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1. Molecular Dynamics Simulation of the Structure of Soda-lime-silica Glass

Taketoshi Taniguchi* and Setsuro Ito*

The structure of soda-lime-silica glass was studied by using a molecular dynamics (MD) simulation technique by two potential parameter sets. Both MD-derived structure was similar to each other. Calculated X-ray interference function of the glass was almost comparable to observed one. The network structure in glass mainly consisted of more than 5-membered rings based on SiO_4 and AlO_4 tetrahedra with 3 or 4 bridging oxygen ions. Modifier ions, such as Mg and Ca ions, clustered in the glass, suggesting that the glass has inhomogeneous structure. On the other hand, physical properties estimated by both MD-derived structures differed each other.

1. Introduction

It is soda-lime-silica glass that has been in the most common use for a long time as window, bottle and so on. There are various investigations about the properties of the glass, such as mechanical, thermal, and chemical properties. Also, there are many reports about the glass structure investigated by X-ray diffraction[1], EXAFS[2], NMR[3], XPS[4], infrared and Raman spectroscopy[5],[6], although most of them described only atomic-level structure, e.g. interatomic distance, coordination number, intertetrahedral angle such as Si-O-Si angle, and the number of bridging oxygen ion around network-forming ions. However, most studies targeted binary and/or ternary system because of the additional complexity with increasing component. Moreover, it is generally difficult to obtain structural information about random network structure and distribution of modifier ion in multi-component glass by the methods described above. In molecular dynamics (MD) simulation[7], it is possible to examine the medium range network structure in addition to atomic-level structure.

In our previous study[8], by MD simulation, we studied the glass having the composition of $12.3Na_2O \cdot 5.5MgO \cdot 8.9CaO \cdot 1.1Al_2O_3 \cdot 72.2SiO_2$ (mol%), which is almost the same composition as a typical commercial window glass. We reported in the paper that Mg and Ca ions were coordinated by non-bridging oxygen ions but Na ion was coordinated by both bridging and non-bridging oxygen ions. On the other hand, Cormack and Du[9] studied $(25\text{-}x)Na_2O\text{-}xCaO\text{-}75SiO_2$ glass and reported that Na ions were surrounded by non-bridging oxygen ions rather than bridging oxygen ions. This difference is due to potential models. We used the empirical potential parameters developed by Matsui[10] while Cormack and Du used potential parameters based on *ab-initio* method[11],[12]. Unfortunately, the parameter sets used by Cormack and Du applies to only $Na_2O\text{-}CaO\text{-}SiO_2$ system but not Al_2O_3 and MgO containing system. Miyake[13] reported empirical potential parameter sets for $K_2O\text{-}Na_2O\text{-}MgO\text{-}CaO\text{-}Al_2O_3\text{-}SiO_2$ system. Principal difference between Matsui's and Miyake's parameter sets is that the former set applied to interatomic energy function consists of Coulombic, the short range repulsion, and the van der Waals attraction terms while the latter set applied to the function consists of Morse potential term besides the terms applied by Matsui's parameter set. Actually, Coulomb and repulsive potential curves by Matsui's set are similar to those by Miyake's set though van der Waals attraction potential curves by Matsui's set is larger than that by Miyake's set. This difference of potential curves,

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as a whole, means that the bottom of potential curve by Matsui's set are deeper and narrower than that by Miyake's set. In this study, we report the glass structure simulated by Matsui's and Miyake's parameter sets.

2. Calculation method

As a MD program, MXDORTO developed by Kawamura[14] was used. In this MD program, the modified Verlet's method is adopted as algorithm for calculation between two ions. The calculation of Coulomb's energy is followed by Ewald's method. The temperature and pressure was controlled by normal scaling method under the isothermal-isobaric ensemble (constant temperature, constant pressure, and constant number of particles in the system). The number of particles for the glass sample was 2860. The usual periodic boundary conditions were imposed with orthorhombic cell, and the equations of motion were solved numerically with the time increment of 1 fs. The system was equilibrated at 3000 K starting from a random configuration. The cooling process was shown in **Fig. 1**. A run of more than 50 ps was performed at each temperature. Quantum corrections to MD simulations were applied at 300 K, considering that Debye temperature of the glass in the system of Na_2O-CaO-SiO_2 is lower than 441 K[15].

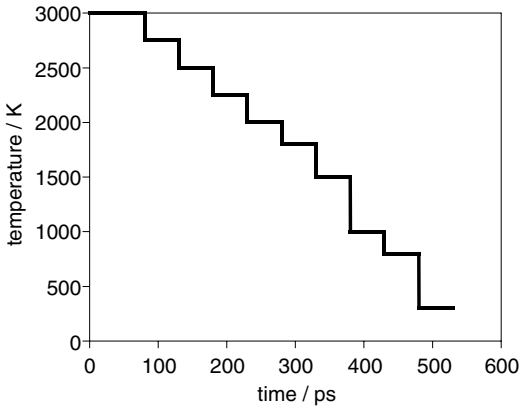

Fig. 1 Plot of the relationship between temperature and time.

3. Results and Discussion

Snapshots of structures of MD-derived glass calculated by Matsui's and Miyake's parameters were shown in **Fig. 2**. Both structures can be seen that the glass had polymerised network (represented by line in the figure) composed of Si, Al and O ions. Modifier ions, such as Na, Mg, and Ca ions (denoted green, orange, and blue circles, respectively) dispersed in the network of glass.

3.1 Atomic distance and coordination number

The calculated atomic distances, coordination numbers, and bond angles are summarised in **Table 1**. The previous reports[16]~[30] of atomic distance, coordination number, and bond angle are also shown in the table, where the Si-O distance, coordination number of oxygen ion around Si, and

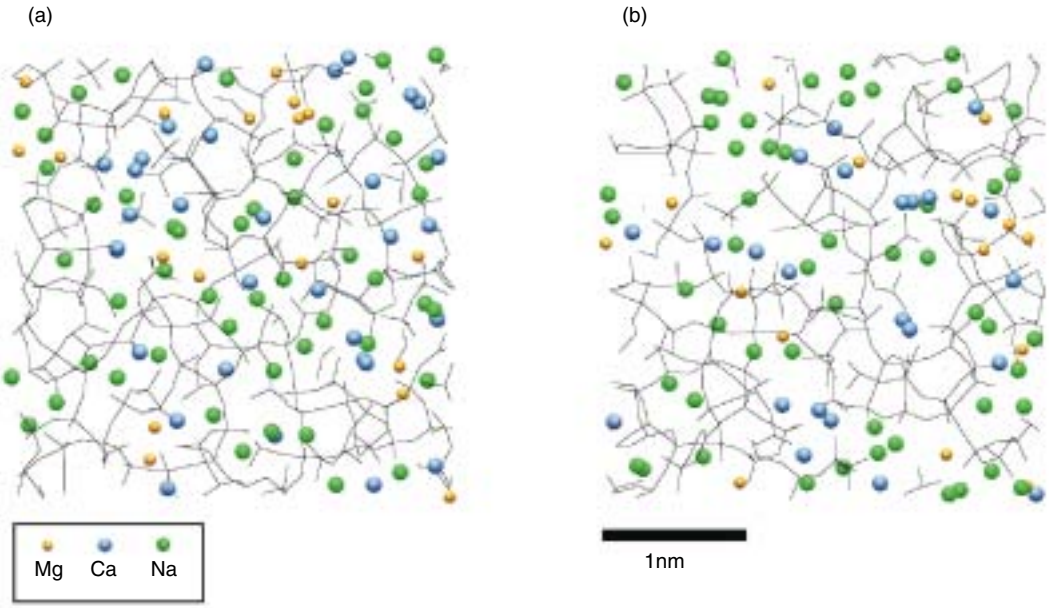

Fig. 2 Snapshots of MD-derived structures (3×3×1nm) of (a) MD-derived glass with Matsui's parameter and (b) by Miyake's parameter. The line represents the network formed by Si, Al, and O ions and orange, blue, and green circles are Mg, Ca, and Na ions, respectively.

Table 1 Interatomic Distance, Coordination Number, and Bond Angle.

Parameter set		Matsui's	Miyake's	obs.
Atomic pair distance (nm)				
	Si-O	0.164	0.163	0.163[16]
	Al-O	0.175	0.176	
	Mg-O	0.202	0.207	0.190-0.208[17]~[22]
	Ca-O	0.241	0.235	0.237-0.249[19]~[21], [23]~[26]
	Na-O	0.251	0.240	0.230-0.262[27]~[30]
	O-O	0.267	0.266	0.266[16]
	Si-Si	0.314	0.316	0.314[16]
Maximum bonding distance (nm)				
	Si-O	0.179	0.179	
	Al-O	0.194	0.192	
	Mg-O	0.219	0.224	
	Ca-O	0.258	0.254	
	Na-O	0.269	0.267	
Coordination number [total (O_b/O_{nb})]				
	Si-O	4.0 (3.3/0.7)	4.0 (3.3/0.7)	3.9[16]
	Al-O	4.0 (3.6/0.4)	4.0 (3.8/0.7)	
	Mg-O	3.9 (0.3/3.6)	4.0 (0.3/3.7)	4.0[17]~[22]
	Ca-O	4.9 (1.0/3.9)	4.4 (0.7/3.7)	6.0[19]~[21], [23]~[26]
	Na-O	4.3 (2.2/2.1)	3.0 (0.6/2.4)	5.0-6.0[27]~[30]
Bond angle (°)				
	O-Si-O	109.3	109.4	109[16]
	O-Al-O	109.2	109.1	
	Si-O-Si	145.9	151.1	149[16]
	Si-O-Al	143.1	147.2	

Si-O-Si angle were quoted from the structural data[16] of the glass having the composition of $12.78Na_2O \cdot 0.58K_2O \cdot 6.01MgO \cdot 8.01CaO \cdot 0.86Al_2O_3 \cdot 71.67SiO_2$ (mol%), which was similar to the glass composition in this study. The pair atomic distances and coordination numbers were estimated as the average distance from cation to oxygen ion existed within the distance to the inflection point in the atomic potential surface. Detailed definition was interpreted in our previous paper[8]. The difference of maximum bonding distance between Matsui's and Miyake's parameter sets was within 0.05 nm. As regards atomic distance, Si-O and Al-O distances were similar to each other though Mg-O from Matsui's set was shorter than that from Miyake's set. While, Ca-O and Na-O distances from Matsui's set were longer than those from Miyake's set. Coordination numbers of oxygen ion around Si, Al, and Mg were almost similar to each other though those around Ca and Na from Matsui's set were somewhat large as compared with Miyake's set. Moreover, the numbers of bridging and non-bridging oxygen ions around Na ions by Matsui's set remarkably differed from those by Miyake's set. This difference was discussed in the section 3.3. These comparisons showed that Mg-O polyhedra by Miyake's set were larger and Ca-O and Na-O polyhedra were smaller than those by from Matsui's set. Comparing these calculated results with observed ones, the atomic distances and the coordination numbers of Si and Al ions were almost equal. However, the calculated coordination numbers of modifier ions, Ca and Na, were smaller than observed ones. Namely, the modifier-oxygen polyhedra calculated by both sets suggested to be small rather than observed ones. The observed coordination number around cation is generally estimated by the area under peak of radial distribution function curve at cation-oxygen atomic pair distances. However, the peak is participated by mainly first-neighbour shell but not only first-neighbour shell of modifier ion because modifier-oxygen polyhedra are not clear shape as compared with SiO_4 tetrahedra. Therefore, both MD results

Table 2　Q-species and Rings.

Parameter set	Matsui's	Miyake's
Q0	0.0	0.0
Q1	0.8	1.2
Q2	12.9	11.8
Q3	39.6	41.5
Q4	46.7	45.5
Ave.	3.32	3.31
2-membered ring	0.00	0.00
3-membered ring	0.42	0.70
4-membered ring	6.56	8.23
5-membered ring	16.04	14.78
6-membered ring	18.27	21.06
7-membered ring	21.48	18.55
8-membered ring	23.29	17.29

showed that real coordinated number of oxygen ion around modifier ion was probably small rather than observed ones.

3.2 Network structure

Table 2 shows the Q_n species and the average number of bridging oxygen ions around network former ions. The bridging oxygen ion O_b, was defined as the oxygen ion bonded to two silicon ions or each one silicon and one aluminium ion within 0.179 nm for Si-O maximum bonding distance and 0.194 nm (Matsui's set) and 0.192 nm (Miyake's set) for Al-O maximum bonding distance (**Table 1**). The Q_n is defined as species with **n** bridging oxygen ions in each SiO_4 and AlO_4 tetrahedron. In both MD results, glass almost consisted of Q_3 and Q_4 species. Moreover the average number of bridging oxygen ions by Miyake's (3.31) were almost the same as that by Matsui's (3.32) and agree with the expected value (3.30) from the glass composition.

The number of ring per 100 Si and Al, which are network former ions, are also shown in **Table 2**. The ring size was determined by the number of SiO_4 and AlO_4 tetrahedra involved in the closed chains. The number of rings increased with increasing ring size in the case of Matsui's set, but not Miyake's set. However, in both case, more than 5-membered rings were predominant.

3.3 Local structure around modifier ions

The distribution curves between modifier ion (Mg, Ca, and Na) and bridging (O_b) or non-bridging oxygen (O_{nb}) ion are shown in **Fig. 3**. From the results by Matsui's and Miyake's sets, the first peaks of Mg-O_b and Ca-O_b curves were much lower than those of Mg-O_{nb} and Ca-O_{nb} one, respectively. These showed that Mg and Ca ions were almost surrounded by non-bridging oxygen ions. On the other hands, the first peak of Na-O_b curve by Matsui's set was almost the same height as that of Na-O_{nb} one though Na-O_b curve by Miyake's set was smaller than that of Na-O_{nb} one as the same as the case of Mg-O and Ca-O pairs. The latter result agreed with that by Cormack and Du[9]. The both results by Matsui's and Miyake's sets showed that the ratio of the number of bridging oxygen ion to the number of non-bridging oxygen ion increased in the order of Mg, Ca, and Na ions. These result means that modifier ions with stronger field strength was surrounded by more non-bridging oxygen ions than bridging oxygen ions. However, the effect of field strength was clearer by Matsui's than by Miyake's.

The Mg-Mg, Ca-Ca, and Na-Na distributions are shown in **Fig. 4**. The results by Matsui's and Miyake's sets showed that Mg-Mg and Ca-Ca distribution curves had several peaks. Especially, the first peaks of Mg-Mg and Ca-Ca pair distribution curves were found around 0.28 nm and 0.35 nm, respectively. This indicates that Mg and Ca ions were clustered in glass. Eckersley et al.[24] reported that the existence of Ca-Ca peak at 0.35 nm was found in $CaSiO_3$ glass by neutron diffraction. This result suggested that Ca ions are arranged at intervals of around 0.35 nm in silicate glass, independent of its contents. However, though Na-Na distribution curve by Matsui's set had no remarkable peak till 0.65 nm, Na-Na distribution curve by Miyake's set had noticeable peak at 0.37 nm. The former result indicates that Na ions distributed homogeneously though the latter result suggests that Na ions were clustered, but the clustering of Na is less than those of Mg and Ca ions. The distribution between modifier ions is strongly related to the distribution between modifier ion and non-bridging oxygen ion. Namely, Na ion in the glass by Matsui's was surrounded by non-bridging and bridging oxygen ions so that this ion arranged randomly in the glass. On the other hand, Na ion in the glass by Miyake's set was mostly surrounded by non-bridging ion. Therefore, it is more stable for Na ions in the glass by Miyake's set clustered together rather than distributed randomly for making the linkages of modifier ions to non-bridging ion, which was fewer than bridging ion in the glass. It is concluded that there was remarkable difference about the local structure around Na ion by Matsui's and Miyake's sets.

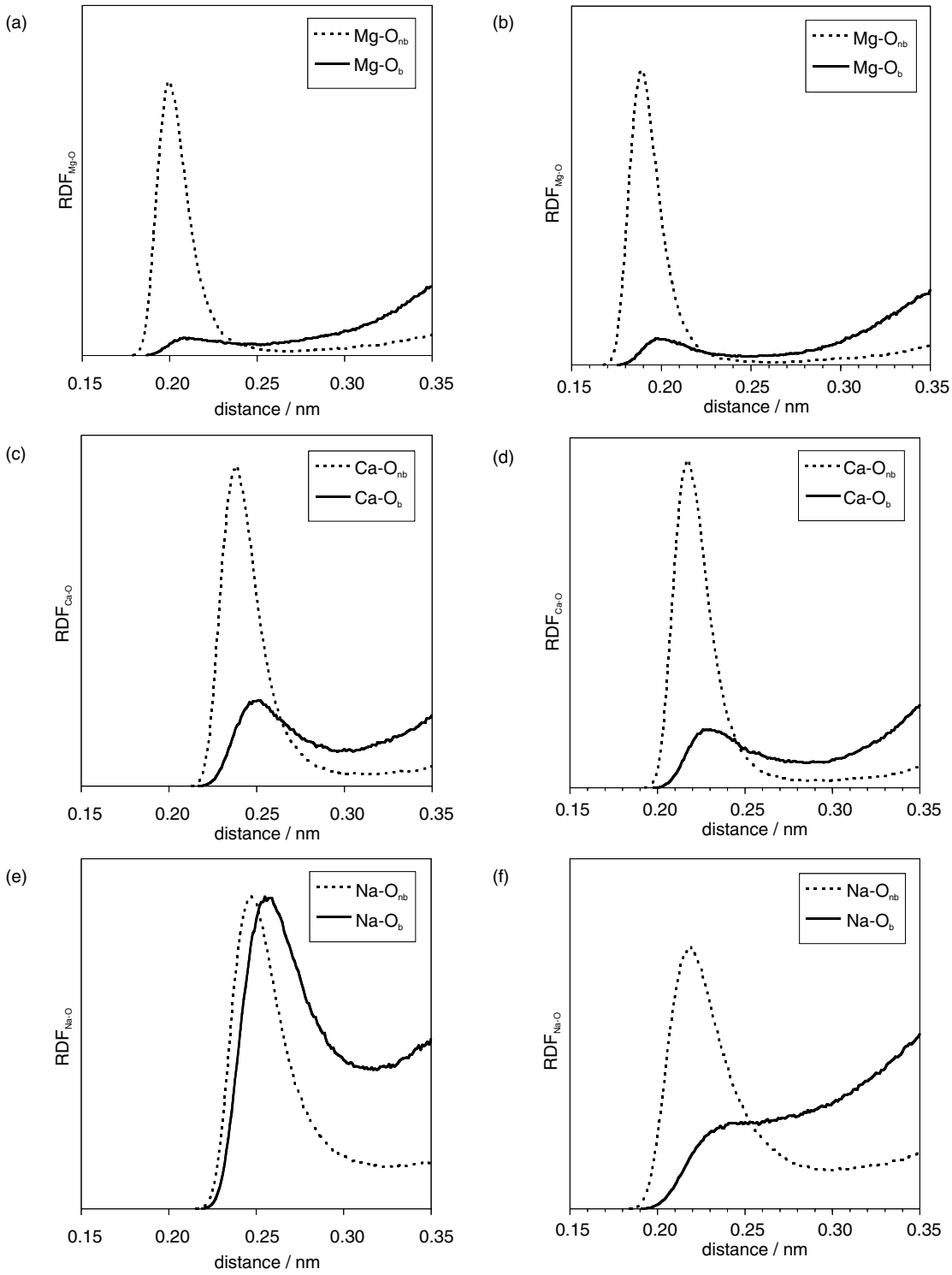

Fig. 3 Distribution curves of (a), (b) Mg-O, (c), (d) Ca-O, and (e), (f) Na-O. Figures (a), (c), and (e) were derived by using Matsui's set and figures (b), (d), and (f) were derived by using Miyake's set.

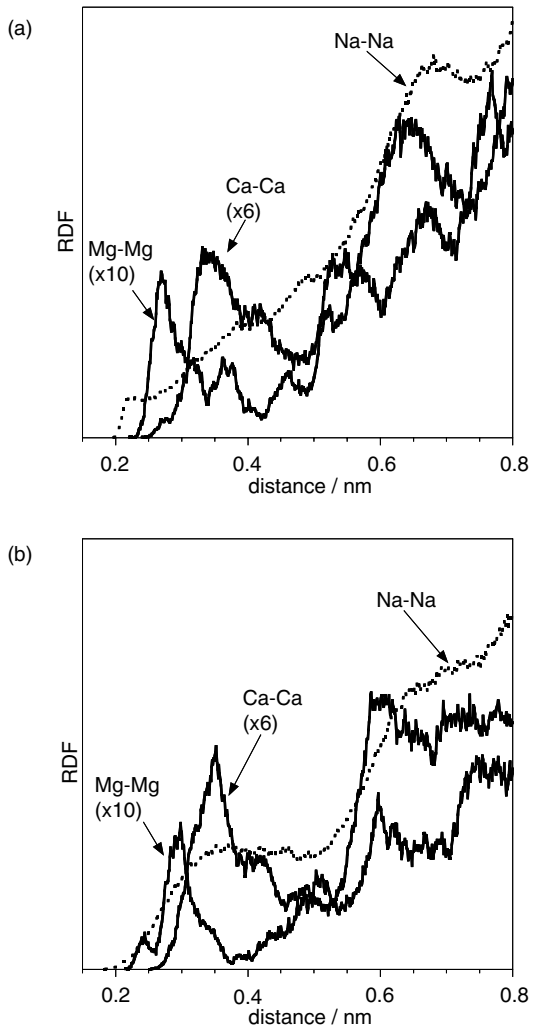

Fig. 4 Distribution curves of modifier-modifier pairs. Figure (a) was derived by using Matsui's set and figure (b) was derived by using Miyake's set.

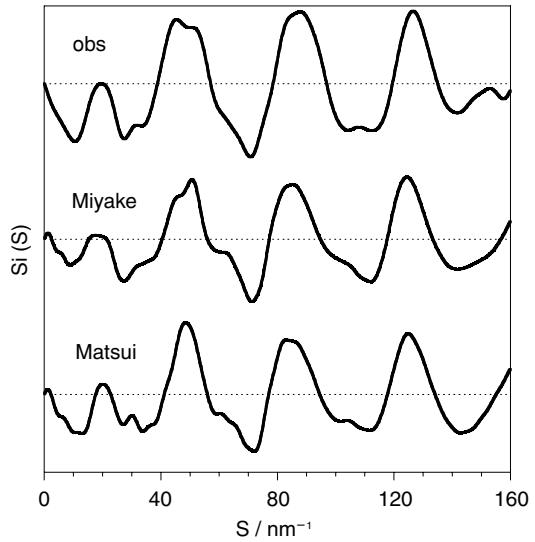

Fig. 5 Calculated *S•i(S)* curve with the observed one[32].

3.4 Physical properties

The density of glass by Matsui's was 2.70 gcm^{-3}, while that of glass by Miyake's was 2.23 gcm^{-3}. The main reason of smaller density by Miyake's was probably fewer bridging oxygen ions around Na ions as described above section. The calculated density by Matsui's was about 8% larger while that by Miyake's was 11% smaller as compared with the observed density (2.50 gcm^{-3})[31]. However, since the X-ray interference function, *S.i(S)* calculated from the glass structure by Matsui's and Miyake's sets were comparable to observed one[32], as shown in **Fig. 5**, the accumulation of a little difference between calculated and observed structures is considered to cause the difference of the density. This result means that it cannot be concluded from X-ray interference function curve alone which of glass structures by Matsui's or Miyake's is correct.

Figure 6 showed reduced volume versus static pressure and strain versus stress, from -4 to 4 GPa.

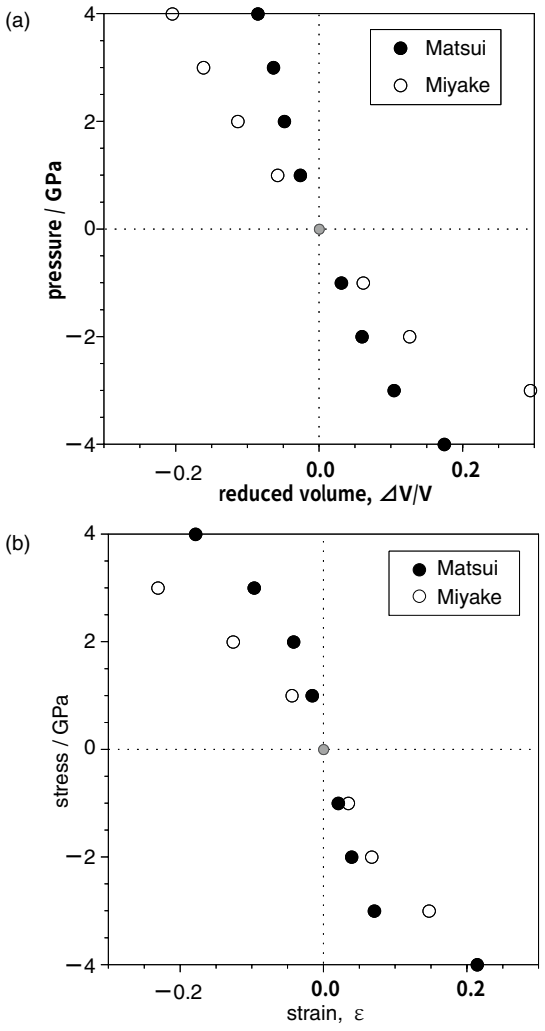

Fig. 6 (a) Volume change and (b) strain of glass versus pressure and stress from −4 to 4 GPa.

In MD simulation under pressure of -4 GPa and stress of ±4 GPa, the glass by Matsui's set was not fractured though the glass by Miyake's set was fractured. It is found that volume and strain at each pressure and stress by Miyake's were larger than those by Matsui's. From the data of -2 to 1 GPa, which was the region of elastic deformation, the bulk and Young's moduli were calculated to be 47 GPa and 68 GPa at 0 GPa by Matsui's and 24 GPa and 35 GPa at 0 GPa by Miyake's, respectively. Compared with observed values (46 GPa [33] for bulk modulus and 74 GPa. [34] for Young's modulus), the calculated values by Matsui's were comparable to but those by Miyake's were smaller than observed ones.

4. Conclusions

Structure of silicate glass having the composition of $12.3Na_2O \cdot 5.5MgO \cdot 8.9CaO \cdot 1.1Al_2O_3 \cdot 72.2SiO_2$ (mol%) was investigated by MD simulation, using Matsui's and Miyake's potential parameter sets. Two models of glass structure showed the same network structure. Namely, Si-O and Al-O polyhedra formed tetrahedral, and the number of bridging oxygen ions around Si and Al ions were almost 3 and 4. The number of rings increased with increasing the size for Matsui's set, but not Miyake's set. The ratio of non-bridging oxygen ion to bridging oxygen ions decreased in the order of Mg, Ca and Na ions. Namely, Mg and Ca ions were surrounded by mostly non-bridging oxygen ion. Moreover, Mg and Ca ions clustered, suggesting that the glass has inhomogeneous structure. However, the local structure around Na ion by Matsui's was different from that by Miyake's. In the glass by Matsui's set, Na ion was surrounded by almost the same number of bridging oxygen ion as non-bridging oxygen ion and distributed randomly in the glass. On the other hand, in the glass by Miyake's set, Na ion was surrounded by mostly non-bridging oxygen ion and clustered in the glass. Nevertheless, calculated X-ray interference functions derived from each glass structure calculated by Matsui's and Miyake's sets were almost coincident with observed one. As regards mechanical properties, however, the value of bulk and Young's moduli calculated by the glass structure by Matsui's set were almost equal to observed ones though those calculated by the glass structure by Miyake's set was smaller than observed ones.

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