COMPARISON OF SODIUM ION DIFFUSION BETWEEN SIMPLEXES IN DIFFERENT SILICATE GLASS SYSTEMS USING MOLECULAR DYNAMICS SIMULATIONS

SO SÁNH SỰ KHUẾCH TÁN CỦA ION NATRI GIỮA CÁC SIMPLEX TRONG CÁC HỆ THỦY TINH SILICAT KHÁC NHAU BẰNG MÔ PHỎNG ĐỘNG LỰC HỌC PHÂN TỬ

Pham Thi Lien*

University of Economics - Technology for Industries, Vietnam

*Corresponding author: ptlien@uneti.edu.vn

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Abstract - This study investigates sodium ion (Na^+) diffusion in sodium silicate glasses $Na_2O.mSiO_2$ (NSm, m = 1, 2, 3, 4) at 1173K using molecular dynamics simulations. Instead of traditional Radial Distribution Function (RDF) or Coordination Number methods, simplex analysis identifies diffusion pathways, revealing structural dynamics and ion mobility. Key findings include differences in the number of simplexes (NSP), bridging oxygens in a simplex (ZBO), and simplex size (SPS), which significantly affect Na^+ diffusion. Simplexes with fewer bridging oxygens facilitate Na^+ movement. Na^+ ions often leave and return to their original simplex, creating a correlation effect on diffusion. Parameters like mean squared displacement (d^2) and average residence time (t_s) in simplexes are linked to Na^+ diffusion coefficients, contributing to a better understanding of the Na^+ diffusion mechanism.

Key words - Simplex; sodium silicate glass; molecular dynamics simulations

Tóm tắt - Nghiên cứu này khảo sát sự khuếch tán ion natri (Na^+) trong thủy tinh silicat $Na_2O.mSiO_2$ (NSm, m = 1, 2, 3, 4) ở 1173K bằng mô phỏng động lực học phân tử. Thay vì sử dụng hàm phân bố xuyên tâm hay số phối trí truyền thống, phân tích simplexs được dùng để xác định các con đường khuếch tán, làm rõ cấu trúc và tính linh động của ion. Kết quả cho thấy sự khác biệt về số lượng simplexs (NSP), oxy nối cầu (ZBO), và kích thước simplex (SPS) ảnh hưởng đến khuếch tán Na^+. Các simplex ít oxy nối cầu giúp Na^+ di chuyển dễ dàng hơn. Ion Na^+ thường rời và quay lại simplex ban đầu, tạo hiệu ứng tương quan làm ảnh hưởng đến khuếch tán. Các tham số như độ dịch chuyển bình phương (d^2) và thời gian lưu trú trung bình (t_s) liên quan trực tiếp đến hệ số khuếch tán Na^+, giúp hiểu rõ hơn cơ chế khuếch tán Na^+.

Từ khóa – Simplex; thủy tinh silicat natri; mô phỏng động lực học phân tử

1. Introduction

Sodium silicate glasses are vital materials widely applied in areas such as nuclear waste immobilization, ion-conductive devices, and chemical processing, owing to their unique combination of chemical durability, structural flexibility, and ionic conductivity [1]. A key factor influencing the performance of these materials is the diffusion of sodium ions (Na^+), which plays a critical role in maintaining structural integrity and functional properties [2]. Previous studies have primarily employed methods such as Radial Distribution Function (RDF) and Coordination Number analysis to investigate Na^+ diffusion [3-5]. While these techniques provide valuable insights into the structural environment and average ion behavior, they often fail to fully capture the dynamic and localized nature of sodium diffusion pathways. Specifically, interactions between sodium ions and structural features like bridging oxygens (BO) and non-bridging oxygens (NBO) remain insufficiently explored [6,7]. This study introduces a novel approach using simplex analysis to identify diffusion pathways for Na^+ ions. This method enables the characterization of critical factors such as the number of bridging oxygens (ZBO) and their impact on diffusion efficiency [8]. By focusing on the dynamic transitions of sodium ions within clearly defined simplex structures, the study provides deeper insights into how local structural variations influence ion mobility.

Through molecular dynamics (MD) simulations of sodium silicate glass systems $Na_2O{\cdot}mSiO_2$ (NSm, where m = 1, 2, 3, 4) at 1173K, this research aims to bridge the gap between structural complexity and ion transport dynamics. The findings offer new perspectives on the interplay between structural connectivity and sodium mobility, contributing to the development of advanced glass materials for industrial applications [9, 10].

2. Computational Methods

Molecular dynamics (MD) simulations were performed for NSm glass under a pressure of 0.1 MPa at 1173K. To replicate the material's structure, we conducted simulations and analysis using the MXDORTO code [11], incorporating interaction potentials with both two-body and three-body components. A full description of these potentials can be found in other references [2]. The NSm systems consisted of approximately 10^4 atoms, with the initial configuration generated by Noritake F. The model production was carried out using a time step of 1 fs under constant pressure and temperature (NPT) conditions at 1873K, followed by a cooling rate of 10^{11} K/s to reach the desired temperature, followed by annealing for 5 ns under constant volume and energy (NVE) conditions to achieve equilibrium. In this

study, a simplex (SP) is defined as a sphere passing through the centers of four oxygen atoms (either NBO or BO) without containing any Si or O atoms internally. The simplex radius (SPR) is not fixed but is determined solely by the positions of the four oxygen atoms.

Sodium ions can move in and out of the same SP multiple times. During each entry into the SP, some sodium atoms may reside there for a certain period before leaving. The t_s is the duration that the sodium ion stays in the simplex, which can be calculated using a specific formula. This allows us to compare the time between two movements with the residence time to evaluate the diffusion capability of sodium ions in the system. To calculate the residence time of sodium in each simplex, the total time sodium ions spend in the simplex is divided by the total number of visits to the simplex. The sodium's difusion constant is given by

$$D = \lim_{t\to\infty} \frac{SMSD}{6t} = \frac{1}{6} \lim_{t\to\infty} (\frac{N_{VS}}{t}) \ (\frac{SMSD}{N_{VS}}) = \frac{1}{6t_s} d^2 \quad (1)$$

$$\frac{1}{t_s} = \lim_{t\to\infty} < \frac{N_{VS}}{t} >; \quad d^2 = \lim \frac{SMSD}{< N_{VS} >} \quad (2)$$

Where, N is the total count of sodium visits to the SP; SMSD denotes the mean squared displacement of sodium, calculated directly from MD simulations, D is the diffusion coefficient, and d^2 is the mean squared displacement of sodium per simplex, N_{VS} represents the number of times sodium moves into a specific simplex over time. It was observed that the relationship between $\langle N_{vs} \rangle$ and t, as well as between SMSD and N_{VP}, is linear.

3. Results and Discussion

Data collection involved recording 76 configurations (atomic positions) at 2 ps intervals over a span of 150 ps for subsequent analysis. From these configurations, the pair radial distribution function (PRDF) and coordination statistics were calculated. A cutoff distance of 2.4 Å was used to determine the coordination number for the Si–O pair. The resulting PRDF showed good agreement with experimental observations [9, 10]. The produced structure included various oxygen types, such as non-bridging oxygen (NBO), bridging oxygen (BO), and free oxygen (FO).

A comparison of the RDF from MD simulations with neutron scattering experiment results [11] reveals a good match in both the peak positions and heights, as shown in Fig 1a. This similarity strongly supports the accuracy and reliability of the MD simulation models. During the simulation time of 150 ps, we recorded 76 configurations corresponding to 76 atomic positions. Note that in the simulation box, all simplexes are calculated as fixed spheres. The structure obtained from the simulation contains a network of SiO_4 tetrahedrons possessing both bridging and non-bridging oxygen (BO and NBO).

We calculated the oxygen simplexes based on the positions of Si and O atoms in the first configuration among the 76 recorded configurations. The simplexes were categorized into five types based on the number of bridging oxygens (ZBO = 0, 1, 2, 3, 4). The distribution of simplexes containing bridging oxygens (BO) in the NSm systems reflects structural complexity and connectivity differences. As shown in Figure 1b, NS1 has the highest proportion of simplexes with low ZBO values (0, 1), indicating an open structure with minimal connectivity. This facilitates easier diffusion of sodium ions due to the less constrained structure and lower energy barriers. In contrast, NS2 shows the highest concentration of simplexes at ZBO = 2, indicating a moderate level of connectivity and a more complex structure. Notably, NS3 and NS4 peak at ZBO = 3, representing the highest level of connectivity and the densest structures. This stronger connectivity restricts the diffusion of sodium ions due to increased electrostatic interactions and tighter packing within the silicate network. The progression from ZBO = 0 to ZBO = 3 highlights the critical role of bridging oxygens in influencing the structural and mechanical properties. As ZBO increases, the silicate network becomes denser and more stable. However, this densification significantly reduces the sodium ion diffusion capacity, as evidenced by the lower diffusion coefficients in NS3 and NS4 compared to NS1. Furthermore, the reduced number of simplexes with low ZBO in NS3 and NS4 further explains why sodium diffusion is restricted, as there are fewer favorable pathways for diffusion.

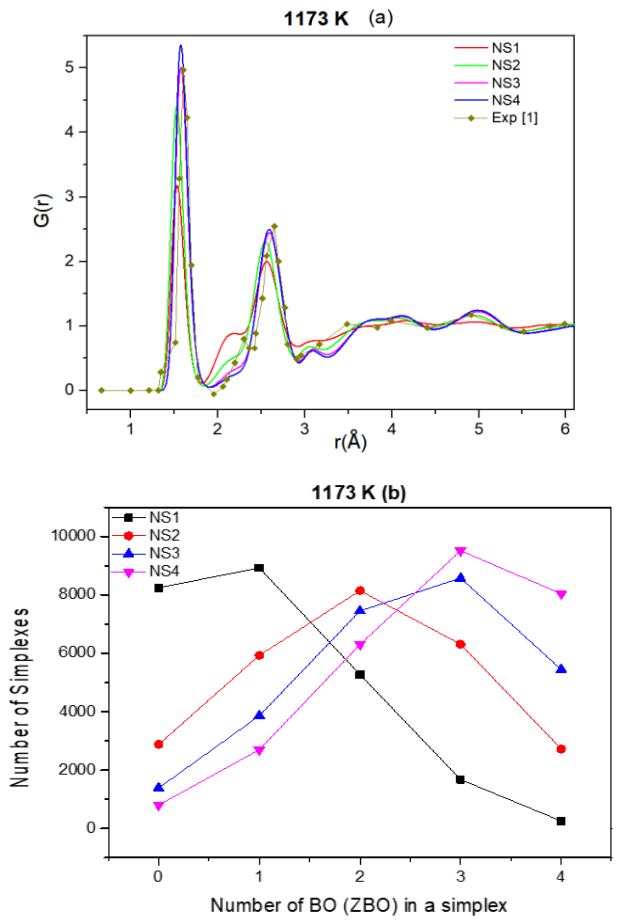

Figure 1. *The total RDF of NSm (m=1, 2, 3, 4) at 1173 K compared with experimental data from [11](a), The simplex number distribution of NSm symtems according to ZBO (b), 20ps*

Table 1. *The proportion of simplexes containing x Na, (x=0,1,2,3) and the ratio of the number of simplexes to the total number of oxygen (N_{SP}/N_O) and sodium atoms (N_{SP}/N_{Na}), The ratio of bridging oxygen to the total oxygen (N_{BO}/N_O)*

1173 K (20ps)				
System	x=0	x=1	x=2	x=3
NS1	0.020674	0.468906	0.376938	0.114653
NS2	0.121753	0.615154	0.223342	0.036056
NS3	0.237755	0.600516	0.139575	0.020174
NS4	0.321504	0.563811	0.102332	0.011695
System	Number simplexes (N_{SP})	N_{SP}/N_O	N_{SP}/N_{Na}	N_{BO}/N_O
NS1	24,378	4.88	7.32	0.3473
NS2	25,987	4.68	11.7	0.6016
NS3	26,724	4.58	16.04	0.7146
NS4	27,362	4.56	20.54	0.7779

Figure 2a shows that sodium ions are primarily concentrated in simplexes with low ZBO levels (0 and 1) and significantly decrease in complex simplexes with high ZBO levels (2, 3, and 4). As ZBO increases, diffusion channels narrow due to stronger structural constraints, limiting Na+ ion movement and reducing diffusion efficiency. The simulation results indicate that over 98% of the simplexes contain fewer than three sodium atoms, with the highest proportion in all systems consisting of just one sodium atom (Table 1, Figure 2b). From NS1 to NS4, the number of simplexes without sodium increases, while those containing more than two sodium atoms decrease. Figure 2c illustrates an inverse relationship between NBO/NO and N_S/NO, where NBO/NO increases and N_S/NO decreases with increasing SiO_2 content. This trend reflects the densification of the network structure, resulting in fewer and narrower diffusion pathways, which significantly restrict Na+ ion mobility. The difference between the number of Na ions entering (N_{Na}) and the number of distinct Na ions (N_{DNa}) in the same simplex throughout the simulation provides evidence of a strong correlation effect (Table 2, Figure 2d). This trend indicates that Na ion diffusion decreases from NS1 to NS4 due to the increasing correlation effect and spatial constraints within the network structure. For a more visual perspective, Figure 3 illustrates the distribution of sodium within 8 simplexes separated by distances greater than 7 Å in the NS1 model at 1173 K. It can be observed that, at different moments, the number of sodium atoms per simplex (NSP) fluctuates and is mostly less than 3. At different time points (12 ps, 62 ps, and 112 ps), the positions and quantities of sodium within the simplexes change. Sodium tends to concentrate in specific regions within the simplexes, and its positions vary over time, reflecting its mobility and interactions within the system.

Table 2. *Distribution of Na in simplexes with different numbers of ZBO*

Number of Na in a simplex -1173 K					
System	0 BO	1 BO	2 BO	3 BO	4 BO
NS1	137.47	124.8	112.99	102.42	83.74
NS2	122.85	106.67	91.21	75.61	54.24
NS3	117.72	101.56	84.59	65.4	39.97
NS4	114.27	96.75	79.18	58.79	32.19
Number of difference Na in a simplex -1173 K					
System	0 BO	1 BO	2 BO	3 BO	4 BO
NS1	22.09	19.34	16.56	13.75	10.06
NS2	15.46	12.88	10.48	8.16	5.57
NS3	18.19	15.38	12.68	9.73	6.33
NS4	10.35	8.59	6.97	5.46	3.42

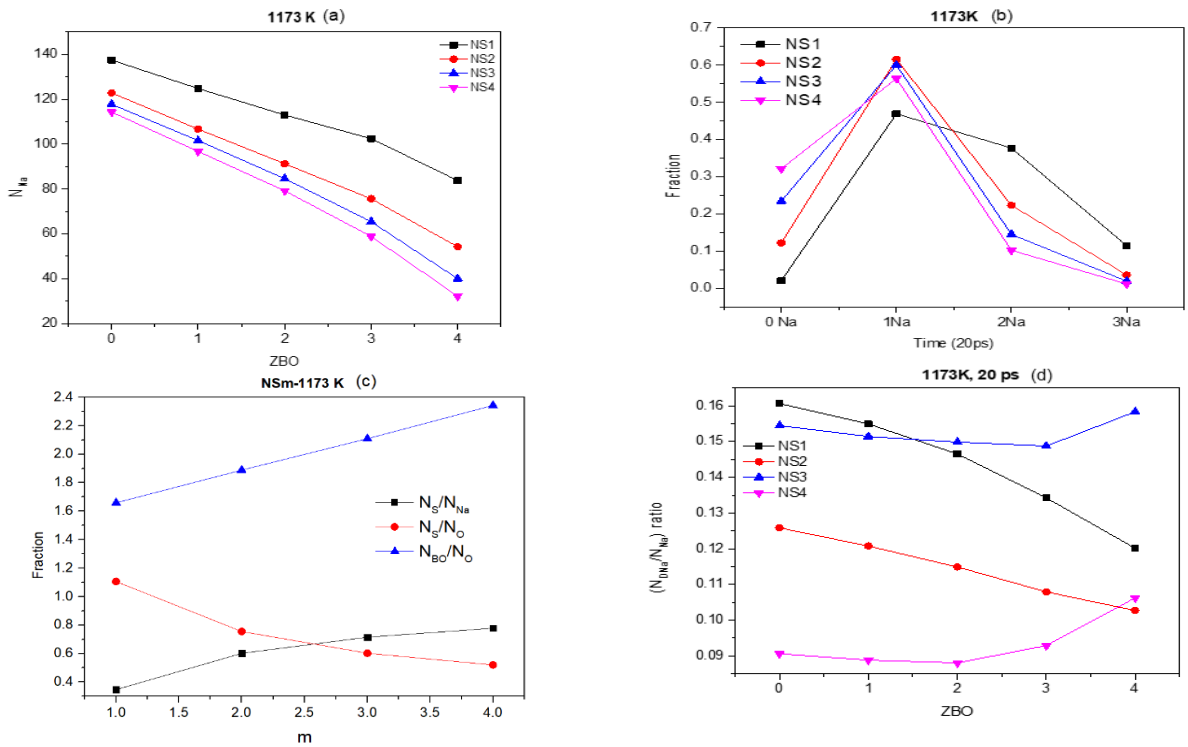

Figure 2. *Distribution of sodium ions in simplexes with different (ZBO) over the entire simulation (a); The distribution ratio of Na in simplex over time (20 ps) at 1173 K (b); The fraction N_{BO}/N_O, N_S/N_O and N_S/N_{Na} for NSm (m = 1, 2, 3 and 4) where N_{BO}, N_O, N_{Na} is the total number of BO, O and Na, respectively; N_S is the total number of selected simplexes (c); The ratio of N_{DNa}/N_{Na} by ZBO (d)*

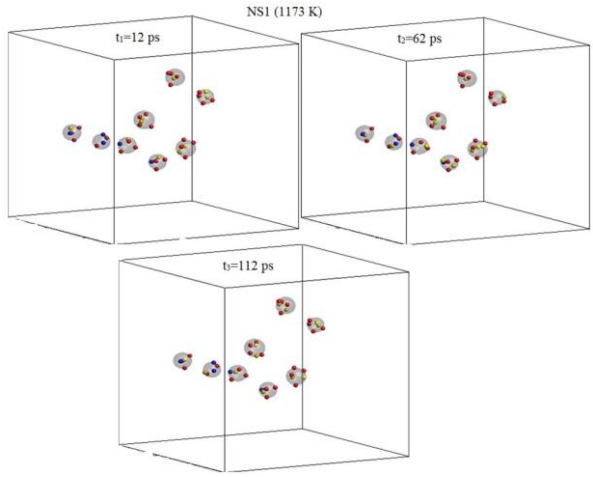

Figure 3. *Snapshots of 8 simplexes of NS1 (1173 K) at 12 ps, 62 ps, and 112 ps. Other simplexes are omitted from the figure. The red spheres represent NBO (Non-Bonding Oxygen), the green spheres represent BO (Bonding Oxygen), and the yellow spheres represent Na (Sodium)*

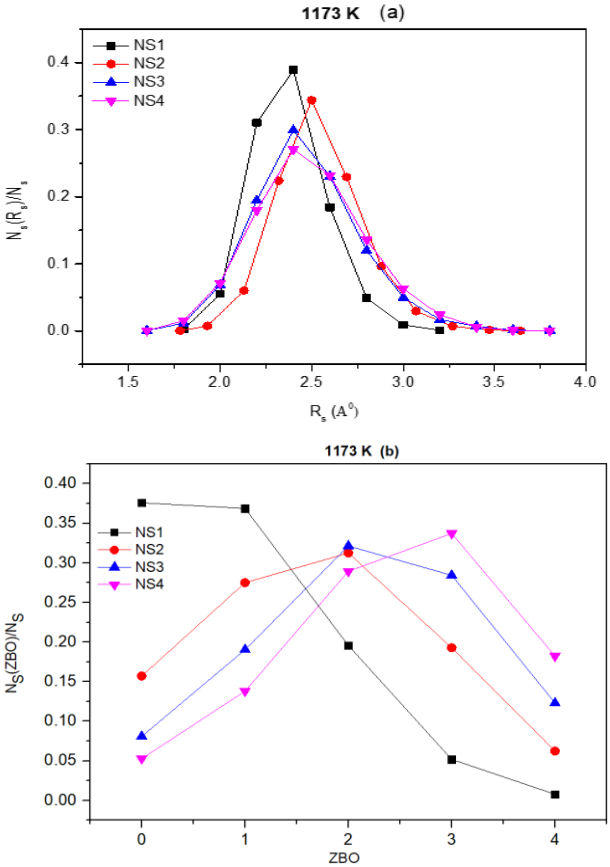

Figure 4. *The simplex distribution through R_S (a) (DSR). Here $N_S(R_S)$ is the number of simplexes with corresponding R_S. The distribution of simplexes through ZBO (DSZB) (b), $N_S(ZBO)$ represents the number of simplexes with bridging oxygens equal to ZBO*

Here we show some cases, but the similar trend is observed across all studied models. As seen Figure 4.a, DSR displays a broad range and possesses a peak near R_S = 2.4 – 2.5 Å. In addition, DSR slightly varies with SiO_2 content. We denote $N_S(0)$, $N_S(1)$, $N_S(2)$, $N_S(3)$, etc., as the number of simplexes containing 0, 1, 2, 3 bridging oxygens, respectively. We see that $N_S(0)$, $N_S(1)$ decreases from NS1 to NS4, while $N_S(3)$, $N_S(4)$ increases (Figure 4.b). Unlike DSR that varies slightly with SiO_2 content, DSZB for NS1 decreases with increasing ZBO, but for NS2 and NS4, it possesses a peak at ZBO(2) or ZBO (3).The analysis of simplex distribution by radius (R_s) and ZBO clearly establishes a consistent structural framework across all studied models, primarily determined by local connectivity. Notably, the increase in SiO_2 content from NS1 to NS4 significantly enhances the number of bridging oxygens within the network. This enhancement is directly reflected in the changes in ZBO distribution, which in turn impacts ion dynamics and overall structural properties. Calculations from MD simulations provide the mean squared displacement and the number of polyhedra visited by sodium over time. By combining equations (1) and (2), d^2, t_s , D can be determined.

Table 3. *Mean square displacement per simplex d^2, residence time $<t_s,>$, diffusion coefficient (D) of NSm at 1173K*

	NS1	NS2	NS3	NS4
d^2	1.04824	0.85048	0.74424	0.70057
Slope ($<N_{VS}>$-$<t>$)	0.79956	0.66185	0.61666	0.57596
t_s (ps)	1.25068788	1.51091637	1.62163915	1.7362316
D ($10^{-4} cm^2/s$)	0.139947	0.093977	0.076793	0.06725

The results from Table 3 show that the diffusion coefficient (D) of sodium ions decreases significantly from 0.139947 (NS1) to 0.06725 (NS4), reflecting a substantial reduction in the diffusion capability of sodium as the structure becomes more complex. This decrease is explained by two main factors: the mean square displacement (d^2) and the mean residence time (t_s). The value of d^2 decreases by approximately 33% from NS1 to NS4, indicating narrower diffusion pathways that limit the free movement of sodium. However, the residence time (t_s) increases by about 39% from 1.2507 ps (NS1) to 1.7362 ps (NS4), indicating that sodium is retained longer within the simplex. This contributes to a significant "diffusion resistance", leading to a marked reduction in D. The analysis suggests that the impact of t_s dominates over d^2 in reducing diffusion efficiency in more complex systems like NS4.

4. Conclusion

Molecular dynamics (MD) simulations performed at 1173 K and 0.1 MPa for NSm systems revealed distinct diffusion behaviors influenced by simplex complexity and sodium interaction dynamics. From NS1 to NS4, the diffusion coefficient (D) decreases significantly, primarily due to the interplay between the mean square displacement (d^2) and the residence time (t_s). While d^2 decreases, reflecting narrower diffusion pathways, t_s increases, indicating stronger sodium retention within a simplex. These trends highlight the critical role of local structural constraints in limiting sodium mobility. Notably, sodium ions often return to the same simplex, reducing the number of visited simplexes and emphasizing the influence of structural overlap. Sodium tends to concentrate in SP with

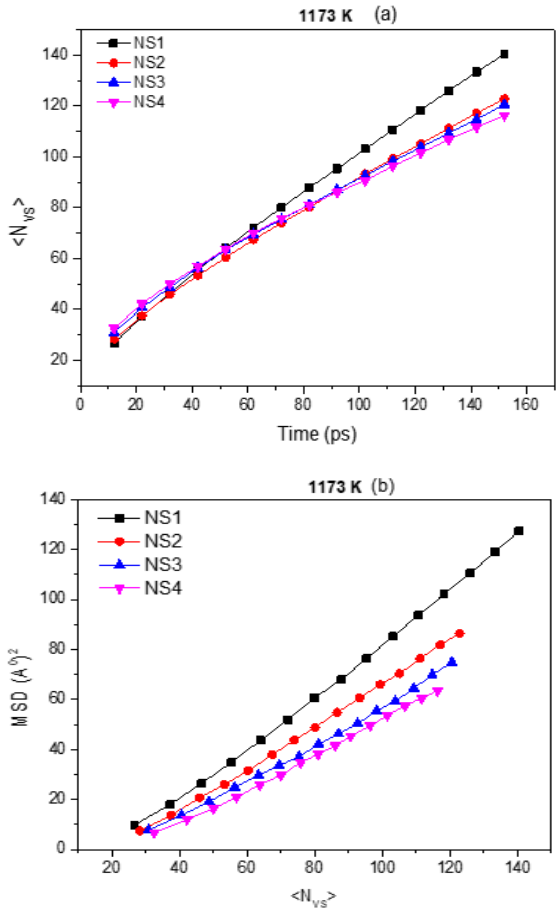

Figure 5. *The dependence of <N_{VS}> on time (a) and MSD as a function of <N_{VS}> (b), where <N_{VS}> is the average number of simplexes visited by a Na*

fewer bridging oxygens (BO). Linear relationships observed in Figure 5 between <N_{VS}> vs. time and MSD vs. <N_{VS}> provide additional insights into sodium diffusion mechanisms. These findings highlight the importance of optimizing glass structures to improve sodium diffusion, enabling applications in advanced glass technologies, energy storage systems, and optical materials. Future studies should investigate the effects of temperature, pressure, and composition to deepen our understanding of sodium ion dynamics in silicate glasses.

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