Study on Micro Structural Properties of Sodium in Na_2O - Doped SiO_2 Melt using Molecular Dynamics Simulation

Abstract. Molecular dynamics (MD) simulation could provide details about local microstructure at atomic level, so we use this method to investigate micro-structural properties of sodium in Na_2O-doped SiO_2 melt. Additionally, we calculated the Voronoi polyhedrons to determine the spatial distribution of atoms in the simulation models. The result shows that many bridging oxygen (BO) polyhedrons and all Si-polyhedrons do not contain Na atoms. Most non-bridging oxygen (NBO) polyhedrons contain 2, 1 or no Na atoms, where BO, NBF is the O bonded with 2 and 1 or no Si, respectively. Average volume per polyhedron decreases in order: NBFx-polyhedron → BOx-polyhedron → Six-polyhedron. Na atoms are found in NBFx-polyhedrons and frequently move through them leading to very fast diffusivity of Na in comparison with Si and O. The simulation shows that the number of neighbors around the NBFx-polyhedron is larger than that around the BOx-polyhedron.

Keywords: Na_2O-doped SiO_2, sodium, Voronoi polyhedron, micro-structure, subnets.

1. Introduction

The micro-structure of silica (SiO_2) is an archetypal network-forming system containing SiO_4 tetrahedra. The addition of doped Na atoms generates non-bridging oxygen (NBO) in SiO_4. Consequently, the Na_2O-doped SiO_2 gives various anomalous properties which are essential for industrial applications, ceramics, and understanding the fundamentals of minerals [1-5]. The Na_2O-doped SiO_2 melt has been intensively investigated by experimental techniques including photoelectron spectroscopy, X-ray diffraction, in situ Raman spectroscopy and elastic neutron scattering, and various simulation techniques [6-11]. The addition of doped Na ions to pure SiO_2 melt leads to a decoupling of alkali diffusion and diffusive transport in the Si-O network [10-17]. Davidenko et al. in ref. [7] suggested that the distribution where the increasing alkali oxide content causes the homogeneous increasing disruption of Si-O network of pure SiO_2 is in conflict with highly nonlinear dependence of viscosity on alkali concentration. In accordance with studies [18-21], the pre-peak at 0.9 $Å^{-1}$ in the micro-structure factor measured experimentally for alkali silicates is evidence for the diffusion pathway.

Various experimental results found that the micro-structure of these silicates is found to comprise micro-regions with high sodium concentration. The two micro structural samples, the modified random network and the compensated continuous random network predict some clustering of alkali atoms in the silicate's microstructure [22-24].

The structure as well as applications of silica and sodium silicate have also been shown in references [25-27]. However, the spatial distribution of Na in the Na_2O-doped SiO_2 melt remains not fully clarified yet. Therefore, in present study, we focus on Na_2O-xSiO_2 melt (x = 1, 2, 3, 4) at pressure of 0.1 MPa and temperatures of 1573 K. Based on the features of pair radial

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distribution function (PRDF), topographies of the Voronoi Ax- polyhedrons, and subnets Si-O in system.

2. Computational method

We conduct the MD simulation for NSx, i.e. Na_2O-SiO_2 (NS1), Na_2O-$2SiO_2$ (NS2), Na_2O-$3SiO_2$ (NS3) and Na_2O-$4SiO_2$ melt at pressure of 0.1 MPa and temperature of 1573 K. The total number of particles in each system is approximately equal to 10,000. The interaction potentials used includes two- and three-body terms, which reproduce well the micro structural and transport properties of sodium silicates. The complete description of these potentials can be found elsewhere [4,28]. In order to collect the micro-structure and dynamics data we additionally run the simulation for 150 ps to produce 76 configurations separated by 2 ps. The structure is analyzed by PRDF and by the one determined separately for BO and NBF. Here BO, NBO and FO are the oxygen which is bounded respectively with two, one or no Si; both NBO and FO are denoted to NBF.

Si-BO subnet, Si- and O-centered Voronoi polyhedrons have been calculated for every system. It turns out that the simulation box is fully filled by those polyhedrons. Each Na is placed inside one among them. Several typical polyhedrons are shown in Figure 1. The following, A-centered polyhedron is called an Ax-polyhedron, where A is the Si, O, BO or NBF; *x* is the number of Na placed in A-centered polyhedron. We call that all Six-polyhedrons and a part of Ox-polyhedrons are A0-polyhedron type. Moreover, Na often moves between Ox-polyhedrons leading to very fast sodium diffusivity. Fig.1 illustrates the system comprising a large Si-O subnet. The Si-O subnet is defined as a subset of Si and BO connected by Si-O bonds, where BO is bonded with two Si, while Si is bonded with four O forming the SiO_4 unit.

3. Results and discussions

To check the value of the simulation samples, we compared the position of the first peak of PRDF with experimental data. Table 1 lists the interatomic distances obtained from simulation, and experimental data [29]. Although r_{SiNa} and r_{NaNa} show some discrepancies, the built models overall are consistent with the experiments. In particular, they reproduce the experimental data for r_{SiSi}, r_{SiO}, r_{OO}, and r_{NaO}.

Table 1. Interatomic distance (Å)

Samples	r_{SiSi}	r_{SiO}	r_{OO}	r_{SiNa}	r_{ONa}	r_{NaNa}
NS1	3.10	1.60	2.60	3.00	2.20	3.25
NS2	3.10	1.60	2.60	3.30	2.25	3.50
NS3	3.10	1.55	2.60	3.35	2.25	3.65
NS4	3.10	1.60	2.60	3.40	2.25	3.60
Exp. [29]	3.05	1.62	2.62	3.50	2.29	2.6-3.05

Figure 2 shows the PRDF determined for BO-Na, NBF-Na and O-Na pairs. A clear peak is seen for the NBF-Na pair, with a significant increase in height from NS1 to NS4. The location of this peak is slightly different. For the BO-Na pair, the height of the first peak is much lower than for the NBF-Na pair. This result indicates that Na atoms are mostly located around NBF and

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rarely near BO. Furthermore, the local sodium density in BOx and NBFx polyhedra changes strongly with SiO concentration. Unlike the NBF-Na pair, the first peak of the Si-Na pair is located at 3.0-3.6 Å, which is significantly larger than that of the NBF-Na pair. This means that Na is not in the Six-polyhedrons. These marks are consistent with the reports in refs. [1-6].

Figure 3 shows snapshots of the distribution of coordination units SiO_x and NaO_y in a model of Na_2O-$3SiO_2$ melt at a pressure of 0.1 GPa (here we only draw a part with size 6×20×20 $Å^3$). Figure 3 indicates that the micro-structure of Na_2O-$3SiO_2$ melt comprises the coordination units SiO_4, and some NaO_4, NaO_5. From Figure 3, it can be seen that the distribution of coordination units SiO_4 is not uniform. Still, it tends to form clusters of SiO_4, and the coordination units SiO_4 tend to connect via a common oxygen atom to form subnet Si-O. Similarly, the coordination NaO_4 tends to connect to create a cluster of NaO_4, and the Na_2O-$3SiO_2$ melt only contains some coordination NaO_5. Therefore, the micro-structure of Na_2O-$3SiO_2$ melt is built up from the intermixture of the clusters SiO_4, NaO_4, NaO_5, and free Na.

Table 2 shows the average volume per polyhedron in descending order: NBFx-polyhedron → BOx-polyhedron → Six-polyhedron, and it slightly varies with SiO_2 content. We note that $\langle x_{NBFx} \rangle$ is significantly larger than $\langle x_{BOx} \rangle$. Moreover, $\langle x_{BOx} \rangle$ changes powerfully with SiO_2 content. This result shows that the spatial distribution of sodium is strongly heterogeneous. In particular, the most important Na atoms are located in NBFx polyhedra with a total volume of 27.11–67.10% of the simulation box. In the system with lower SiO_2 content, more Na diffused into the Box-polyhedron.

Table 2. Characteristics of A*x*-polyhedrons. Here $\langle v_{Six} \rangle$, $\langle v_{BOx} \rangle$ and $\langle v_{NBFx} \rangle$ is the average volume per Six-, BOx- and NBFx-polyhedron, respectively; V_{Six}, V_{BOx}, V_{NBFx} and V_{SB} is the volume occupied by Six-, BOx-, NBFx-polyhedrons and volume of simulation box, respectively; m_{NBF}, N_{Na} is the number of Na in NBFx-polyhedrons and total number of Na, respectively.

System	$\langle v_{Six} \rangle$, $Å^3$	$\langle v_{BOx} \rangle$, $Å^3$	$\langle v_{NBFx} \rangle$, $Å^3$	V_{Six}/V_{SB}	V_{BOx}/V_{SB}	V_{NBFx}/V_{SB}	m_{NBF}/N_{Na}
NS1	8.13	20.12	30.41	0.0920	0.2370	0.6710	0.8682
NS2	7.96	20.25	31.45	0.1140	0.4369	0.4491	0.8081
NS3	7.94	20.37	31.96	0.1260	0.5379	0.3361	0.7909
NS4	7.94	20.44	32.45	0.1324	0.5965	0.2711	0.7798

Different Six-polyhedrons, Ox-polyhedrons either are polyhedrons with $x_{Ox} = 0$ or $x_{Ox} > 0$. As shown in Figure 4, the number of BO0-polyhedrons increases from 78.1 to 95.8% with increasing SiO_2 content. Figure 4 shows that most Box-polyhedrons are BO0 and BO1 polyhedrons, while the most important NBFx- polyhedrons are either NBF0, NBF1, and NBF2 polyhedrons. In addition, the Na atoms are concentrated in the NBFx-polyhedrons instead of being uniformly distributed in the Ox- polyhedrons. The obtained result makes it possible to propose a simple diffusion model. Consequently, Na moves from BOx and NBFx- polyhedron sites. Each slot is empty or occupied by one Na in BO_x- polyhedron, an NBFx polyhedron has one and two points respectively. There are also torus polyhedrons with more than 2 sites, but their concentration is very low. Na transfer between Ox- polyhedrons results in very fast diffusion of Na compared to Si and O [10,20].

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The sodium distribution in polyhedrons shown in Figure 5, it can be wide and asymmetrical. A pronounced peak is seen. This result confirms the fact that Na atoms are concentrated in NBF-polyhedrons instead of uniformly distributed through O-polyhedrons.

In summary, Na atoms are concentrated in NBF-polyhedrons instead of uniformly spreading through O-polyhedrons. The frequent displacing of Na between polyhedrons mainly contributes to the sodium's diffusion. The system consists of the NBO-FO, interfacial and Si-BO regions. The rate of A*x* → A*x*' happening in those regions reduces in the order: NBO-FO region → interface region → Si-BO region. Therefore, our results can propose that Na atoms diffuse by hopping alone and collective movement, but the major amount of Na moves collectively across O-polyhedrons located nearby. For melt with high SiO_2 content the NBO-FO region can represent the preferential sodium's diffusion pathway.

4. Conclusion

MD simulation is carried out for NSx melt at temperature of 1573 K and pressure of 0.1 MPa. Micro-structural properties are investigated through Voronoi polyhedron. The result shows a pronounced peak for the NBF-Na pair of which the height varies with SiO_2 content. The position of the first peak for Si-Na peak is located at a distance significantly larger than that for the NBF-Na pair. The simulation demonstrates that Na atoms mostly present in the vicinity of NBF and rarely around BO. Simulation reveals that Na atoms are not placed in Six-polyhedrons and in about 32.9 to 72.89 % of total BOx-polyhedrons. Most NBFx-polyhedrons contain 2, 1 or no Na. The average volume per polyhedron decreases dramatically in the order: NBFx-polyhedron → BOx-polyhedron → Six-polyhedron. Although the average volume per polyhedron weakly depends on SiO_2 content, the volume occupied by all NBFx-polyhedrons varies strongly with SiO_2 content. We also discovered that Na atoms are not only located in NBFx-polyhedrons, but they also move frequently through them. Therefore, we suggest that melt with high SiO_2 content the NBO regions and FO regions can represent the preferential sodium's diffusion pathway.

Disclaimer (Artificial intelligence)

We hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of manuscripts.

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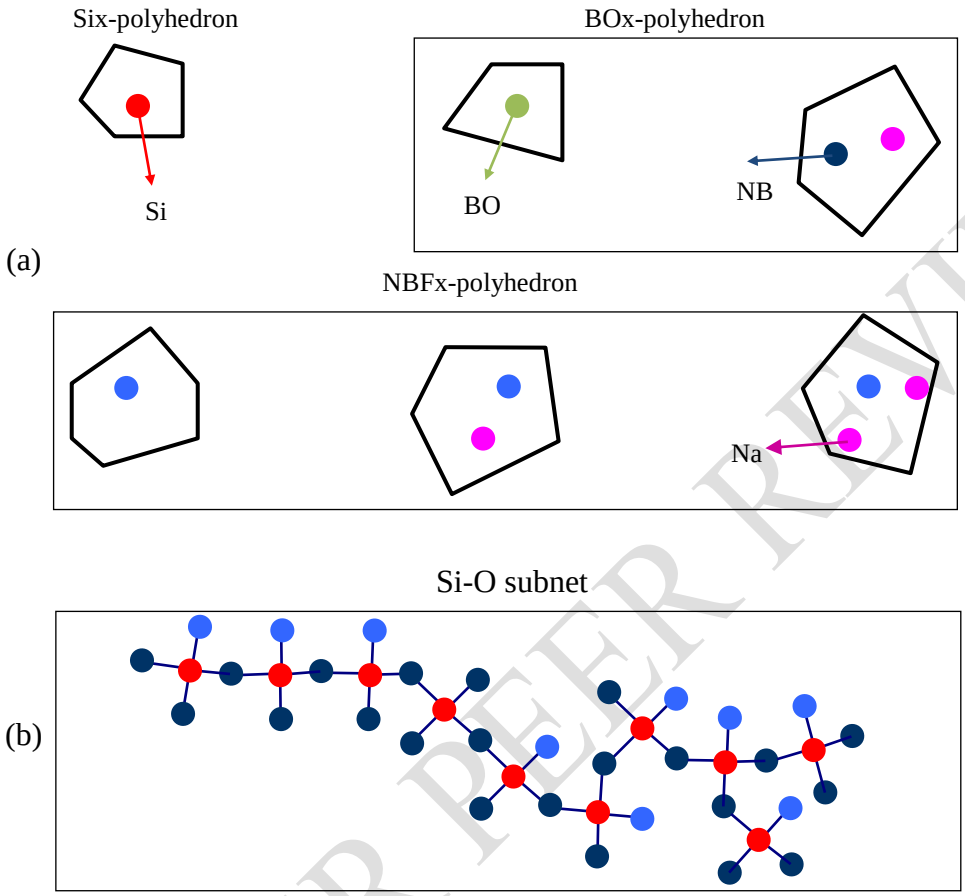

Figure 1. Schematic illustration of Ax-polyhedrons (a) and Si-O subnet (b). Here A is Si, BO or NBF; *x* = 0, 1, 2, 3 and 4. Ax-polyhedron can contain Na atoms.

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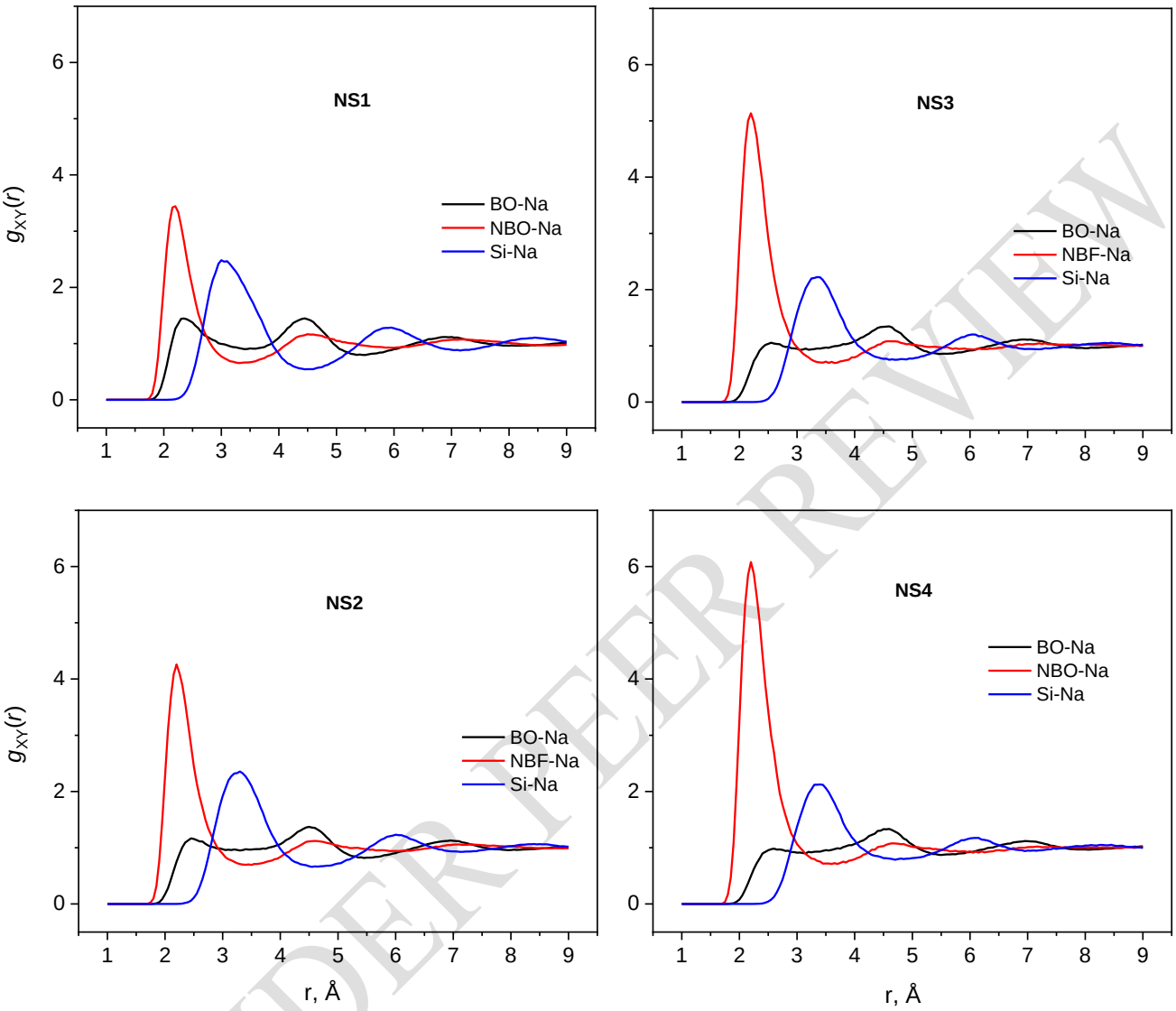

Figure 2. PRDF for NBF-Na, BO-Na, and Si-Na pairs of NSx at temperature of 1573 K and pressure of 0.1 MPa.

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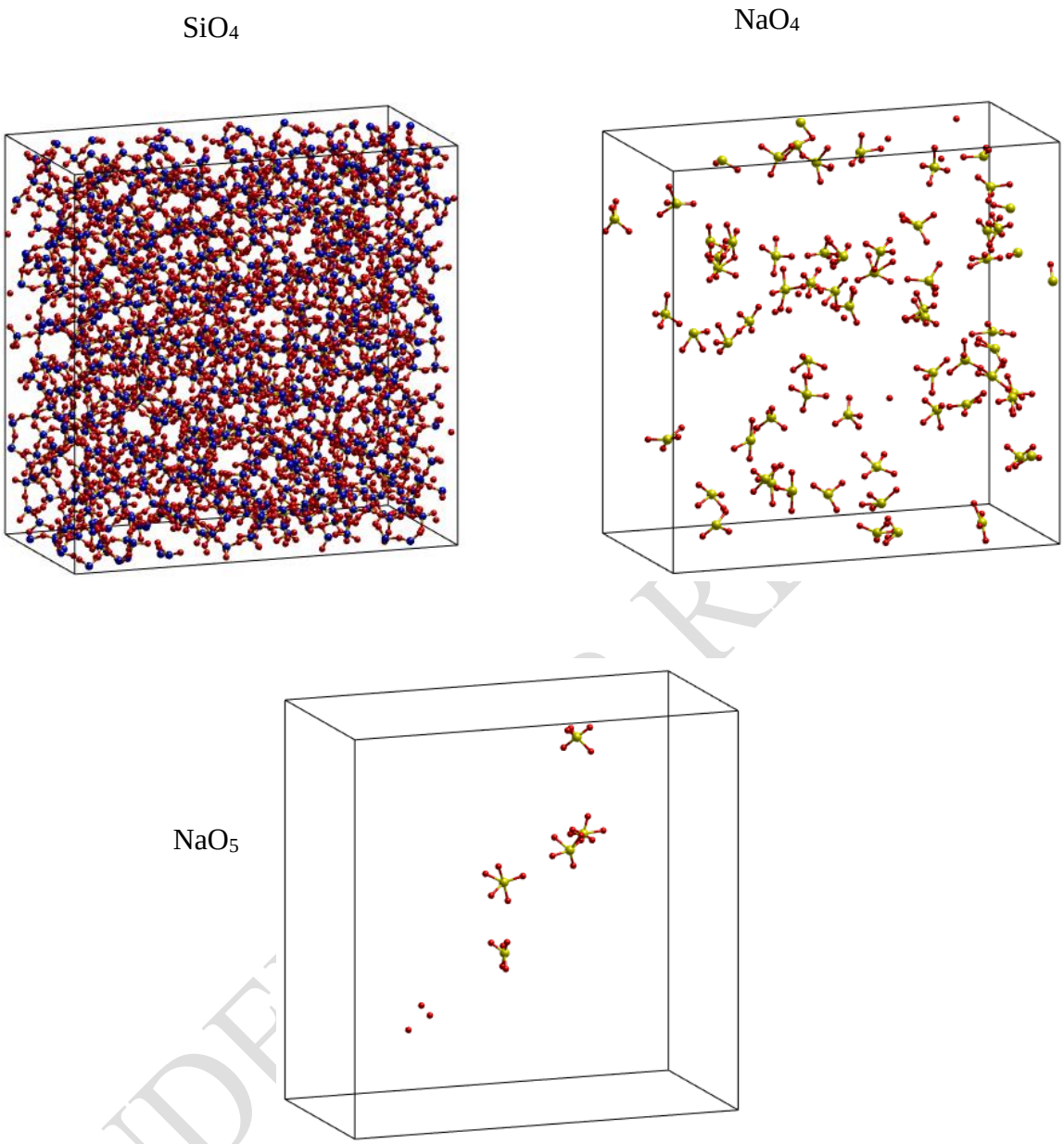

Figure 3. Spatial distribution of SiO_x and NaO_y in sample Na_2O-$3SiO_2$ at temperatue of 1573 K and pressure of 0.1 MPa, here O (red color), Si (blue color), Na (yellow color).

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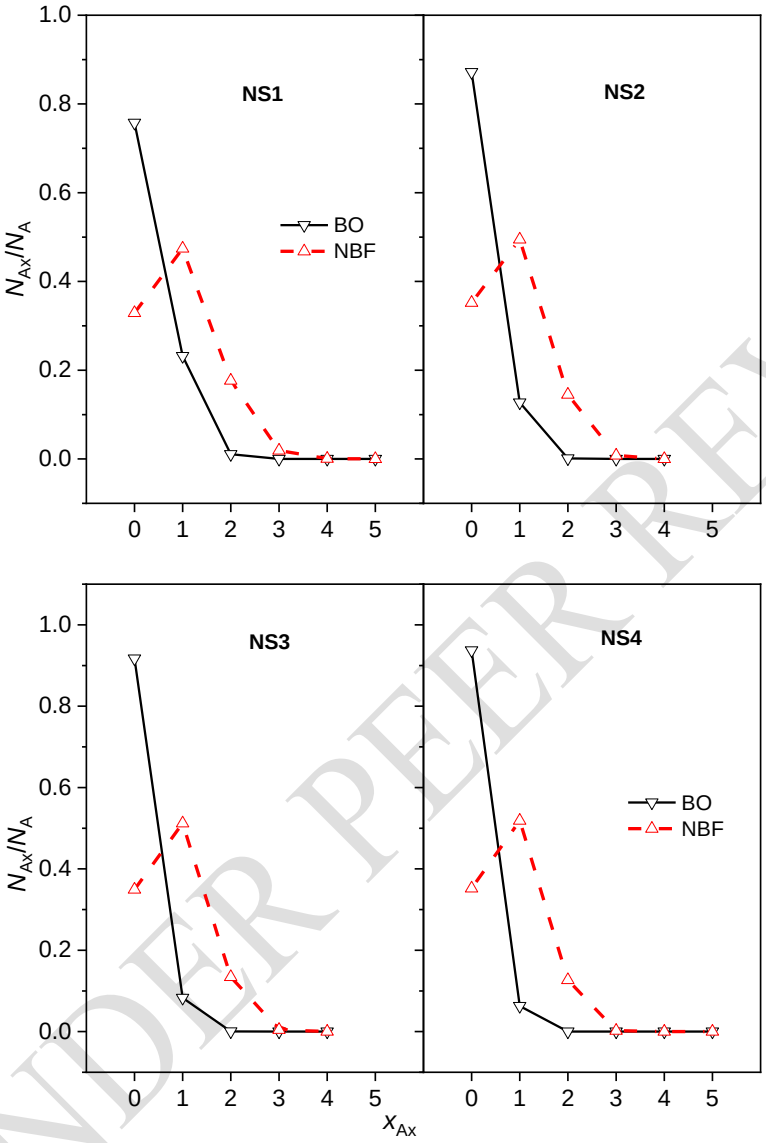

Figure 4. The fraction N_{Ax}/N_A as a function of x_{Ax}. Here N_{Ax}, N_A is the number of Ax-polyhedrons with x_{Ax}, and total number of A; x_{Ax} is the number of Na in Ax-polyhedron; A is the BO or NBF.

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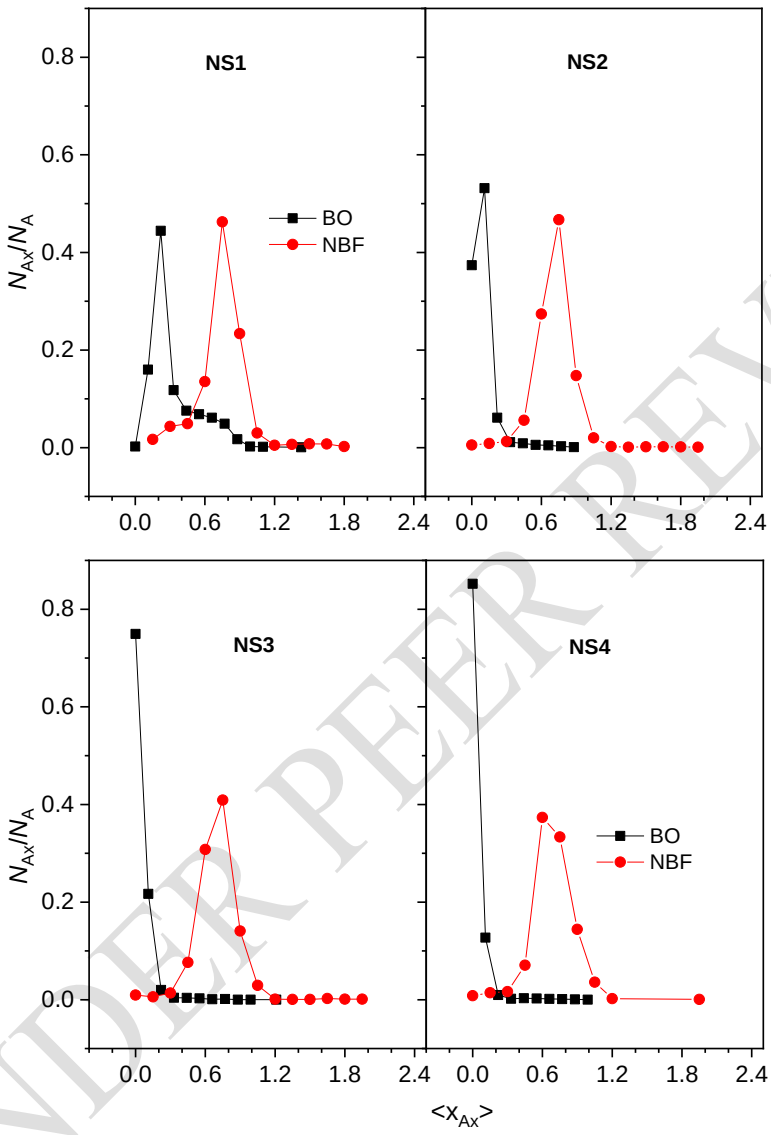

Figure 5. The fraction N_{Ax}/N_A as a function of $<x_{Ax}>$. Here N_{Ax}, N_A is the number of Ax-polyhedrons with $<x_{Ax}>$ and total number of BO or NBF; $<x_{Ax}>$ is the average number of Na in Ax-polyhedron during 150 ps.

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