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MOLECULAR DYNAMICS SIMULATION OF THE DIFFUSION PROCESS OF SODIUM ATOMS IN $Na_2O.3SiO_2$ AND $Na_2O.4SiO_2$ SYSTEMS

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Abstract. The $Na_2O.3SiO_2$ and $Na_2O.4SiO_2$ materials have been investigated in the range of temperatures from 973 K to 1573 K by using molecular dynamics simulations. The diffusion behaviors of sodium atoms in a fixed Si-O network have been assessed by analyzing both the mean square displacement of sodium atoms and the number of O coordination of sodium atoms. The results show that the diffusion behavior of sodium atoms is governed by the rate of change in their oxygen coordination number. This dependence is described by a quadratic equation, applicable to all samples considered at various temperatures and SiO_2 content.

Keywords: O coordination number, diffusion behavior, sodium silicate glass, MD simulations.

1. Introduction

Alkali silicate glasses have attracted considerable scientific interest due to their attractive ionic transport properties [1]. These glasses exhibit significantly higher diffusivity of alkali ions compared to that of Si and O atoms [2]. The specific mobility of alkali ions is attributed to their preferential diffusion along specific pathways [3]. The diffusion of alkali ions via an alkali-rich channel in a fixed Si-O network was observed by a quasi-elastic neutron scattering experiment.

Molecular dynamics (MD) simulation is considered as a useful research method to study the diffusion of alkali ions in amorphous silicates [4,5]. Because this method allows us to observe the change in the atomic coordination number with time, these simulation studies have also shown that the diffusion of alkali atoms in amorphous silicates occurs along preferential paths or channels, forming a subnet in the simulation box [6,7]. These channels have been inferred through techniques such as extended x-ray absorption spectroscopy [8], and inelastic neutron scattering [9].

In previous work [10], we conducted an analysis of BO (bridging oxygen), NBO (non-bridging oxygen), and FO (free oxygen) polyhedra in MD models of sodium silicate glass and investigated the distribution of sodium atoms between these polyhedra.

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Although this simulation improved our knowledge about the dynamics in alkali silicate glass, numerous aspects of this phenomenon remain poorly comprehended. For instance, how the distribution and movement of sodium atoms are in the structure of the Si-O network, and the relation between the movement of sodium atoms and the O coordination number. To provide detailed insights into the diffusion of sodium atoms, in this paper, we have determined the number of oxygen coordination for Si and Na atoms in MD models of sodium silicate glass at various temperatures and SiO_2 contents. We then derive an expression for the diffusion coefficient of sodium atoms and the rate of change in their number. This study has also shown the influence of temperature and SiO_2 concentration on the properties of diffusion behaviors of sodium atoms.

2. Content

2.1. Computational method

Molecular dynamics simulation is used to construct the Na_2O. $3SiO_2$ and Na_2O. $4SiO_2$ systems, commonly referred to as NS3 and NS4 systems, respectively. These systems are generated under a pressure of 0.1 MPa and temperatures ranging from 973 K to 1573 K. The NS3 system contains 9996 atoms with 5555 O atoms, 2499 Si atoms, and 1666 Na atoms. On the other hand, the NS4 system contains 9990 atoms with 5994 O atoms, 2664 Si atoms, and 1332 Na atoms. The interaction potentials employed to describe the interactions between the atoms in the system consist of two-body and three-body terms. The system is initially generated by randomly distributing atoms within the simulation box. Subsequently, the sample undergoes thermal annealing at 1573 K, employing the NPT ensemble, for a duration of 5 ns, which corresponds to 5 million simulation steps. Following the annealing process, the systems are cooled down to 973 K at a cooling rate of 10^{11} K/s.

To study the structure and dynamics of the systems, a simulation is conducted for a duration of 150 ps, resulting in 76 configurations, each recorded at 2 ps intervals. The structural analysis involves the calculation of the pair radial distribution function (RDF) and the temporal distribution of the number of coordinated atoms. The diffusion behavior of sodium atoms is investigated by determining the mean square displacement (MSD) of sodium atoms and the rate of change of the oxygen coordination number of Na atoms. The diffusion coefficient (D) for sodium atoms is derived from the slope of the graph depicting the relationship between MSD and time. Similarly, the rate of O coordination number change of Na atoms is determined from the slope of the graph illustrating the dependence of the O coordination number on time. Thus, the correlation between diffusion and the variation in the O coordination number of Na atoms can be determined.

2.2. Results and discussion

The radial distribution function (RDF) for NS3 and NS4 samples at a temperature of 1573 K is shown in Fig.1. The first peak of the RDF for both NS3 and NS4 samples occurs at a distance of 1.55 Å. The height of this peak is 4.54141 and 4.8489 for NS3 and NS4 samples, respectively. A comparison between the RDF obtained from MD simulations and the results from a neutron diffraction experiment [11] shows good agreement in the position and height of peaks. This congruence provides compelling evidence regarding the accuracy and reliability of the MD simulation models.

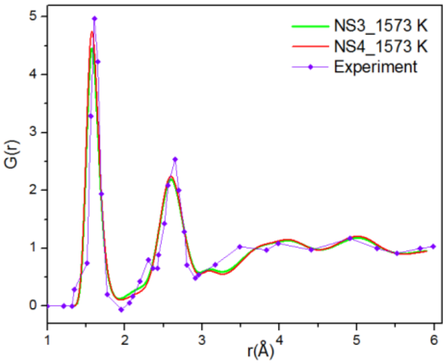

Figure 1. The total RDF for NS3 and NS4 samples at 1573 K, and the comparison with experimental data [11]

The spatial distribution of atoms is examined at intervals of 2 ps using the coordination numbers of these atoms. Fig.2 displays the distribution of different coordination atoms (DCA) of Si and Na atoms across a range of temperatures from 973 K to 1573 K. Specifically, Si atoms exhibit a consistent coordination number of 4, indicating the presence of 4 O atoms surrounding each Si atom throughout the temperature range. The number of DCA for Na atoms increases rapidly with time and depends on both temperature and SiO_2 content. As temperature increases, the rate of increase in the number of O coordination atoms diminishes. This observation lends support to the notion that Na atoms move within a fixed Si-O network, and their mobility is modulated by temperature and SiO_2 content.

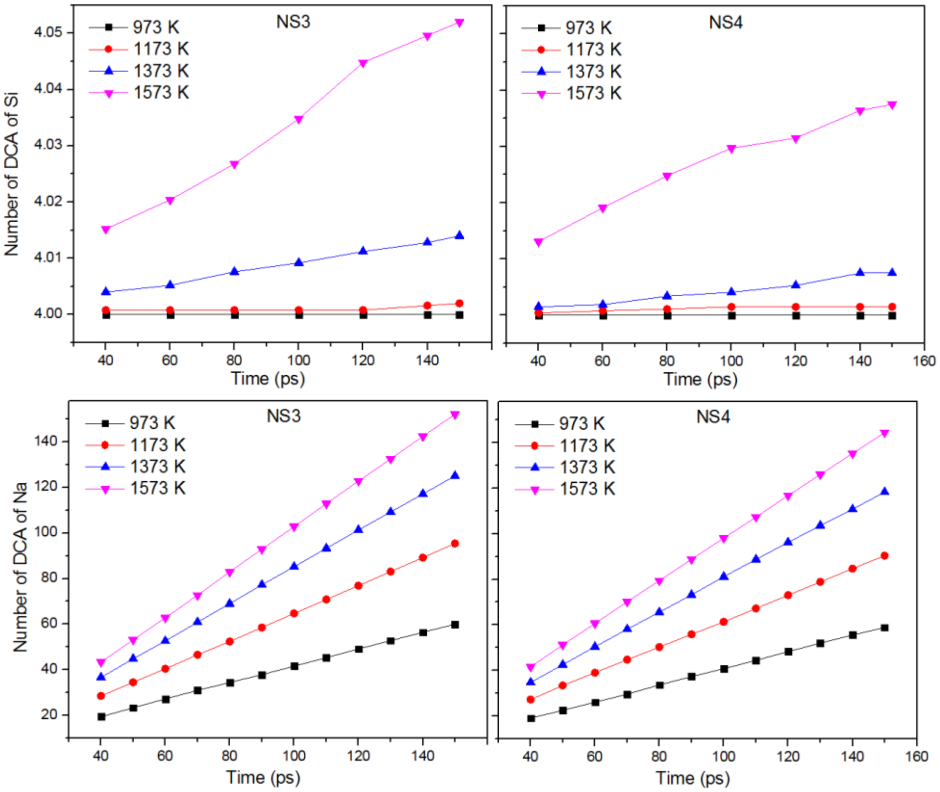

Figure 2. The change of the number of DCA of Si and Na atoms with time

The diffusion behavior of Na atoms in a fixed Si-O network is considered through the calculation of the mean squared displacement (MSD) of these atoms over time. The MSD of Na atoms over an interval of 150 ps is presented in Fig.3. Notably, the MSD of Na atoms exhibits a linear increase with time. The rate of this temporal increase in the MSD depends on both temperature and concentration of SiO_2. Higher temperature facilitates the more accessible thermal motion of Na atoms in systems, leading to a more rapid increase in the MSD of these atoms. Conversely, increasing the concentration of SiO_2 decreases the MSD of Na atoms due to a reduction in the number of Na atoms and an increase in the number of fixed Si-O networks. From the slope of the graph on the dependence of MSD on time, the values of diffusion coefficients of NS3 and NS4 samples are calculated at various temperatures. Table 1 provides an overview of the obtained values of D for Na atoms at different temperatures. It is evident that the D of Na atoms increases with increasing temperatures and decreases with increasing SiO_2 concentration, reflecting the temperature and concentration of SiO_2 dependences of Na atoms mobility within the fixed Si-O network.

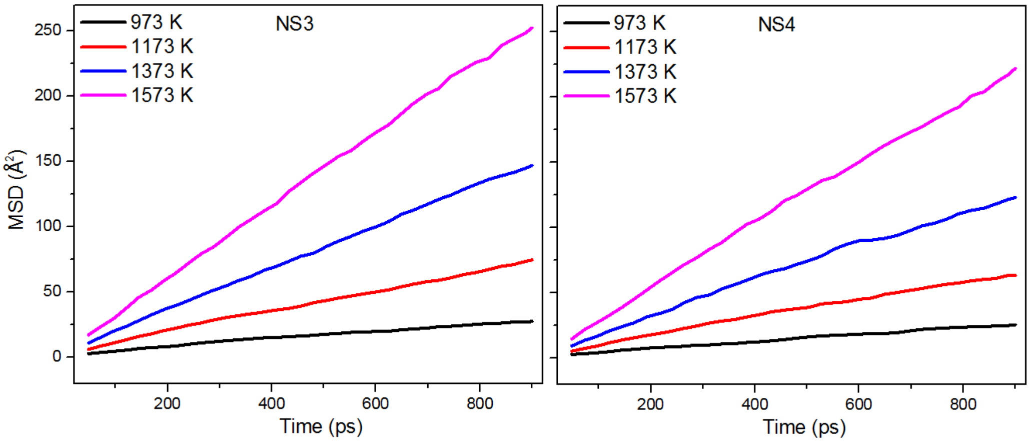

Figure 3. The temporal evolution of the MSD of Na atoms

Table 1. The diffusion coefficient D (10^{-4} cm^2/s) of NS3 and NS4 samples at various temperatures

T(K)	973	1173	1373	1573
NS3	0.0276	0.07554	0.15913	0.27764
NS4	0.02665	0.06661	0.13048	0.23672

When Na atoms move within a fixed Si-O network, they encounter an increasing number of coordinated O atoms (referred to as N_{CO}) over time. The variation of N_{CO} of each Na atom over time is shown in Fig.4. One can see that the ratio of N_{CO}/Na increases linearly with time. The rate of temporal increase is particularly accelerated under high temperature conditions and lower concentration of SiO_2. Therefore, the change rate of N_{CO}/Na is a critical factor influencing the diffusion of sodium atoms in systems. From the slope of the graph of N_{CO}/Na versus time, calculate the rate of change of N_{CO}/Na, denoted as shown in Table 2. As seen, it increases with increasing temperature.

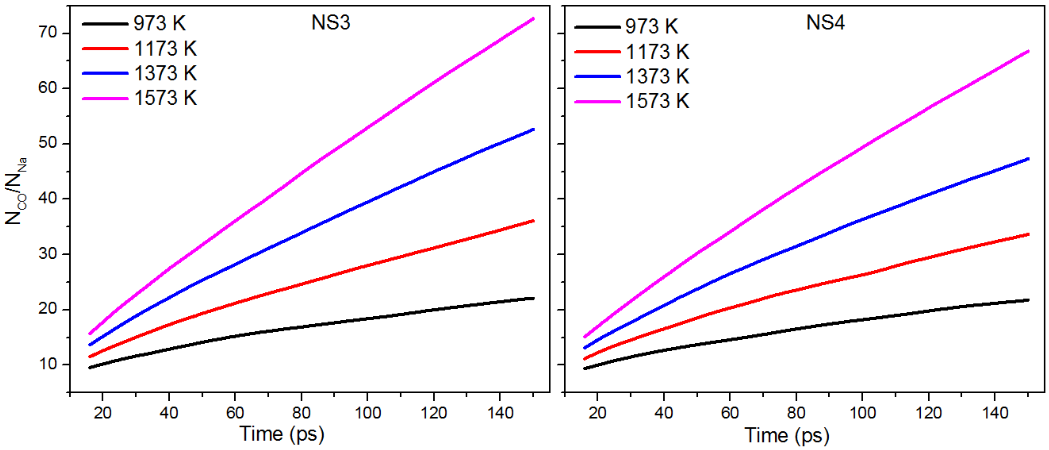

Figure 4. The variation of N_{CO}/Na as a function of time at various temperatures

Table 2. The **rate of change of** *N_{CO}/Na (λ - ps^{-1}) of NS3 and NS4 samples at different temperatures*

T(K)	973	1173	1373	1573
NS3	0.08747	0.17464	0.28326	0.4188
NS4	0.0881	0.15947	0.24756	0.3785

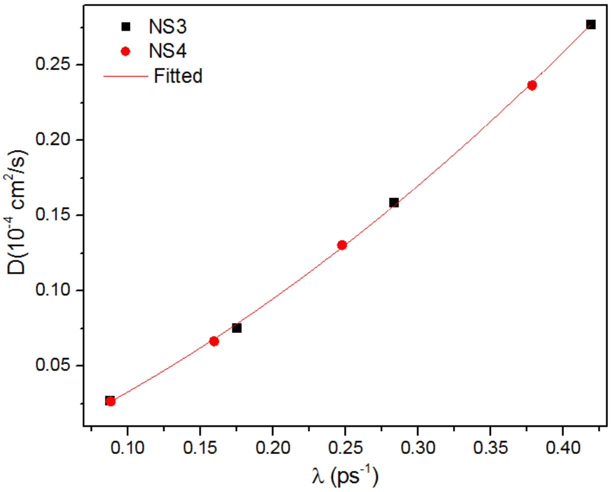

Figure 5. The dependence of D on λ

The correlation between the diffusion coefficient *D* and is visually depicted in Fig. 5. One can see that the diffusion of Na atoms increases with increasing of λ. Moreover, at high, temperatures the influence of the concentration of atoms on sodium's diffusion becomes more pronounced. It is noteworthy that these relationships can be approximated by the second - order polynomial fit, represented as:

$$D = 0.66943\lambda^2 + 0.41824\lambda - 0.01551$$

This observation suggests consistent and uniform diffusion behavior among all the samples examined.

3. Conclusions

MD simulations were performed for Na_2O. $3SiO_2$ and Na_2O. $4SiO_2$ systems in the range of temperature from 973 K to 1573 K. Structural analysis such as the coordinated O numbers (CO), the mean square displacement (MSD), and the variation of coordinated O numbers of Na (N_{CO}) has provided insights into the diffusion behavior of Na atoms in these systems. These systems consist of fixed Si-O networks and Na atoms moving within this network. The diffusion coefficient of Na atoms increases with increasing temperature and decreasing SiO_2 concentration. Additionally, the rate of change of N_{CO} (λ) increases with increasing temperature. Moreover, the diffusion coefficient of Na atoms depends on the second-order polynomial relationship, and the diffusion law of Na atoms remains consistent in all the investigated systems.

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