

# MD study of sodium borate glasses containing $\text{Al}_2\text{O}_3$

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The short range structure of  $0.05\text{Al}_2\text{O}_3 \cdot x\text{Na}_2\text{O} \cdot (0.95-x)\text{B}_2\text{O}_3$  glasses ( $0.10 < x < 0.45$ ) has been investigated using molecular dynamics calculations employing a fully ionic model. Regardless of  $x$ , the coordination number of oxygen atoms around the Al atom was approximately four. It was found that these Al atoms are present as network formers of  $\text{AlO}_4$  units in the glasses in the same manner as are  $\text{BO}_4$  units, and that they cause a decrease of the coordination number of O around Na. It is suggested that the exclusively formed  $\text{AlO}_4$  units may suppress the conversion of the  $\text{BO}_3$  unit to the  $\text{BO}_4$  unit caused by an increase of  $\text{Na}_2\text{O}$ . The decrease of the fraction of four coordinated boron atoms,  $N_4$ , due to the addition of  $\text{Al}_2\text{O}_3$  is supported by the results obtained from preliminary neutron diffraction measurements.

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## 1. Introduction

The compositions of alkali and alkaline earth borate mixtures have limited glass forming ranges. Their behaviour is somewhat complicated: it is known that certain alkaline earth borate mixtures have non-glass forming ranges at a low alkaline earth metal oxide content.<sup>(1)</sup> Aluminium oxide,  $\text{Al}_2\text{O}_3$ , has been empirically known as an effective additive for the extension of the glass forming range of these glasses. Although this means that Al ions should effectively enhance the stability of the vitreous state of alkali and alkaline earth borates, the change of the glass structure and the role of Al ions have not yet been elucidated from the viewpoint of the stability of the glasses.

So far, through the use of molecular dynamics (MD) and neutron diffraction methods, we have focused on the constitutional units in the network to investigate the short range structure of a series of alkaline earth borate glasses in the entire glass-forming range, compared with that for sodium and

potassium borate glasses.<sup>(2–4)</sup> The results showed the presence of well defined triangular and tetrahedral constitutional units,  $\text{BO}_3$  and  $\text{BO}_4$ , respectively, in these glasses. As well, the behaviour of the fraction of  $\text{BO}_4$  unit of all boron atoms,  $N_4$ , was elucidated. It follows  $x/(1-x)$  at a low metal oxide content, where the  $x$  indicates the molar fraction of metal oxide, but tends to deviate from this, as the radius of metal cation decreases in the higher  $x$  range.

On the basis of these findings, therefore, it is important to investigate the changes in short range structures such as the constitutional units (changes which are caused by small amounts of additives such as  $\text{Al}_2\text{O}_3$ ) and to clarify the role of a modifier such as Al in the network, in regard to the stability of the glass structure. For this purpose, in the present study we have performed MD simulation for sodium borate glasses containing 5 mol%  $\text{Al}_2\text{O}_3$  using fully ionic potentials, and have investigated the short range structure around B, Al, and Na. Furthermore, we present some results from our current neutron diffraction experiments, and compare results of simulation and experiment, focusing

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on  $5\text{Al}_2\text{O}_3 \cdot 29\text{Na}_2\text{O} \cdot 66\text{B}_2\text{O}_3$  glass. A comprehensive report on the neutron diffraction experiments will be presented elsewhere.

## 2. Calculation and experimental procedure

### 2.1. MD calculation

The simulated compositions of the alumina sodium borate glass system were  $0.05\text{Al}_2\text{O}_3 \cdot x\text{Na}_2\text{O} \cdot (0.95-x)\text{B}_2\text{O}_3$  with  $x=0.10, 0.19, 0.29, 0.38, \text{ and } 0.45$ , where  $x$  denotes the mole fraction of  $\text{Na}_2\text{O}$ . All MD calculations were carried out using the *NPT* ensemble. The total number of ions,  $N$ , was chosen to be slightly over 1000. The pressure,  $P$ , during the calculations had been adjusted using the Andersen method<sup>(5)</sup> so as to maintain the density evaluated from the experimentally determined values for each real glass, using a pycnometer method, within  $\pm 0.01 \text{ g/cm}^3$ . The temperature was controlled using the Nose–Hoover thermostat.<sup>(5)</sup> The function used for pair potential energy,  $U_{ij}$ , between the ions  $i$  and  $j$  was a form of the Busing approximation of the Born–Mayer–Huggins' type without the dispersion terms. The function is given as

$$U_{ij}(r_{ij}) = \frac{e^2}{4\pi\epsilon_0} \frac{Z_i Z_j}{r_{ij}} + f_0 (b_i + b_j) \exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) \quad (1)$$

where  $Z$  is the ionic charge,  $e$  is the unit charge,  $r$  is the interionic distance, and  $f_0$  is a constant ( $=6.9472 \times 10^{-11} \text{ N}$ ). Since the model used in this study is fully ionic,  $Z_{\text{B}}=+3$ ,  $Z_{\text{O}}=-2$ ,  $Z_{\text{Na}}=+1$ , and  $Z_{\text{Al}}=+3$ . The parameters,  $a$  and  $b$ , are the values related to the radius and the compressibility of each ion, respectively, and their values for each ion were those proposed by Xu *et al.*,<sup>(6)</sup> as shown in Table 1. The Coulomb interactions were treated using the Ewald method<sup>(7)</sup> under periodic boundary conditions.

The initial atomic configuration was generated randomly and the initial atomic velocities were also provided randomly in accordance with the Maxwell distribution of velocities. The equations of motion were integrated using the RESPA algorithm.<sup>(8)</sup> Initially, the system was kept at 5000 K for 303 ps with a calculation time step of 1 fs in order to obtain a fully disordered configuration in the equilibrium state. The molten state was confirmed by checking the mean square displacement of the atoms. Subsequently, it was gradually cooled to 300 K for vitrifying at a rate of 50 K/ps; the time step was 1 fs at above 3000 K, and was 2 fs below 3000 K. In the process of

Table 1. Potential function parameters used in the MD calculations

Ion	Z	$a$ (nm)	$b$ (nm)
Na	1	0.1260	0.0080
Al	3	0.1064	0.0080
B	3	0.0720	0.0080
O	-2	0.1629	0.0085

cooling, the system was kept at 3000, 2000, 1000 and 300 K for 40, 40, 40, 40, and 800 ps, respectively, to relax the structure. The trajectories of the positions for the subsequent 100 ps were analysed to obtain the structural information. On the basis of the obtained pair distribution functions,  $g_{ij}(r)$ , the partial static structure factor,  $S_{ij}(Q)$ , in the Faber–Ziman form<sup>(9)</sup> was evaluated for each pair of ions  $i$  and  $j$ , as follows

$$S_{ij}(Q) = 1 + 4\pi\rho_0 \int_0^{r_{\text{max}}} r^2 [g_{ij}(r) - 1] \frac{\sin(rQ)}{rQ} dr \quad (2)$$

where  $\rho_0$  is the average number density of atoms and  $r_{\text{max}}$  is the cutoff value of  $r$  for the Fourier transformation. The neutron weighted static structure factor,  $S(Q)$ , is given by

$$S(Q) = \frac{\sum_i \sum_j x_i x_j b_i b_j S_{ij}(Q)}{\left(\sum_k x_k b_k\right)^2} \quad (3)$$

where  $b_i$  is coherent scattering length of the  $i$ th nuclear species and  $x_i$  is the atomic fraction. The total structure function,  $Q \cdot i(Q)$ , is defined as follows:

$$Q \cdot i(Q) = Q(S(Q) - 1) \quad (4)$$

The neutron weighted total pair distribution function,  $g^N(r)$ , is expressed by

$$g^N(r) = \sum_i \sum_j x_i x_j b_i b_j g_{ij}(r) / \left(\sum_k x_k b_k\right)^2 \quad (5)$$

The coordination numbers,  $n_{\text{BO}}$  and  $n_{\text{OB}}$ , for O around B and B around O were estimated from the integration of  $g_{\text{BO}}(r)$  using the upper integration limit,  $r_{\text{cutoff}}$  of 0.200 nm. In the same way, the  $n_{\text{AlO}}$  and  $n_{\text{NaO}}$  for O around Al and Na were obtained from corresponding  $g_{ij}(r)$  with a  $r_{\text{cutoff}}$  of 0.200 and 0.300 nm, respectively.

### 2.2. Sample preparation

The compositions of the glass samples used in the present neutron diffraction study were  $0.05\text{Al}_2\text{O}_3 \cdot x\text{Na}_2\text{O} \cdot (0.95-x)\text{B}_2\text{O}_3$  with  $x=0.29, 0.38, \text{ and } 0.45$ . These glasses were made from analytical reagent powders of  $\text{H}_3\text{BO}_3$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{Al}_2\text{O}_3$ . The  $\text{H}_3\text{BO}_3$  was enriched with 99.27 at%  $^{11}\text{B}$  to avoid neutron absorption by  $^{10}\text{B}$ . The details of sample preparation are described in a previous paper.<sup>(4)</sup>

### 2.3. Neutron diffraction

Pulsed neutron diffraction experiments were carried out using a time-of-flight method employing the High Intensity Total scattering spectrometer (HIT-II)

at the KENS Neutron Scattering Facility of the High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. Each sample was contained in a thin walled vanadium cell that was 8 mm in inner diameter and 25  $\mu\text{m}$  in thickness. The neutrons scattered from each sample filled in the cell at 298 K were detected at nominal angles  $2\theta$  of 15, 20, 25, 30, 50, 90, and 150°, which covered a region of momentum transfer,  $hQ/2\pi$ , where  $Q=(4\pi/\lambda)\sin\theta$  and ranged from 1–500  $\text{nm}^{-1}$ . The observed intensity was corrected for the cell, background, absorption, and multiple and incoherent scattering. The coherent scattering intensity,  $I(Q)$ , was normalised with respect to the scattering intensity from a vanadium rod used as a standard. The total structure factor,  $S(Q)$ , in the Faber–Ziman form was derived from the  $I(Q)$ , and the neutron weighted total pair distribution function,  $g^N(r)$ , was obtained from the  $S(Q)$ . The average coordination number of O around B,  $n_{\text{BO}}$ , was based on the simple integration of  $g^N(r)$  for the B–O correlation. The upper limit of integration,  $r_{\text{cutoff}}$  was fixed at 0.170 nm for the glasses containing the additive in order to avoid the Al–O correlation, while the  $n_{\text{BO}}$  was evaluated both at  $r_{\text{cutoff}}=0.170$  and 0.200 for the glasses not containing the additive for comparison with the MD results. The experimental error of  $n_{\text{BO}}$  was estimated to be  $\pm 0.05$  from the reproducibility. The value of  $N_4$  can be determined experimentally from  $n_{\text{BO}}$  using the relation:

$$n_{\text{BO}}=3(1-N_4)+4 N_4=N_4+3 \quad (6)$$

The details of the analytical procedure are provided in a previous paper.<sup>(4)</sup>

### 3. Results and discussion

The pair distribution functions,  $g(r)$ , obtained from MD calculation are shown in Figure 1(a) for  $5\text{Al}_2\text{O}_3 \cdot 29\text{Na}_2\text{O} \cdot 66\text{B}_2\text{O}_3$  glass. Although the first peak position in all these functions is reasonably close to the approximate sum of ionic radii of each pair, the peak height is approximately twice the experimental value in the neutron weighted radial distribution function,  $g^N(r)$ , as shown in Figure 1(b), owing to the use of a fully ionic model. However, since this is due simply to a strong ionic interaction that should suppress excessively interionic thermal fluctuations, these disagreements are not problems critical to discussion in this paper.<sup>(2–4)</sup> Actually, the first peak positions in the simulation and experiment are in close agreement, as shown in Figure 1(b). Furthermore, as shown in Figure 2, the neutron-weighted total structure function from MD simulation is in good agreement with that derived from the experiment, although strong oscillations observed up to the high  $Q$  range in the MD result are also caused by the intense first B–O and O–O peaks in the  $g^N(r)$ , as

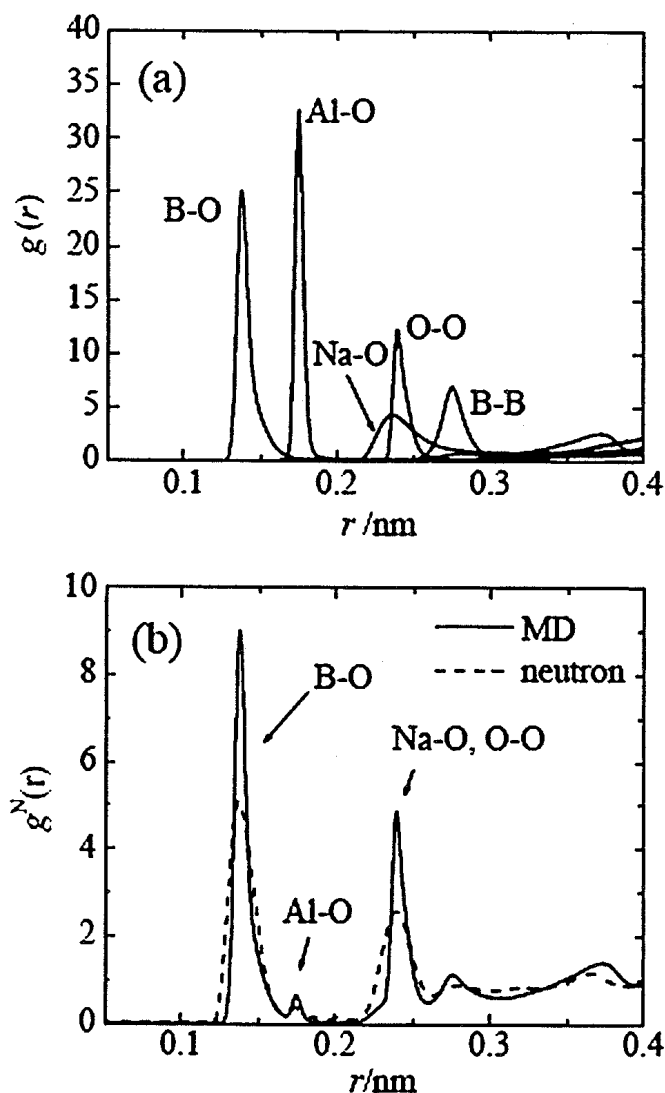


Figure 1. (a) Pair distribution functions obtained from MD calculation for  $5\text{Al}_2\text{O}_3 \cdot 29\text{Na}_2\text{O} \cdot 66\text{B}_2\text{O}_3$  glass. (b) Neutron weighted radial distribution functions,  $g^N(r)$ , from MD calculation for  $5\text{Al}_2\text{O}_3 \cdot 29\text{Na}_2\text{O} \cdot 66\text{B}_2\text{O}_3$  glass. The dashed line denotes  $g^N(r)$  from the neutron diffraction experiment

shown in Figure 1(b).

Table 2 shows the coordination numbers evaluated from the B–O, Al–O, and Na–O pair distribution functions. The coordination number of O around Al,  $n_{\text{AlO}}$ , was found to be approximately four, regardless of  $x$ . This shows that Al atoms are usually present as  $\text{AlO}_4$  units in these glasses, which was confirmed also by direct evaluation of coordination number distribution of O around Al. These results are consistent with those from NMR studies.<sup>(10,11)</sup> Both the  $n_{\text{BO}}$  and  $n_{\text{OB}}$  for the glasses added with  $\text{Al}_2\text{O}_3$  are smaller than those without  $\text{Al}_2\text{O}_3$ . As a result, the fraction of four-coordinated B,  $N_4$ , decreases on addition of  $\text{Al}_2\text{O}_3$  for the entire simulated  $x$  range, as is shown in Figure 3(a).

On the other hand, the fraction of four-coordinated B and Al atoms,  $N_4$ , was evaluated without distinction between B and Al, and shows the same quantitative dependence on  $x$  as that for the glasses without  $\text{Al}_2\text{O}_3$ , except for the high  $x$  range, as is shown in Figure 3(b).

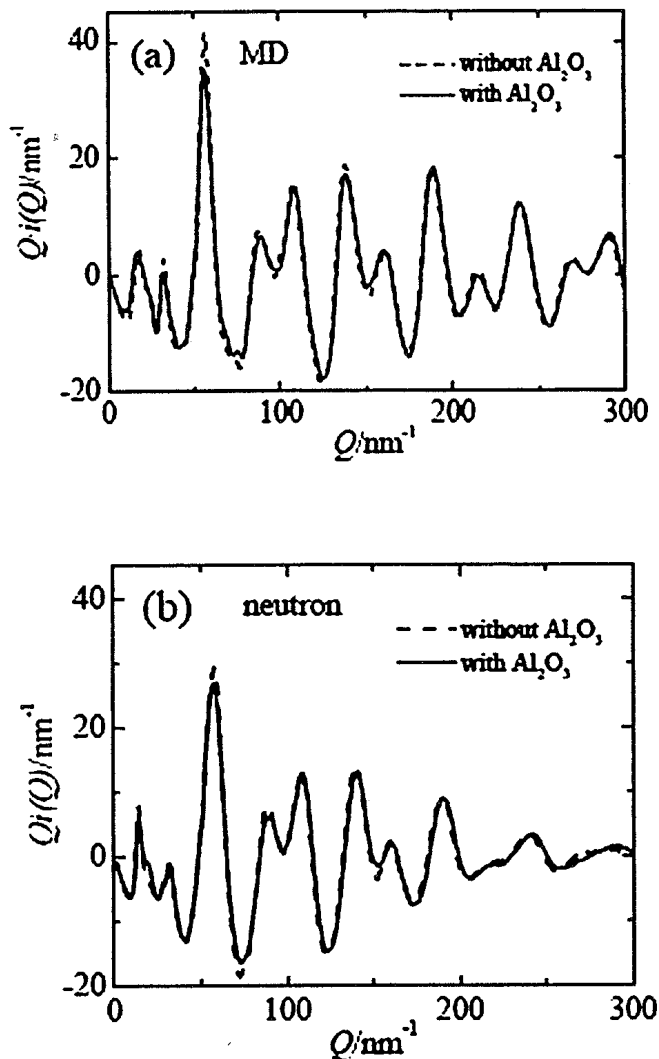


Figure 2. Comparison of structure functions  $Q \cdot i(Q)$  between (a) MD calculation and (b) neutron diffraction for  $5\text{Al}_2\text{O}_3 \cdot 29\text{Na}_2\text{O} \cdot 66\text{B}_2\text{O}_3$  glass. The dashed line denotes  $Q \cdot i(Q)$  for  $30\text{Na}_2\text{O} \cdot 70\text{B}_2\text{O}_3$  glass

Furthermore, in the same way as described above, the coordination numbers of B and Al around O,  $n_{\text{OBAL}}$  obtained without distinction between B and Al, also show the same dependence as the  $n_{\text{OB}}$ . That is, the fraction of nonbridging oxygen (NBO) evaluated without distinction between B and Al shows the same  $x$ -dependence quantitatively as that for the glasses without Al<sub>2</sub>O<sub>3</sub>, as is shown in Figure 4, except for

Table 2. Average coordination numbers from MD calculation and neutron diffraction

Composition	$n_{\text{BO}}^{(a)}$	$n_{\text{BO}}^{(b)}$	$n_{\text{OB}}^{(a)}$	$n_{\text{OB}}^{(b)}$	$n_{\text{OBAl}}^{(a)}$	$n_{\text{AlO}}^{(a)}$	$n_{\text{NaO}}^{(a)}$
B <sub>2</sub> O <sub>3</sub>	3.00	-	2.00	-	-	-	-
5Al <sub>2</sub> O <sub>3</sub> ·10Na <sub>2</sub> O·85B <sub>2</sub> O <sub>3</sub>	3.07	-	1.86	-	2.00	4.05	6.30
5Al <sub>2</sub> O <sub>3</sub> ·19Na <sub>2</sub> O·76B <sub>2</sub> O <sub>3</sub>	3.18	-	1.83	-	1.99	4.01	6.19
5Al <sub>2</sub> O <sub>3</sub> ·29Na <sub>2</sub> O·66B <sub>2</sub> O <sub>3</sub>	3.33	3.22	1.82	1.76	1.98	4.05	6.38
5Al <sub>2</sub> O <sub>3</sub> ·38Na <sub>2</sub> O·57B <sub>2</sub> O <sub>3</sub>	3.44	3.24	1.77	1.67	1.93	4.03	6.07
5Al <sub>2</sub> O <sub>3</sub> ·45Na <sub>2</sub> O·50B <sub>2</sub> O <sub>3</sub>	3.46	3.21	1.66	1.54	1.84	4.00	5.70
10Na <sub>2</sub> O·90B <sub>2</sub> O <sub>3</sub>	3.11	3.11	2.00	2.00	-	-	6.41
20Na <sub>2</sub> O·80B <sub>2</sub> O <sub>3</sub>	3.24	3.23	1.99	1.98	-	-	6.55
30Na <sub>2</sub> O·70B <sub>2</sub> O <sub>3</sub>	3.38	3.37	1.97	1.96	-	-	6.43
40Na <sub>2</sub> O·60B <sub>2</sub> O <sub>3</sub>	3.53	-	1.93	-	-	-	6.63
50Na <sub>2</sub> O·50B <sub>2</sub> O <sub>3</sub>	3.61	-	1.80	-	-	-	6.42

(a) MD calculation, (b) Neutron diffraction experiment

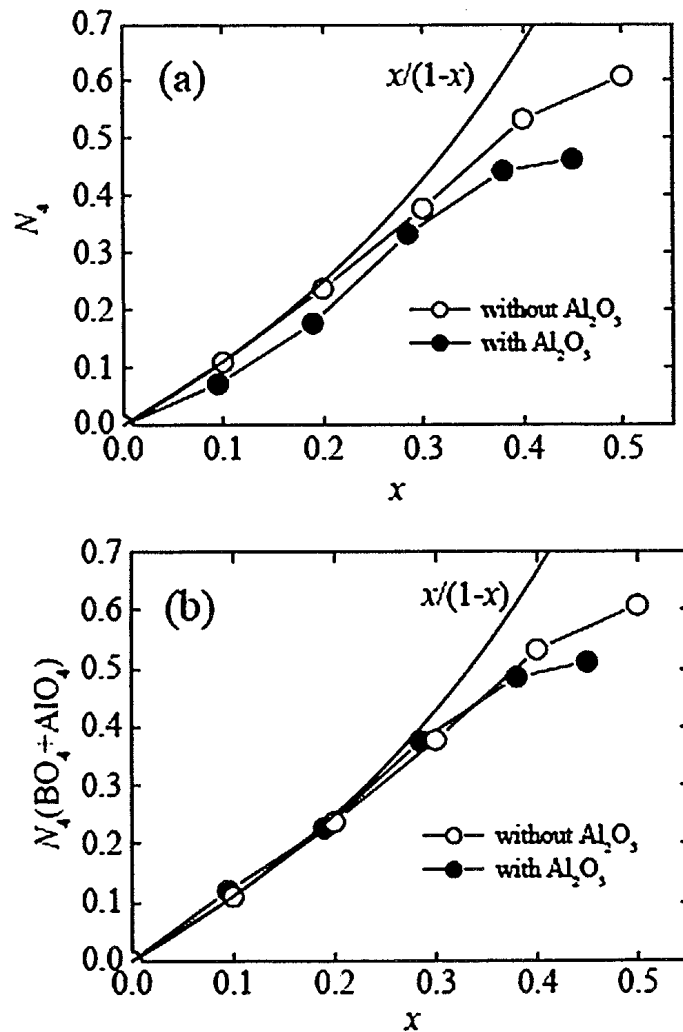


Figure 3. (a) Fraction of four-coordinated B atoms,  $N_4$ , and (b) that of four-coordinated B and Al atoms,  $N_4(\text{BO}_4 + \text{AlO}_4)$ , as a function of the mole fraction of alkali oxide content

the high  $x$  range. These results show that Al atoms participate in the B–O glass network as glass-forming  $\text{AlO}_4$  units.

If all the B atoms are three-coordinated by O in pure B<sub>2</sub>O<sub>3</sub> glass, and all the O atoms added as Na<sub>2</sub>O into B<sub>2</sub>O<sub>3</sub> participate in the formation of four-coordinated B atoms by bridging two boron atoms, then  $N_4$  follows  $x/(1-x)$ , as shown in the low  $x$  region in Figure 3. Actually, O atoms supplied by a small addition of metal oxide to borate glass convert  $\text{B}\text{O}_3$  to  $\text{B}\text{O}_4^-$  units, where  $\text{O}$  indicates the bridging oxygen atom. However, as the added amount increases, the formation of units containing NBO such as  $\text{B}\text{O}_2\text{O}^-$  could occur even at low Na<sub>2</sub>O content as shown in Figure 4,<sup>(12,13)</sup> (where O denotes NBO), and  $N_4$  then deviates downward from  $x/(1-x)$ . Therefore, the results described above suggest that the exclusive formation of  $\text{AlO}_4$  units from Al atoms could suppress the conversion from  $\text{B}\text{O}_3$  to  $\text{B}\text{O}_4^-$  units, compared with the glasses without Al<sub>2</sub>O<sub>3</sub>. It is concluded that Al<sub>2</sub>O<sub>3</sub> has an effect of suppressing the formation of the  $\text{BO}_4$  unit in the case of sodium borate glasses with a composition of  $x \sim 0.4$ .

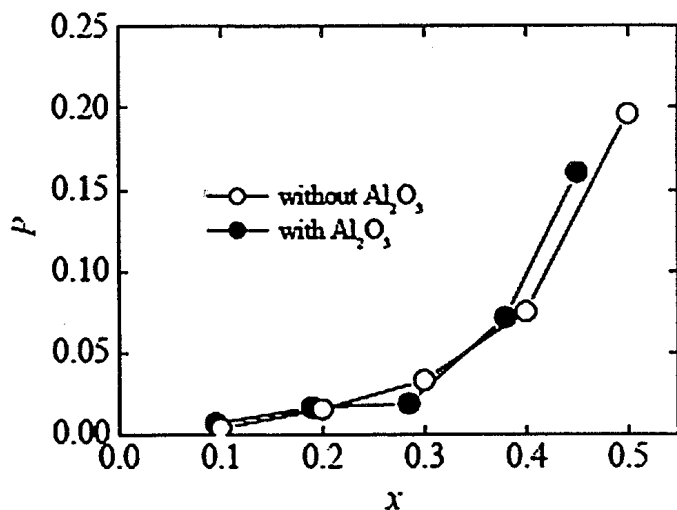


Figure 4. Fraction of nonbridging oxygen,  $p$ , evaluated without distinction between B and Al as a function of the mole fraction,  $x$ , of alkali oxide content

Although the coordination number of O around Na,  $n_{\text{NaO}}$ , could not be definitively estimated since the coordination shell is somewhat ambiguous, the values were estimated with a given  $r_{\text{cutoff}}=0.30$  nm. The  $n_{\text{NaO}}$  for the glasses with  $\text{Al}_2\text{O}_3$  shows a decrease by a few percent on average from those for the glasses without  $\text{Al}_2\text{O}_3$ . This result suggests that the additive  $\text{Al}_2\text{O}_3$  inclines to draw O atoms around Na and to form  $\text{AlO}_4$  units.

Figure 5 shows the  $N_4$  obtained from neutron diffraction experiments as a function of  $x$ . Although the  $r_{\text{cutoff}}$  was always 0.200 nm in MD simulation, it was 0.170 nm for the experimental results of glasses with  $\text{Al}_2\text{O}_3$  and 0.200 nm for those without  $\text{Al}_2\text{O}_3$ , since the B–O correlation cannot be separated from the Al–O correlation in the former case. The  $N_4$  was then also evaluated using a  $r_{\text{cutoff}}$  of 0.170 nm in the experimental results of the glasses without  $\text{Al}_2\text{O}_3$ . In both cases, the decrease in  $N_4$  resulting from the addition of  $\text{Al}_2\text{O}_3$  is seen in a comparison of  $N_4$  between the glasses with and those without  $\text{Al}_2\text{O}_3$ . Therefore, both the simulation and experimental results show similar behaviour regarding the decrease in  $N_4$  due to the addition of  $\text{Al}_2\text{O}_3$ .

#### 4. Conclusions

The short range structure of  $0.05\text{Al}_2\text{O}_3 \cdot x\text{Na}_2\text{O} \cdot (0.95-x)\text{B}_2\text{O}_3$  glasses ( $0.10 < x < 0.45$ ) has been investigated using MD calculations. The  $n_{\text{AlO}}$  was approximately four, regardless of  $x$ . On the basis of the analysis of other coordination numbers and the fraction of four-coordinated B and Al, it was concluded that these Al atoms are present as network-formers of  $\text{AlO}_4$  units in the glasses in the same manner as the  $\text{BO}_4$  unit and causes a decrease of the coordination number of O around Na. This summary suggests that the exclusively formed  $\text{AlO}_4$  units could suppress the conversion of the  $\text{BO}_3$  unit to the  $\text{BO}_4$  unit caused by

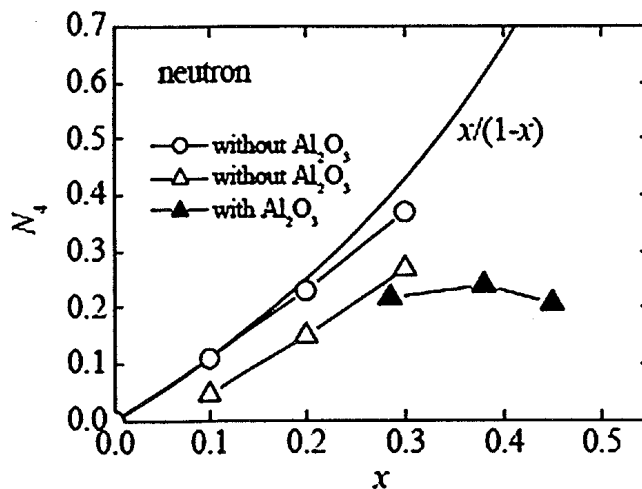


Figure 5. Fraction of four-coordinated B,  $N_4$ , obtained from neutron diffraction as a function of the mole fraction of alkali oxide content. The values evaluated using the upper integration limit of 0.170 and 0.200 nm are indicated by triangles and circles, respectively

an increase of  $\text{Na}_2\text{O}$ . The decrease of the fraction of four-coordinated boron atoms,  $N_4$ , due to the addition of  $\text{Al}_2\text{O}_3$  was supported by the results obtained from preliminary neutron diffraction measurements.

#### Acknowledgements

The authors thank Professors M. Misawa & K. Maruyama and Dr E. M. Anghel for their enlightening discussion. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan (No. 16560599).

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