

COMPUTER SIMULATION OF LOCAL STRUCTURE AND DIFFUSION MECHANISM THROUGH VORONOI POLYHEDRONS IN SODIUM SILICATE GLASS

Giap Thi Thuy Trang¹ and Nguyen Thi Thao^{2,*}

¹*Department of Physics, Thai Nguyen University of Education*

²*Faculty of Physics, Hanoi National University of Education*

Abstract. The Na₂O.SiO₂ glass has been studied at different temperatures from 300 K to 1173 K by using molecular dynamics simulations. The Voronoi Si and O polyhedrons are analyzed to evaluate the displacement of sodium between these polyhedrons. The results show that more than 90% of the total number of Na is located in NBF polyhedrons that contain non-bridging (NBO) and free oxygen (FO) polyhedrons. The site energy for Na atoms located in NBF is smaller than one in BO polyhedron. The diffusion process of Na atoms is occurred in two ways: the first one is the alone jumping of Na in BO polyhedrons and the second one is the mixed alone jumping of Na and the cooperative movement of Na in NBF polyhedrons. The calculation of the average time between two consecutive jumps and the visiting time for Na atoms leads to the correlation effect for the diffusion of Na atoms. This effect depends on the temperature of the samples.

Keywords: structure, dynamics, sodium-silicate, simulation, Voronoi polyhedron.

1. Introduction

Sodium silicate is a highly applicable material. It is widely used in many fields such as cement making, ceramics, cleaning agents, and wood treatment. This is also a compound that exists in nature. Therefore, understanding these systems has important implications for the fields of Materials and Earth Science. Up to now, sodium silicate has attracted many experimental studies such as neutron diffraction [1-3], X-ray diffraction [4-5], and simulation [6-10]. The research results have provided quite a lot of information about the structure and dynamics of this material. For example, some experiments have determined the average distance of Si-O to be 1.61 - 1.65 Å, Na-O to be 2.3 - 2.4 Å, and Na-Si to be 3.4 - 3.8 Å [3-5]; The phenomenon of short-distance shoulder appearance in the Si-O radial distribution obtained from the experimental results of neutron diffraction is believed to be caused by the existence of NBO [1]; In addition, ref. [2] have shown that the Na element does not diffuse randomly but follows its paths in the Si-O network called channels. The results obtained above are also

Received October 7, 2021. Revised October 22, 2021. Accepted October 29, 2021.

Contact Nguyen Thi Thao, e-mail address: thaont@hnue.edu.vn

confirmed in studies by the simulation method [6-10]. Specifically, in accordance to study [8], the NBOs and BOs which exist in the sodium silicate model have an average bond length of Si-NBO of 1.56 - 1.58 Å and Si-BO of 1.61 - 1.65 Å. Huang and Cormack found from simulations that sodium silicate at 293K consisted of 35% NBO and 65% BO [6]. In a study with a model at 1000 K, W. Smith reported that when sodium was added to the silica network, it partially broke the S-O bonds, leading to the conversion of some bridged oxygen into unbridged oxygen with the formation of Na-O bonds in the sodium silicate glass network structure [10]. In addition, information on the presence of unbridged oxygen can also be found through the survey results of Q_n oxygen bridges ($n = 1\div 4$, n is the number of oxygen atoms bridged in each SiO_4 structural unit); where Q_4 corresponds to the structure consisting of all bridged oxygen and Q_1 - Q_3 corresponds to the structure with unbridged oxygen. Surveying the model with about 30% of sodium oxide, the proportion of Q_4 accounts for only about 29.5 - 33.6%, and the proportion of Q_1 - Q_3 accounts for 66.4 - 70.4% [8, 11]. In another study [9], surveying the sodium silica model at 2100 K showed that: Q_3 oxygen bridge accounted for 45% - 60% and Q_4 accounted for 40% - 55% with NS2 and NS3 systems. The presence of Q_1 - Q_3 bridging oxygens with a large percentage also indicates that many NBOs are present in the model. Several studies [7, 10, 12] have shown that sodium element diffuses much faster than silicon and oxygen elements, especially at low temperatures due to the existence of channels in the Si-O lattice. The ref. [10] also confirmed that the diffusion of sodium is carried out by the oscillation of these elements around a position and after a period of time jumping to a new position and determined sodium. It diffuses strongly in the sodium silicate system at 1600 K with a diffusion coefficient of about $2.6 \cdot 10^{-4} \text{ cm}^2/\text{s}$. The difference between the diffusion of sodium and silicon, oxygen decreases with increasing temperature. It is shown in ref. [9] that silicon and oxygen diffuse with a coefficient of $0.78 \cdot 10^{-5} \text{ cm}^2/\text{s}$ and $D_O = 1.17 \cdot 10^{-5} \text{ cm}^2/\text{s}$; Meanwhile, the diffusion coefficient of sodium is about $2.35 \cdot 10^{-5} \text{ cm}^2/\text{s}$. At the temperature of 2000 K, the results showed that the sodium distribution is not uniform but forms aggregates with the size of about 3 - 6 Å (pockets) and sodium movement in these aggregates [12]. Also, the mean squared displacement of bridging and non-bridging oxygen is similar; therefore, it can be assumed that all oxygen is almost frozen in the lattice at low temperature and the main contributor to diffusion in the network is the sodium element in the channels. Therefore, at low temperatures, the diffusion of sodium in the channel is significantly higher than that outside the channel [13]. Work [14-16] has shown that sodium often preferentially diffuses to a site already occupied by other sodium; This is evidence of sodium channel movement, but the cause of this phenomenon has not been explained by the authors. In summary, experimental and simulation studies have provided quite a bit of information on the structure and dynamical properties of the sodium silicate system. However, there are still some issues that need to be further clarified in this study, such as information on $NBO \leftrightarrow BO$ variation over time, sodium distribution around NBO and BO, and the diffusion mechanism of sodium. We believe that this information plays an important role in material manufacturing technology as well as in controlling natural phenomena occurring in the Earth's crust.

2. Content

2.1. Computational method

MD simulation is carried out for sodium silicate glass at temperatures ranging from 300 to 1173 K and pressure of 0.1 MPa. The model is made of 9996 particles including 4998 O, 1666 Si, and 3332 Na. It is well known that it is very important to select reliable interatomic potentials for MD simulations. We adopt the inter-atomic potential consisting of two- and three-body terms to the model [17]. To collect the dynamical and structural data we also produce 15 configurations separated by 10 ps from well-annealed models. The local structure is analyzed by pair radial distribution function (PRDF). The calculation of Voronoi polyhedron is performed on both Si and O. It turns out that the simulation box is filled by O-centered and Si-centered polyhedrons, and Na are placed inside these polyhedrons. For convenience, A-centered polyhedron is denoted by A-polyhedron, Ax-polyhedron, or Ax, where A is the Si, BO, or NBF; x is the number of Na in A-polyhedron. For example, BO-polyhedron, NBF2 are the BO-centered polyhedron and NBF-centered polyhedron containing 2 Na, respectively. The local sodium density in the vicinity of the A atom is specified by the average number of Na in A-polyhedron $\langle x_A \rangle$.

2.2. Results and discussion

The partial RDF for BO-Na, NBF-Na, and Si-Na pairs at the temperature of 300 and 1173 K is shown in Figure 1. The partial RDF at temperatures of 573, 773, and 973 K that are not shown here has a similar shape. One can see that the height of the first peak of $g_{\text{NBF-Na}}(r)$ is about three times higher than that of $g_{\text{BO-Na}}(r)$. This suggests that Na mostly are located around NBF and rarely present in the vicinity of BO. The position of the first peak of RDF for BO-Na; NBF-Na and Si-Na pairs shows the distance between O and Na atoms, Si and Na atoms at 2.35 and 3.25 Å, respectively. These positions do not change at different temperatures, but the height of these peaks decreases with increasing temperature.

The distribution of Na in BO and NBF polyhedrons and the number of different types of polyhedrons are calculated in Table 1. Here, n_{BO} and n_{NBF} are the numbers of BO- and NBF- polyhedrons, respectively. The number of Na in these polyhedrons is called x . Most of these polyhedrons are BO0, BO1, NBF0, NBF1, and NBF2, fewer NBF x with $x > 2$. As seen in Table 1, the number of BO1 and NBF1 polyhedrons increase significantly as the temperature increases. Meanwhile, the number of BO0, NBF2, and NBF $x > 2$ polyhedrons decreases with the increasing temperature. The BO0 and NBF0 describe the empty O-polyhedrons. According to the single diffusion model, Na atoms will move from one to empty sites located in BO or NBF polyhedron that has one site and two sites, respectively. The displacement of Na atoms between the polyhedrons leads to the formation of different types of polyhedrons and the fast diffusivity of Na atoms.

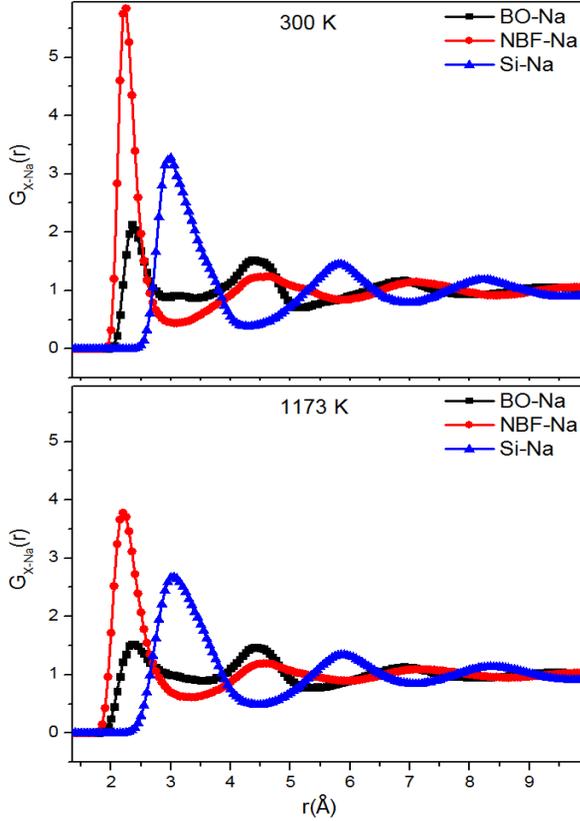


Figure 1. The partial radial distribution function for BO-Na, NBF-Na and Si-Na pairs at temperature of 300 K and 1173 K

Table 1. Distribution of Na in Ax-polyhedrons

T (K)	n_{BO0}	n_{BO1}	n_{NBF0}	n_{NBF1}	n_{NBF2}	$n_{NBF>2}$
300	1478	252	1039	1482	647	97
573	1416	311	1044	1520	621	80
773	1389	334	1056	1518	617	75
973	1361	360	1060	1535	602	69
1173	1344	378	1066	1537	589	68

In Table 1, n_{Ax} is the number of Ax-polyhedrons; A is the BO or NBF; x is the number of Na in Ax-polyhedron; n_{NBF} , n_{BO} is the total number of NBF and BO polyhedrons, respectively.

The fraction of volume of different types of Voronoi polyhedrons and the fraction of the number of Na that reside in O-polyhedrons are presented in Table 2. Results show that the volume per polyhedron increased in the order: Si-polyhedron \rightarrow BO-polyhedron \rightarrow NBF-polyhedron. The volume of Si-polyhedron only accounts for less than 9.5% of the simulation box. So, the total volume of BO and NBF polyhedrons is more than 90.5% of the simulation box. We can see that the fraction of the number of

Na residing in NBF polyhedrons is more than ten times bigger than that of BO polyhedrons. This result indicates that Na atoms are non-uniformly concentrated in O polyhedrons, but instead of they are concentrated mainly in NBF polyhedrons. The fraction f_{NaBP} (the fraction of the number of Na residing in BO polyhedron) slightly increase with increasing temperature pointed out that more sodium resides in BO polyhedrons at a higher temperature. This clarifies the fact that sodium diffuses through specific pathways.

Table 2. The fraction of volume of Voronoi polyhedrons measured in \AA^3

T(K)	f_{Si} (%)	f_{BO} (%)	f_{NBF} (%)	f_{NaBP} (%)	f_{NaNP} (%)
300	9.41	24.37	66.22	7.77	92.23
573	9.43	24.27	66.30	9.99	90.01
773	9.36	24.13	66.51	9.60	90.40
973	9.36	24.01	66.64	10.92	89.08
1173	9.29	23.98	66.74	11.97	88.03

In Table 2 ($f_{\text{Si}} = V_{\text{Si}}/V_{\text{SB}}$, $f_{\text{BO}} = V_{\text{BO}}/V_{\text{SB}}$, $f_{\text{NBF}} = V_{\text{NBF}}/V_{\text{SB}}$); V_{Si} , V_{NBF} , V_{SB} is the volume occupied by Si-, BO-, NBF-polyhedrons and volume of simulation box, respectively; and the fraction of number of Na residing in BO (f_{NaBP}) and NBF (f_{NaNP}) - polyhedrons ($f_{\text{NaBP}} = n_{\text{NaBP}}/n_{\text{Na}}$, $f_{\text{NaNP}} = n_{\text{NaNP}}/n_{\text{Na}}$)

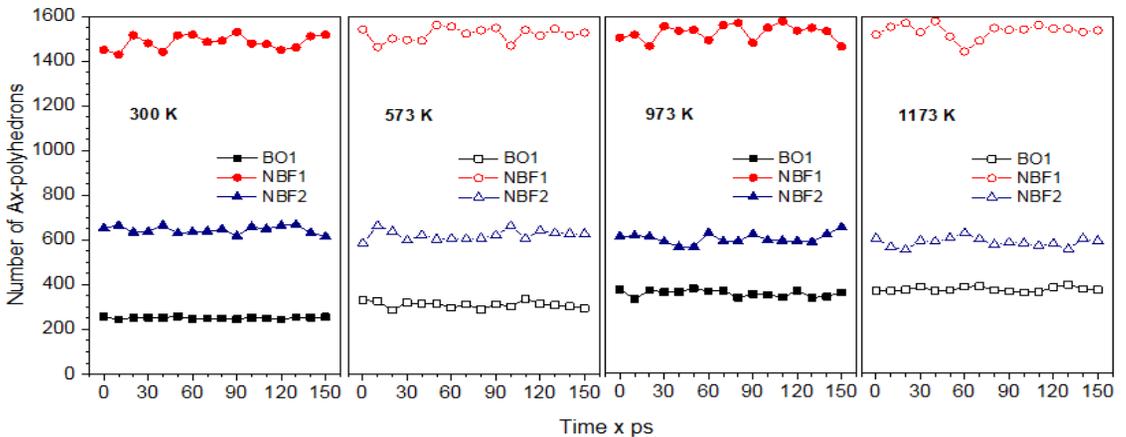


Figure 2. The variation of the number of Ax-polyhedrons at 300, 573, 973 and 1173

The number of BO1, NBF1, and NBF2 are shown in Figure 2. One can see that the number of these polyhedrons fluctuates around finite values because of the frequent displacement of Na atoms between O-polyhedrons. The number of BO1 is the smallest and it increases with the increase of temperature. This indicates that more Na shifts to the BO polyhedrons when temperature increases. The number of NBF2 is the biggest and its fluctuation is also the strongest. Therefore, Na atoms are constantly shifting from one NBF to another. This leads to the variation of the average number of Na in polyhedrons over time. Figure 3 shows the dependence of the fraction of BO and NBF polyhedrons on the average number of Na in these polyhedrons for 150 ps. For the distribution of NBF polyhedrons, it has a pronounced peak at the average number of Na equals 0.75 and spread on a wide range. Meanwhile, the major BO polyhedrons have

small values of the average number of Na. When the temperature increases, the curve of distribution for NBF spreads on the narrower range. This result confirms the diffusion pathway which is composed of NBF-polyhedrons. As seen from Figure 3, the average number of Na for NBF is significantly larger than that for BO. Thus, the site energy for Na located in BO polyhedrons must be larger than in NBF polyhedrons.

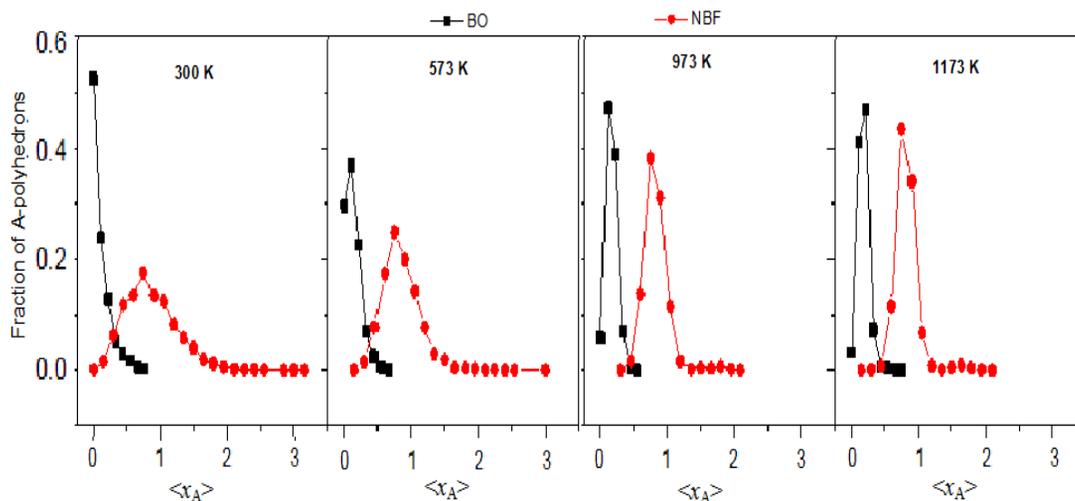


Figure 3. The dependence of the fraction of BO and NBF-polyhedrons on the average number of Na in A-polyhedron $\langle x_A \rangle$ for 150 ps

The time dependences of deviation for BO and NBF polyhedrons at different temperatures are plotted in Figure 4. One can see that the derivation decreases fast with time for both BO and NBF polyhedrons at all considered temperatures. The δ_{Ax} for NBF is higher than that for BO at the same temperature. At higher temperatures, the derivations are close to each other for BO and NBF polyhedrons. These values proceed to smaller values as the temperature increases.

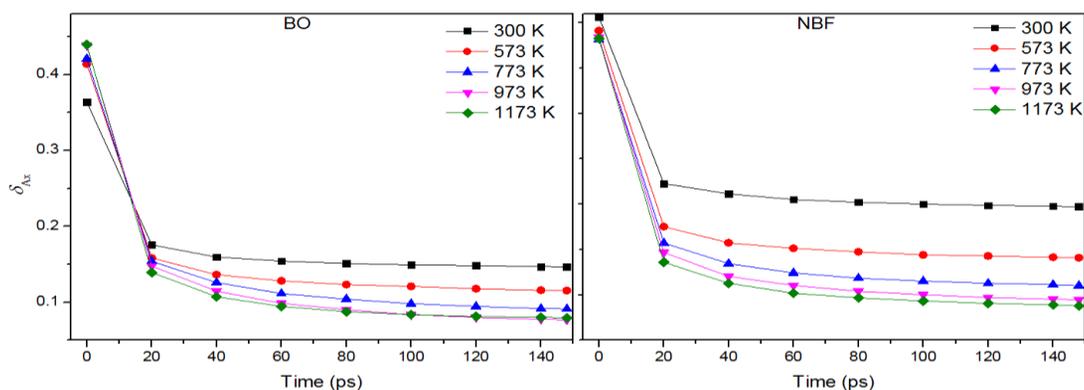


Figure 4. The variation of deviation δ_{Ax} of BO and NBF polyhedrons over time at different temperatures

The variation of the average number of Na that stays in A polyhedron or moves from A polyhedron to another one within 2 ps at different temperatures is shown in Figure 5. It can be seen that the number of staying Na decreases with increasing temperature for both BO and NBF polyhedrons. The number of Na moving from BO to NBF is significantly larger than BO to BO. For NBF polyhedrons, the number of Na moving from NBF to NBF is larger than NBF to BO. So, the diffusion pathways are derived from Na atoms either staying in NBF polyhedrons or moving from NBF to NBF polyhedrons. From the displacement of Na in the O polyhedrons, we conclude that Na performs the alone jumping and cooperative motion in NBF-polyhedrons. The cooperative motion is realized in more NBF-polyhedrons at higher temperatures.

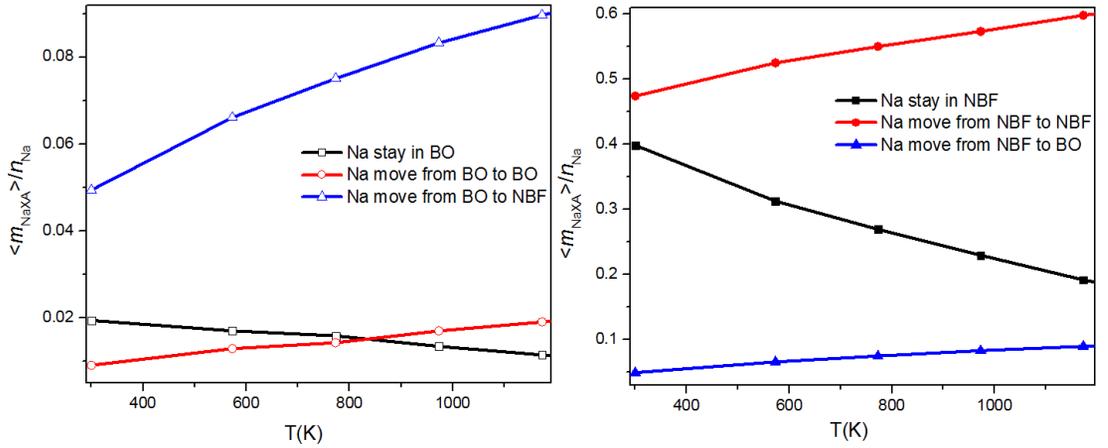


Figure 5. The temperature dependence of the average number of Na staying in A-polyhedrons or moving from A-polyhedron to another one within 2 ps

Table 3. Characteristics of the average time between two consecutive jumps in BO-, NBF-polyhedrons and average visiting time for a polyhedron

Temperature (K)	300	573	773	973	1173
$\langle \tau_{\text{jumpB}} \rangle$, ps	1.32	1.21	1.17	1.13	1.11
$\langle \tau_{\text{jumpN}} \rangle$, ps	1.72	1.51	1.42	1.34	1.27
$\langle \tau_{\text{polyhedron}} \rangle$, ps	17.7	13.87	8.71	4.82	2.94

When Na atoms move between polyhedrons, they spend different visiting times in these polyhedrons. We call the time between two consecutive jumps in the given polyhedron is equal to τ_{jump} . Thus, the average visiting time for O, BO, and NBF polyhedrons are equal to $\langle \tau_{\text{polyhedron}} \rangle$, $\langle \tau_{\text{jumpB}} \rangle$, and $\langle \tau_{\text{jumpN}} \rangle$, respectively. Values of these average times at different temperatures are calculated in Table 3. As the temperature increase, these values decrease. The larger value of $\langle \tau_{\text{polyhedron}} \rangle$ is due to the forward-backward jumps of Na and Na visits many times at the same polyhedron.

Therefore, the correlation effect is significant for the diffusion of Na atoms. This phenomenon increases significantly with decreasing temperature.

3. Conclusions

The structural and dynamical properties of $\text{Na}_2\text{O} \cdot \text{SiO}_2$ glass were studied at different temperatures from 300 K to 1173 K by molecular dynamics simulations. More than 90% of Na atoms are located in NBF polyhedrons. Analysis of the displacement of Na atoms between different types of O polyhedrons shows that the diffusion of Na atoms is done by the alone jumping in both BO and NBF polyhedrons, and by the cooperative movement in NBF polyhedrons. There are empty sites located in O polyhedrons, then the diffusion process occurs when Na moves from one to other empty sites. The major shift takes place from NBF to NBF because the site energy for Na located in NBF polyhedrons is smaller than that in BO polyhedrons. The average time between two consecutive jumps decreases with increasing temperature. Therefore, the correlation effect is significant for the diffusion of sodium at lower temperatures.

Acknowledgement. This research is funded by the Thai Nguyen University of Education, Thai Nguyen University, under project number CS.2021.17.

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