NETWORK STRUCTURE AND POLYAMORPHISM OF BOROSILICATE

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Abstract

Network structure and polyamorphism of borosilicate melts are investigated by molecular dynamics simulation. The local structure of elements is investigated via radial distribution function, coordination number distribution. The topology of tetrahedral SiO₄ and BO₄, and triangular BO₃ is analyzed via O-T-O bond angle and T-O bond length distribution (where T = Si, B). Glassy network structure is investigated via distribution of linkages Si-O-Si, B-O-Si and B-O-B and Qⁿ (Q is SiO₄ and n is the number of bridging oxygen (BO) in SiO₄ units). Specially, the polyamorphism as well as structural and compositional heterogeneities are also presented and discussed in detail.

Keywords and phrases: polyamorphism, borosilicate, heterogeneity, simulation, network structure.

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1. Introduction

Boron trioxide (B_2O_3) and silica (SiO_2) are two major components of many industrial glasses. Specially, the borosilicate systems $(B_2O_3-SiO_2)$ have been applied in many areas of high technology such as bioactive glasses or the storage of nuclear waste. Because of their important applications, many studies (both experiment and simulation) have been conducted to clarify the structural characteristics and physical properties of borosilicate glasses and melts [1-10].

Many nuclear magnetic resonance (NMR) experiments show that the concentration of BO4 tetrahedra in sodium borosilicate glasses is strongly dependent on the modifier oxide content [1-3]. By using Raman spectroscopy, the investigation in the works [4, 5] have shown the existence of boroxol, trigonal and tetrahedral units in B_2O_3 -based glasses. By neutron- and high-energy synchrotron x-ray diffraction experiments for sodium borosilicate glasses with different compositions [6], Fábián and coworker have shown that the glassy network is formed by trigonal BO_3 and tetrahedral BO_4 , SiO_4 units, forming mixed ${}^{[4]}\mathrm{Si-O}\text{-}{}^{[3,\,4]}\mathrm{B}$ linkages and $\mathrm{Na_2O}$ oxide have the role of network modifier. The tetrahedral SiO₄ network in the system is very stable. The Si–O bond length and Si–Si distance are 1.60 and 3.05Å, respectively and not dependent on the mole ratio SiO_2/B_2O_3 as the Na₂O content is constant. The behaviour of network former (boron atoms) is very complex. It exists two distinct values of B–O bond length at 1.3 and 1.50Å, both trigonal BO_3 and tetrahedral BO_4 units are present. The number of BO_4 and BO_3 units depends on the SiO_2/B_2O_3 and Na_2O/B_2O_3 ratios. The number of BO_4 decreases with the increase of B_2O_3 content. The B-O-B average bond angles are around 121° and 149° corresponding to OB₃ and OB₂ linkages. The O-B-O bond angles distribution has a peak at $106^{\circ} \pm 5^{\circ}$ for BO₄ units. For the Si-O-Si and O-Si-O angle distribution, the peak positions are at $147^{\circ} \pm 3^{\circ}$ and $107^{\circ} \pm 5^{\circ}$, respectively, which are very close values to the ideal tetrahedral configuration [6-8].

Besides experimental methods, classical molecular dynamics simulation (MDS) is still one of the most useful methods to investigate the structure of borosilicate as well as multi-components glasses [9-15]. By MDS, it has been shown that the structure of B_2O_3 -SiO₂ system consists of two network formers: Si forming SiO₄ coordination units; B forming $\mathrm{BO}_4\,$ and $\mathrm{BO}_3\,$ coordination units. The B atoms with two kinds of coordination are an important characteristic of the borosilicate glass, which shown a non-linear structural change with respecting to the composition. This is known as the boron anomaly. As alkaline is added into borosilicate glass, the alkaline content has a direct impact on the network structure (fraction of BO_3 and BO_4). On the one hand, they incorporate into network via [BO₄]⁻ units (alkaline atoms locate near $[\mathrm{BO}_4]^-$ units) and play the role of charge balance. On the other hand, they can also act as network modifiers when they break the network and create NBOs. In this case alkaline atoms will incorporate in network via $[NBO]^-$. For simple network liquids $(B_2O_3, SiO_2, GeO_2, Al_2O_3)$, MDS and considerable experimental data have shown the coordination number of network-forming cation increases under compression that results in the increase of diffusion as density increases [2, 3, 11]. Theoretical studies and molecular dynamics simulations have shown that the increases of cation coordination under compression will be accompanied by the increases of the oxygen coordination number from two to three [5, 6, 12-14]. In more complex systems where a significant fraction of NBO are (typical bonded to single network cations network cations: Si, B, Ge, P, ...) and to multiple, lower- charged modifier cations (typical lower- charged modifier cations: K, Na, Li, ...), it has been suggested [5, 8] that a displacement of the following equilibrium to the right may $NBO + TO_n = TO_{n+1}$, here T is a occur with increasing pressure: network-forming cation.

Although structural and dynamical properties of B_2O_3 based glasses have been investigated for a long time, most of works focus on the multicomponent systems (such as $Na_2O-B_2O_3-SiO_2$; $Na_2O-CaO-SrO-P_2O_5-SiO_2$; ...), the number of works that studied the structure of $B_2O_3-SiO_2$ is very limited. So, in this work the structure of $B_2O_3-SiO_2$ system with different compositions will be investigated in detail. The structural characteristics such as network structure, polyamorphism as well as structural and compositional heterogeneities will be clarified.

2. Computational Method

Models of borosilicate systems ($B_2O_3 - 2.SiO_2$, 5500 atoms [abbreviate: BS2]; $B_2O_3 - 3.SiO_2$, 5320 atoms [abbreviate: BS3]; $B_2O_3 - 4.SiO_2$, 5270 atoms [abbreviate: BS4]), at temperature of 3000K and ambient pressure are constructed by molecular dynamics simulation. The two-body Buckingham potentials are applied in this simulation. This is the empirical potential model developed for application with borosilicate glasses with different compositions. The detail of potential parameters can be referred in the work [16]. To eliminate the surface effect, the periodic boundary condition is applied for all three dimensions.

The software used in our calculation was written by ourselves. It was written in C language and run on Linux operating system. The programs can be applied for simulation of multicomponent oxide glasses and melts. We use the Verlet algorithm to integrate the equation of motion with MD step of 1.6fs. This value assures the requirement to accurately integrate the Newtonian equations of motion in order to track atomic trajectories and the computational cost is reasonable.

In this study, the program is applied for simulation of BS2, BS3 and BS4 systems. Calculation is performed on high performance computing system at RIKEN institute in Japan with MD time step of 1.0fs. This value assures the requirement to accurately integrate the Newtonian equations of motion in order to track atomic trajectories and the computational cost is reasonable. Initial configuration is generated by randomly placing all atoms in a simulation cell. To eliminate the memory effect of initial configuration, the model is equilibrated at temperature of 5000K for a long time (about 2×10^5 time-steps). After that the models at different compositions are cooled down to the desired temperature of 3000K with the rate of about 2.5×10^{12} K/s. A consequent long relaxation (about 10^6 MD steps) has been done in the NPT ensemble (constant temperature and pressure) to obtain equilibrium state. Next, the models are relaxed in NVE ensemble for 10^6 MD steps. In order to improve the statistics, the measured quantities such as the coordination number, partial radial distribution function (PRDF) as well as distribution of bond angle, bond length, NBOs, BOs are computed by averaging over 1000 configurations separated by 20 MD steps.

To calculate the size distribution of SiO_x - and BO_x -clusters, we used our previous program that have been used to calculate the size distribution of SiO_x -clusters in MgO-SiO₂ and Al_2O_3 -SiO₂ systems [17, 18].

To identify SiO_x and BO_x units, we use the cutoff radius of 2.20Å and 1.98Å for Si–O and B–O, respectively. These cutoff distances are the first minimum positions of the Si–O and B–O pair radial distribution function (RDF). Size distribution of SiO_x clusters or subnets is calculated by following algorithm: (i) for the set of SiO_x units, all atoms are labeled from 1 to n (n is the number of atoms in the set). After that, if two Si atoms have at least one common O atom then they will belong to the same cluster and have the same label (value of this common label is the label of the Si atom with the smaller value). Size distribution of BO_x clusters is also calculated similarly to the case of SiO_x .

3. Result and Discussion

Figure 1 shows the PRDFs of Si–O, B–O, Si–Si, B–B, B–Si, and O–O pairs. It can be seen that the PRDFs of Si–O, B–O, and Si–B are almost not changed with varying composition. It means that the average bond length of Si–O, B–O, and Si–B pairs in BS2, BS3, and BS4 models are the same. The average bond lengths of B–O, Si–O, and Si–B pairs are around 1.38, 1.64, and 2.92Å respectively. This reveals that the local structure of Si and B in liquid borosilicate is not dependent on composition, in other word, not depend on mole ratio: B_2O_3/SiO_2 . The PRDFs of Si–Si, B–B, and O–O atomic pairs are slightly changed with composition. The PRDFs of Si–Si, B–B, and O–O atomic pairs relate to the intermediate range order. It means that the intermediate range order structure is slightly dependent on composition. The average distances of Si–Si, B–B, and O–O pairs are around 3.10-3.14, 2.70-2.76, and 2.50-2.56Å, respectively.



Figure 1. The PRDFs of Si–O, B–O, Si–Si pairs (top); B–B, B–Si, O–O pairs (bottom).

Figures 2 and 3 show the B–O and Si–O coordination number distribution. Most of B have coordination number of 3. The number of B with coordination number of 4 is rather small and dependent on composition. It can be seen that the fraction of BO_4 units increases slightly with the SiO_2 content. It means that the number of B atoms that replace the site of Si ones in the SiO_4 tetrahedra increases slightly with the SiO_2 content. The fraction of BO_4 units in BS2, BS3, and BS4 are 6.7, 8.7, and 10.2%, respectively (see Figure 2). The formation of BO_4 units with negative charge is usually applied for storage of the metalcations in multicomponent glass. This is applied to immobilize the hazardous metals in nuclear and industrial waste.

Figure 3 shows that most of Si atoms have coordination of 4. The fraction of Si one with coordination of 3 and 5 is rather small (about several percents). The fraction of SiO₄ in BS2, BS3, and BS4 systems are around 91-92% and almost not dependent on composition. The formation of SiO₃ is due to the Si atoms replacing the B site in BO₃ triangle.



Figure 2. Distribution of B–O coordination number of models BS2, BS3, and BS4.



Figure 3. Distribution of Si–O coordination number of models BS2, BS3, and BS4.

To clarify the local environment of B and Si, the topology structure of BO_3 and SiO_4 units is investigated via bond angle and bond length distribution. Figure 4 shows the bond angle and bond length distribution in BO_3 and SiO_4 units at different compositions. It can be seen that the bond length and bond angle distribution in BO₃ and SiO₄ units for BS2, BS3, and BS4 systems are almost the same. It means that topology of $\mathrm{BO}_3\,$ and $\,\mathrm{SiO}_4\,$ units is identical and not dependent on composition. The immediate range order (IRO) in borosilicate relates to the linkages among SiO_x and BO_x (most of SiO_x and BO_x are SiO_4 and BO_3 , see Figures 2 and 3). So, to clarify the IRO, we have investigated the distribution of T-O-T bond angle and O-T bond length (T = B or Si). Figure 5 shows the distribution of B-O-B bond angle, Si-O-Si bond angle, O-B bond length and O-Si bond length. For OSi_x and OB_x linkages, investigation result shows that most of them are OSi_2 and OB_2 ones (see Table 1). The OB_3 tri-cluster is almost not existent and this maybe relate to the B-avoidance principle in borosilicate system.



Figure 4. Distribution of bond angle and bond length in BO_3 units (top) and SiO_4 unit (bottom).



Figure 5. Distribution of bond angle and bond length in OSi_2 linkage (top) and OB_3 linkage (bottom).

Linkages	BS2	BS3	BS4
Si-O-B	1969	1629	1445
В-О-В	443	261	148
Si-O-Si	855	1302	1593
$O-B_3$	1	0	0
O-Si ₃	26	32	36
Si_2 –O–B	79	81	83
$Si-O-B_2$	43	25	24

Table 1. Distribution of all kind of linkages for BS2, BS3, and BS4 model

The distribution of bond angle and bond length for OSi₂ and OB₂ linkage in BS2, BS3, and BS4 system is almost the same. It means that the IRO for Si–O network and B–O network is almost not dependent on composition. The distribution of B–O–B and Si–O–Si bond angles has the peak at around 144-146° and 140-144°, respectively. The distribution of B–O and Si–O bond lengths has the peak at 1.38 and 1.64Å, respectively. It reveals that the distribution of B–O–B and Si–O–Si bond angle is similar and not dependent on composition.

Figure 6 shows the distribution of T–O–T bond angles in OT_x linkages. For OT_x linkages, most of them are OT_2 and OT_3 . The distribution of T–O–T in OT_2 linkages for BS2, BS3, and BS4 system is almost the same (with the peak at around 142-146°). However, the distribution of T–O–T in OT_3 linkages for BS2, BS3, and BS4 system is slightly dependent on composition. They have the peak at around 116-120°.



Figure 6. The T–O–T bond angle distribution in OT_2 and OT_3 linkages.

Figure 7 shows the distribution of O–T bond length in OT_x linkages. It can be seen that the distribution of bond length in OT_x linkages is significantly dependent on composition. The distribution of bond length in OT_2 linkages have two peaks at around 1.38 and 1.64Å corresponding to B–O and Si–O bond length. Similar, the distribution of bond length in OT_3 linkages also have two peaks at around 1.40 and 1.66Å corresponding to B–O and Si–O bond length. This reveals that the B–O and Si–O bond lengths in OT_3 linkages are a little longer than the one in OT_2 ones. However, the number of OT_3 linkages is very small in comparison to the ones of OT_2 (the fraction O–T bonds belong to OT_3 linkages is around 5-6% the total O–T bonds).



Figure 7. The O–T bond length distribution in OT_2 and OT_3 linkages.

To clarify the polyamorphism as well as structural and compositional heterogeneities. The size distribution of SiO_x , and BO_x clusters has been investigated and shown in Tables 2 and 3. It can be seen that the SiO_x units tend to connect each other forming a very large cluster (for BS2 system, the largest -Si-O- cluster consists of 2963 atoms). The number of small clusters is not much (for BS2 system, it exists about 94 clusters with size from 5-10 atoms and 23 cluster with size from 11-44 atoms). The size of the largest -Si–O- cluster increases with SiO_2 content. The number of small clusters decreases with the increase of SiO₂ content. The size of largest clusters for BS2, BS3, and BS4 system are 2963, 4096, and 4384 atoms, respectively. In contrast, the BO_x tends to connect to each other forming small -B-O- cluster with size from several to several tens of atoms. The number of -B-O- clusters for BS2, BS3, and BS4 system are 508, 472, and 446, respectively. For more detail about network structure and polymerization, the distribution of $Q^n(Si)$ units is investigated and shown in Table 4. It can be seen that the number of $Q^{0}(Si)$ ($Q^{0}(Si)$ is the SiO₄ without BO [isolated SiO₄ tetrahedron]) decreases with the increase of SiO₂ content. For BS2 model, most of $Q^{n}(Si)$ belongs to $Q^{1}(Si)$ and $Q^{2}(Si)$. For BS3 and BS4 models, most of $Q^{n}(Si)$ belongs to $Q^{2}(Si)$ and $Q^{3}(Si)$. It means that the degree of polymerization of -Si-O- network increases with SiO₂ content. The intuitive network structure of borosilicate system is shown in Figures 8(a), 8(b) and 8(c). It can be seen that the structure of borosilicate consists of two networks: -B-O- and -Si-O- ones. The distribution of BO_x and SiO_x is not uniform but forming cluster of BO₃ beside SiO₄. This reveals the polyamorphism as well as the structural and compositional heterogeneities.

Table 2. Size distribution of SiO_x clusters for BS2, BS3, and BS4 models, here Nc and Na are number of cluster and the number of atoms in the cluster, respectively

]	BS2		BS3		BS4
Nc	Na	Nc	Na	Nc	Na
94	5-10	19	5-10	13	5
12	11-20	1	12	1	8
8	21-30	1	13	1	4384
1	32	1	4096		
1	37				
1	44				
1	2963				

Table 3. Size distribution of BO_x clusters for BS2, BS3, and BS4 models, here Nc and Na are number of cluster and the number of atoms in the cluster, respectively

В	8S2		BS3		BS4
Nc	Na	Nc	Na	Nc	Na
441	4-10	441	4-10	431	4-10
51	11-20	26	11-20	15	11-20
11	21-30	6	21-30		
2	31-40				
3	41-50				

Table 4. Distribution of $Q^n(Si)$ in BS2, BS3, and BS4 models

Q^n	BS2	BS3	BS4
\mathbf{Q}^{0}	59	29	19
\mathbf{Q}^1	264	177	113
Q^2	386	397	373
Q^3	222	396	510
Q^4	69	142	225



Figure 8(a). Snapshot of borosilicate network structure for BS2 system. The balls from small to large is O, B and Si, respectively. Figures from left to right are -Si-O-B-, -B-O-B-, and -Si-O-Si- network.



Figure 8(b). Snapshot of borosilicate network structure for BS3 system. The balls from small to large is O, B, and Si, respectively. Figures from left to right are -Si-O-B-, -B-O-B-, and -Si-O-Si- network.



Figure 8(c). Snapshot of borosilicate network structure for BS4 system. The balls from small to large is O, B, and Si, respectively. Figures from left to right are -Si-O-B-, -B-O-B-, and -Si-O-Si- network.

4. Conclusion

The structure of borosilicate consists of BO_x and SiO_x (mainly BO_3 and SiO_4) connects to each other forming SiO_x - and BO_x -networks. The topology of BO_3 and SiO_4 units is almost not dependent on composition. In the BS2, BS3, and BS4 systems, the -Si-O- network is the main one. The distribution of SiO_x and BO_x units is not uniform but forming BO_x clusters beside SiO_x ones. This reveals the polyamorphism as well as the structural and compositional heterogeneities in borosilicate systems. The structure of borosilicate maybe also exhibits the B-avoidance principle, that is similar to Alavoidance principle in aluminosilicate systems.

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