic distance calculated from PRDF and diffusion constant of Si, O, and Na atoms. The mean inter-atomic distance is chosen as the first peak of PRDF. These results are compared with both experimental data [1, 3] and simulation data [13]. As seen, although r_{Na-O} and r_{Na-Si} have some discrepancies, this is in good agreement with data in these works. The diffusion constants of Si atoms and O atoms is almost equal and significantly smaller than the diffusion constant of Na atoms. It shows that Na atoms can move easily in an immobile Si-O network.

Table 2. The proportion of polyhedrons corresponding to the difference number of Na atoms

m_{NaP}	n_{PSi}/n_{Si}	n_{PBO}/n_O	n_{PNBO}/n_O	n_{PFO}/n_O
0	1	0.7231	0.0816	0.0001
1	0	0.0534	0.1154	0.0002
2	0	0.0002	0.0252	0.0004
3	0	0	0.0005	0.0001
	PG	n_{PG}/n_O	n_{NaPG}/n_{Na}	
	PBO	0.7767	0.2419	
	PNBO	0.2227	0.7522	
	PFO	0.0006	0.0059	

Table 2 lists the proportion of different types of polyhedrons in NS4. Here, m_{NaP} the number of Na atoms in a polyhedron; n_{PSi} , n_{PBO} , n_{PNBO} , n_{PFO} and n_{PG} are the number of PSi, PBO, PNBO, PFO and PG, respectively; n_{NaPG} is the total number of Na atoms in PG; n_{Si} , n_O and n_{Na} are the total number of Si, O and Na atoms, respectively. The quantities are obtained by averaging over 15 configurations. From Table 2 follows that Na atoms reside in PO, not in PSi. Most PBO also does not contain Na atoms (72.31%). Na atoms are mainly distributed in PNBO, and the number of Na atoms in a polyhedron reaches up to 3. The system also contains a small PBO1, PBO2 and PFOx. More than 75.22% of total Na atoms reside in PNBO, although the number of PNBO is only 22.27%. Figure 1 shows the fraction of PBO1, PNBO1 and PNBO2 as the function of time. It can be seen that these fractions slightly vary over time, although the transition among BO, NBO, and FO is continuously occurring. This reveals that Na atoms always tend to reside in PNBO, and PFO to maintain the local charge neutrality instead of uniformly distributing through PO.

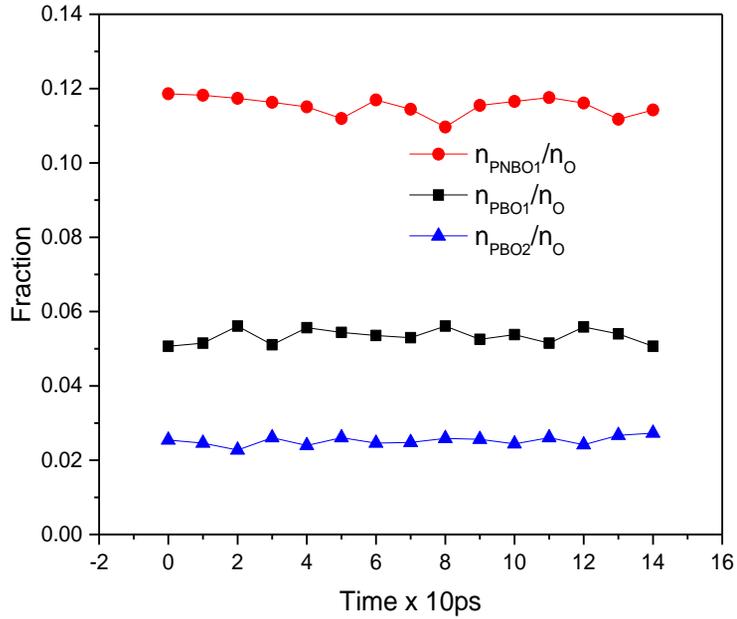


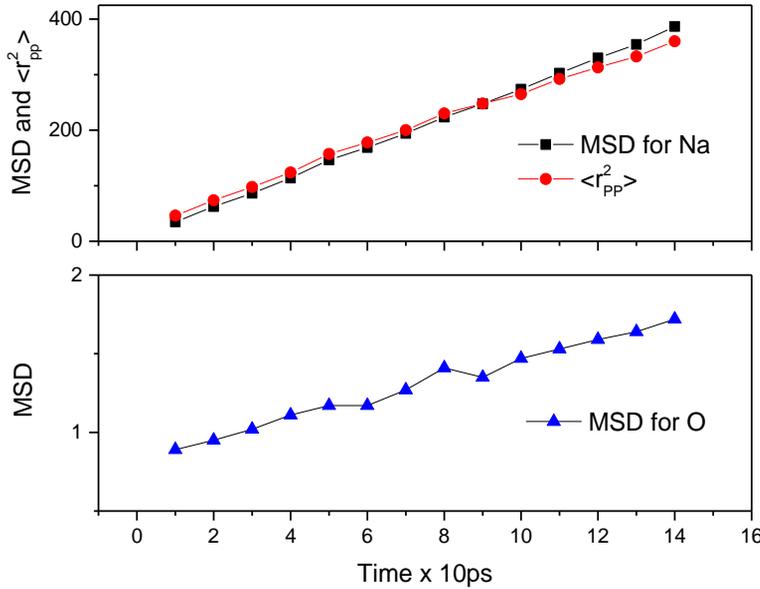
Figure 1. The fraction of PBO1, PNBO1, and PNBO2 as a function of time

To clarify the diffusion mechanism of Na atoms, we calculate the mean square displacement (MSD) for O and Na atoms. We also find distance r_{PP} between two PO, where Na atom resides at the initial and present time. The distance r_{PP} is defined as the distance between two central O atoms of these polyhedrons. As having shown in Figure 2, MSD for O atoms are significantly smaller than that for Na atoms and MSD for Na atoms is close to $\langle r_{PP}^2 \rangle$. The Na-O bond is significantly weaker than Si-O bond [5]. So, the Na-O bond is more likely to rupture than Si-O bond. This result reveals that Na atoms do not move via the collective motion of Na and O (corresponding to keeping chemical bond Na-O). That move mainly by hopping from one polyhedron to another.

Table 3. The fraction of ab polyhedrons

ab	C_{BO}	C_{NBO-FO}	ab	C_{BO}	C_{NBO-FO}
00	0.8645	0.1934	20	0.0011	0.0360
01	0.0626	0.2163	21	0.0001	0.0407
02	0.0002	0.0397	22	0	0.0061
03	0	0.0007	23	0	0.0001
10	0.0668	0.2020	30	0	0.0007
11	0.0047	0.2223	31	0	0.0006
12	0	0.0399	32	0	0.0003
13	0	0.0008	33	0	0.0001

For more detail about the flow of Na atoms through PO, the number of Na atoms that enter and leave a polyhedron has been investigated and shown in Table 3. The index a and b are the number of Na atoms that enter and leave a polyhedron within 10ps, respectively. The PO with index ab is denoted as abPO. Here, $C_{BO} = n_{abPBO}/n_{BO}$, $C_{NBO-FO} = (n_{abPNBO} + n_{abFBO})/(n_{NBO} + n_{FBO})$; n_{BO} , n_{NBO} , n_{FO} , and n_{PG} are the number of PBO, PNBO and PFO, respectively; n_{abPBO} , n_{abPNBO} , and n_{abFBO} are the number of abPBO, abPNBO and abPFO, respectively. From Table 3, one can see that 86.45% of the total PBO is 00 type and 12.94% of total PBO is 01 and 10 types. This means that the movement of Na atoms through PBO resemble the hopping of isolated Na atom and rarely happen. In contrast, only 19.34% of the total PNBO and PFO is 00 type. Fraction of 01 and 10 types reaches up to 41.83%. It also exists some other type (02, 03, 11, 12, 20, 21, 22, 23, 30, 31, 32), total is about 39%. These types correspond to the collective displacement of Na atoms.


Figure 2. MSD for Na and O atoms and $\langle r_{PP}^2 \rangle$ as a function of time

In order to check for more detail about the distribution of Na atoms and the movement of Na atoms through polyhedrons, we consider two groups of PO. The first group includes PO that has either 0 or 1 Na atom during 150ps (called as O1 group). The second group is the remaining PO that contains more than 1 Na atom at least in one configuration (called as O2 group). For convenience, the O atom and polyhedron of O1 group and O2 group are denoted O1, O2, O1-polyhedron and O2-polyhedron, respectively. The fraction of O1 atoms is about 80% of total O atoms, mainly composing BO and a small part of NBO. In contrast, O2 atoms mainly compose NBO and FO. In O2 group, more than 62% of total Na atoms reside in the space with a volume smaller than 24% of the volume of the simulation box through 15 configurations. In Figure 3 we show an average number of Na atoms per polyhedron and density of Na atoms for O1 group and O2 group. It can be seen that the average number of Na atoms per O1-polyhedron is significantly smaller than the one for O2-polyhedron. Similarly, the Na density in regions occupied by O1-polyhedrons is also significantly smaller than the one for O2-polyhedrons. The above analysis demonstrates that O1 group is significantly different from O2 group: the average number of Na per polyhedron, the Na density, and the flow of Na atoms through polyhedrons.

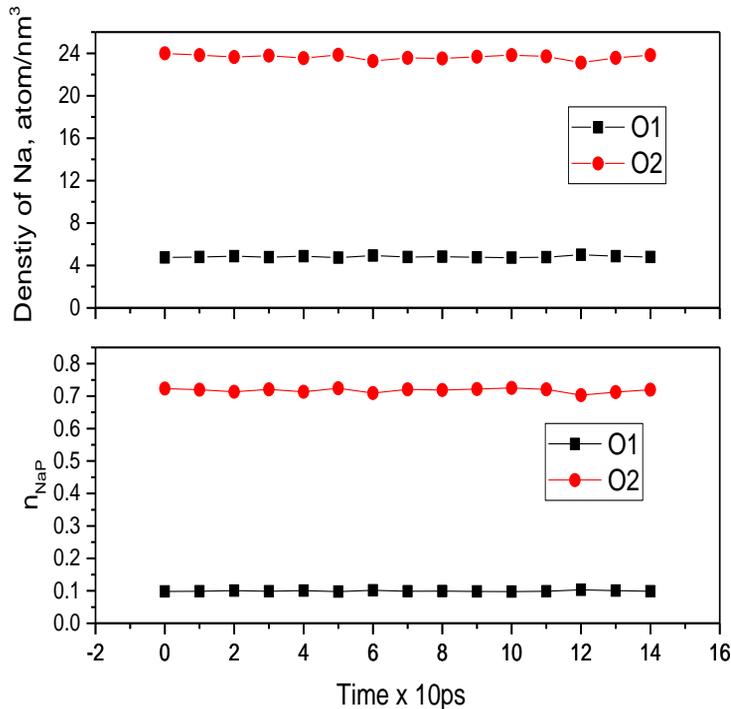


Figure 3. Average number of Na per polyhedron (n_{NaP}) and density of Na for O1 and O2 polyhedrons.

We mention that O1 group and PSi form Si-O subnet. In the subnet, one Si atom links four O atoms of O1 group. The Si-O linkage is formed by Si and O atoms when their distance is smaller than $r_{cutoffSiO}$. We also survey O2 cluster, which consists of a group of O2 linked with each other by O-O linkages. The O-O linkage is found when

the distance between two O atoms is smaller than $r_{cutoffO}$. The cut off distance r_{cutoff} is chosen as the first minimum after the first peak of PRDF. The results have been shown in Table 4. Table 4 shows the size distribution of subnets and clusters. Here, n_s and n_c are the number of subnet and cluster, respectively. The size of subnet or cluster is defined as the number of networks former in subnet or cluster, respectively. By varying different configurations, we made sure that the results obtained do not depend on surveyed configuration. From this table, we recognize immediately that NS4 has a subnet that contains 4501 atoms, corresponding to 65% of total network formers. This subnet forms a large Na-poor region. The remaining subnets are significantly smaller in size. O2 atoms are distributed in a large number of clusters. In particular, 329 clusters have one atom, corresponding to 64.5% of total clusters. These clusters are surrounded only by O1-polyhedron and PSi. The other clusters consist of 2 to 45 O2 atoms which represent as “pocket for sodium”. These pockets form Na-rich regions. Thus, the system consists of separate Na-poor regions which are placed inside matrix of Na-rich regions. We note that a strong correlation between the location of Na-poor regions and the location of PSi and PBO. In contrast, the location of Na-rich regions has a strong correlation with the location of PNBO and PFO. During observation time the chemical composition, Na density as well as type of Na motion through those regions differ strongly from each other. Therefore, the above analysis demonstrates the structural and dynamical heterogeneities in NS4 melt.

Table 4. The size distribution of subnets and clusters

Size of subnets	n_s	Size of clusters	n_c
5	15	1	329
9	2	2	91
13	2	3	36
21	1	4	24
32	1	5	7
4501	1	6	7
-	-	7	5
-	-	8	1
-	-	9	2
-	-	10	3
-	-	12	1
-	-	13	2
-	-	15	1
-	-	17	1

3. Conclusions

Molecular dynamical simulation is carried out for NS4 melt at 1873 K and pressure of 0.1 MPa. A new analysis method was proposed and applied to clarify the structure and dynamics by using Voronoi polyhedron around network former and displacement of Na atoms between them. In summary, the simulation reveals that Na atoms are non-uniformly distributed through polyhedrons. Namely, Na atoms do not reside in PSi and a major part of PBO, but they mainly gather in NBO and FO polyhedrons. More than 75.22% of total Na atoms are placed in PNBO, although the number of PNBO is only 22.27%. This simulation also shows that Na atoms do not move via the collective motion of Na and O. The movement of Na atoms through PBO seems to be just the hopping of isolated Na atoms. In contrast, the movement of Na atoms through PNBO and PFO has two types: hopping of isolated Na atoms and collective displacement of Na atoms. The diffusion process of Na atoms is contributed mainly by two types of motion. During observation time, the system consists of separate Na-poor regions formed by Si-O subnets and Na-rich regions formed by O2 clusters. The largest Si-O subnet has a size up to 65% of the total network former. The size of the O2 cluster reaches up to 45 atoms. The two regions have strongly different in chemical composition, the density of Na atoms as well as motion type of Na atoms (hopping of isolated Na atom or collective displacement). Therefore, the structure and dynamic of NS4 melt are heterogeneous.

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