

A THEORETICAL INTERPRETATION OF ^{17}O NMR SPECTRA IN BOROSILICATE GLASSES

M. Urushihara, T. Nanba, and Y. Miura

Department of Environmental Chemistry and Materials, Faculty of Environmental Science and Technology, Okayama University
3-1-1, Tsushima-Naka
Okayama-shi 700-8530, Japan

S. Sakida

Environmental Management and Safety Section, Health and Environment Center, Okayama University
3-1-1, Tsushima-Naka
Okayama-shi 700-8530, Japan

ABSTRACT

Local structure around oxygen is directly elucidated by ^{17}O nuclear magnetic resonance (NMR). However, the ^{17}O NMR spectra in borosilicate glasses are quite complicated, and hence the assignments of the peaks have been empirically done. In the present study, ^{17}O NMR parameters for the various oxygen sites in the borosilicate system were obtained from the ab-initio molecular orbital calculations using the Gaussian03 programs. As for the oxygen atoms in SiOSi, SiOB[3], and B[3]OB[3] bridging bonds (B[n]: n -fold coordinated boron), the isotropic chemical shift δ_i^{O} decreased with increasing the bond angle. The oxygen atoms coordinated by B[4] as SiOB[4], B[3]OB[4], and B[4]OB[4] bridges showed weak dependency in δ_i^{O} against the bond angle, and B[4]OB[4] showed a maximum in δ_i^{O} at 150°. The quadrupole coupling constant C_q of all the bridging oxygens increased with increasing the bond angle. When the oxygen atoms in SiOB[4], B[3]OB[4] bridges were coordinated by Na ion, δ_i^{O} decreased by 5 ~ 10 ppm. The oxygen atoms in trimeric ring clusters showed different δ_i^{O} from dimeric clusters, indicating that δ_i^{O} was also influenced by the second neighboring cations. The order of δ_i^{O} was expected as SiOSi < SiOB[4] < SiOB[3] < B[4]OB[4] < B[3]OB[4] < B[3]OB[3], which was in accordance with the order of bond covalency.

INTRODUCTION

The structure of borosilicate glasses has been studied for a long time with various spectroscopic methods including NMR, Raman and XPS. A number of structural models have been proposed, in which a model proposed by Dell et al.¹ has been popularly accepted. The Dell model is based on ^{11}B NMR, from which the fraction of 4-fold coordinated boron atoms can be predicted. MacKenzie et al.² also proposed a different model from ^{29}Si MAS NMR, predicting the amount of non-bridging oxygen (NBO) atoms in SiO_4 units. Nanba and Miura³ found an inconsistency between the amounts of NBO estimated from ^{11}B and ^{29}Si NMR. According to the theoretical calculations, Nanba et al.⁴ revealed that some bridging oxygen (BO) atoms in SiOB[4] bridges (B[n]: n -fold coordinated boron) were in similar electronic states to NBOs in SiONa terminals, indicating the difficulty of Si NMR analysis in borosilicate materials. Zhao et al.⁵ pointed out a possibility of “tricluster” units sharing one oxygen by three-tetrahedral SiO_4 and BO_4 units in borosilicate glasses.

Recently, Du and Stebbins⁶ demonstrated the coordination environment of oxide ions

from ^{17}O 3QMAS NMR, in which the spectra were successfully separated into the components assigned to the oxygen sites in SiOSi, SiOB, and BOB bridges. However, the assignments have been done empirically, and theoretical interpretations have never been given in borosilicate glasses. As for aluminosilicate glasses, Xue and Kanzaki⁷ examined NMR parameters from theoretical calculations. Then, in the present study, theoretical calculations were performed based on the procedures used by Xue and Kanzaki⁷ to interpret ^{17}O NMR peaks in borosilicate glasses.

CALCULATION METHODS

Molecular orbital calculations were performed with the Gaussian03 program.⁸ Six kinds of clusters were constructed, containing SiOSi, SiOB[3], SiOB[4], B[3]OB[3], B[3]OB[4], B[4]OB[4] bridges. As shown in Fig. 1, oxygen atoms were placed at the center of the clusters, and the other atoms within the second atomic shells were put into the clusters. Excluding the central bridging oxygens, all oxygens were terminated with hydrogens for the charge compensation. The geometry of the clusters were optimized by using the B3LYP hybrid DFT method and the 6-31+G(d) basis. To examine the dependence of bond angle on the NMR parameters, the central bond angles were fixed at the pre-selected values and the geometry optimizations were also done by the B3LYP/6-31+G(d) level.

As for the clusters containing B[4], that is, SiOB[4], B[3]OB[4], and B[4]OB[4] bridges, clusters containing Na ions were also prepared, in which the atomic configurations were fixed at the positions in NaBSi_3O_8 and $\text{Na}_2\text{B}_4\text{O}_7$ crystals,^{9,10} and only the terminal hydrogens were optimized in position; H atoms were initially positioned in the directions to the next cations in the respective crystal structures. In the case of SiOB[4] and B[3]OB[4], the optimal geometries were obtained, and in the case of B[4]OB[4], however, the optimal geometries were not obtained due to the close H–H pair. In $\text{Na}_2\text{B}_4\text{O}_7$ crystal, B[4]OB[4] bridge is present in a 3-membered ring formed by one BO_3 and two BO_4 units. When this ring was used in the geometry optimization, the optimal positions of hydrogens were successfully determined. Then, as for B[4]OB[4], the results shown below were obtained from the 3-membered ring clusters.

NMR parameter calculations were performed with HF/6-311+G(2df,p), and in the magnetic shielding tensor calculations, the Gauge-Independent Atomic Orbital (GIAO) method¹¹ was used. The isotropic chemical shifts (δ_i^{O}) (in ppm) were estimated from the following equation:

$$\delta_i^{\text{O}}(\text{cluster}) = \sigma_i^{\text{O}}(\text{H}_2\text{O}) - \sigma_i^{\text{O}}(\text{cluster})$$

where σ_i^{O} is the ^{17}O isotropic magnetic shielding (in ppm) obtained from MO calculations. Obtaining the referential σ_i^{O} for H_2O , H_2O cluster was optimized using B3LYP/6-31+G(d) and σ_i^{O} was calculated with HF/6-311+G(2df,p).

The ^{17}O quadrupole coupling constant (C_q) was calculated using the following equation:

$$C_q = e^2 q_{zz} Q / h$$

where eQ is the quadrupole moment of the objective oxygen and the experimental value for H_2O molecule (10.175 MHz).^{7,12} And the eq_{zz} is the largest absolute value of electric field gradient (EFG) tensor at the nucleus in the principal axis.

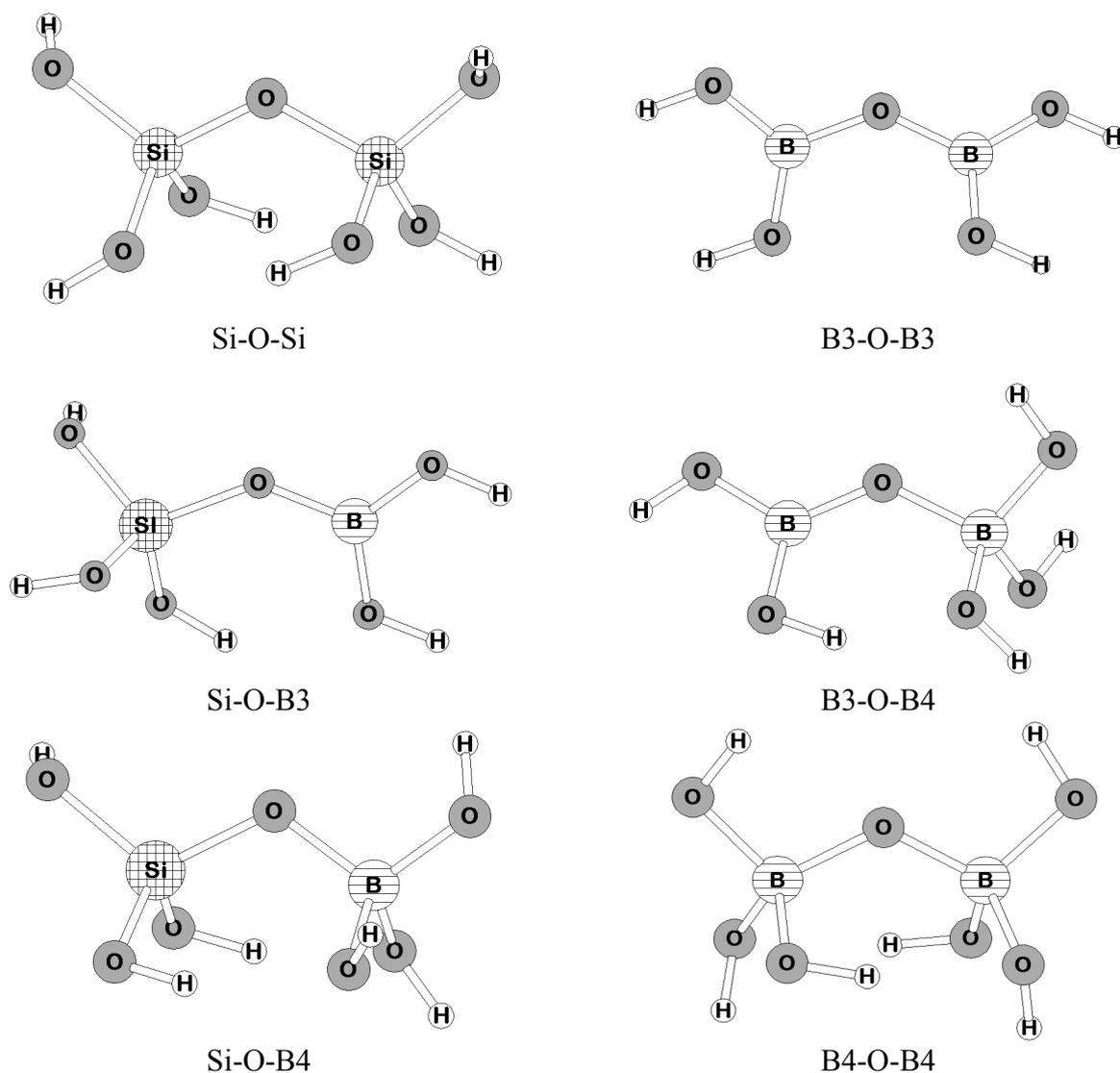


Fig. 1. Cluster models obtained by the geometrical optimizations using the B3LYP/6-31+G(d) level.

RESULTS AND DISCUSSION

Optimal structures

The structural details after the geometrical optimizations are summarized in Table 1. In NaBSi_3O_8 crystal,⁹ the bond length and angle are $\angle\text{SiOSi} = 129 \sim 158^\circ$, $\angle\text{SiOB}[4] = 125 \sim 143^\circ$, $\text{Si}-\text{O} = 1.60 \sim 1.65 \text{ \AA}$ and $\text{B}[4]-\text{O} = 1.44 \sim 1.48 \text{ \AA}$, and in $\text{Na}_2\text{B}_4\text{O}_7$ and $\beta\text{-Na}_2\text{B}_6\text{O}_{10}$ crystals^{10,13} are $\angle\text{B}[3]\text{OB}[3] = 119 \sim 123^\circ$, $\angle\text{B}[3]\text{OB}[4] = 119 \sim 137^\circ$, $\angle\text{B}[4]\text{OB}[4] = 117 \sim 121^\circ$, $\text{B}[3]-\text{O} = 1.30 \sim 1.41 \text{ \AA}$ and $\text{B}[4]-\text{O} = 1.43 \sim 1.50 \text{ \AA}$. The bond lengths and angles are in good agreement between the optimal geometries and crystal structures, and it is therefore judged that the clusters after the optimization are in appropriate structures.

Table 1. Bond angle and length of the central oxygen in the clusters after the geometrical optimization and the NMR parameters, ^{17}O isotropic chemical shifts δ_i^{O} and quadrupole coupling constant C_q of the central oxygen

| Cluster | Bond angle ($^{\circ}$) | Bond length (\AA) | | | δ_i^{O} (ppm) | C_q (MHz) |
|-----------|---------------------------|------------------------------|--------|--------|-----------------------------|-------------|
| | | Si–O | B[3]–O | B[4]–O | | |
| SiOSi | 127.6 | 1.65 | | | 58.6 | 5.01 |
| SiOB[3] | 133.8 | 1.65 | 1.36 | | 70.5 | 4.94 |
| SiOB[4] | 118.4 | 1.63 | | 1.49 | 72.5 | 5.45 |
| B[3]OB[3] | 133.5 | | 1.36 | | 79.4 | 5.88 |
| B[3]OB[4] | 127.6 | | 1.34 | 1.50 | 91.9 | 5.14 |
| B[4]OB[4] | 125.3 | | | 1.45 | 76.7 | 5.70 |

Isotropic chemical shift δ_i^{O}

Fig. 2 shows the relations between the isotropic chemical shift δ_i^{O} and the bond angle of central oxygen. As for SiOSi, SiOB[3], and B[3]OB[3] bridges, δ_i^{O} decreases with increasing the bond angle. On the other hand, SiOB[4] and B[3]OB[4] bridges show weak dependency of the bond angle, and B[4]OB[4] shows a maximum in δ_i^{O} at 150° .

Comparing δ_i^{O} in the clusters with full optimizations (solid markers in Fig. 2), δ_i^{O} increases in the order of SiOSi < SiOB < BOB, and this order is consistent with the assignments given from the experiments.⁶ However, it is quite difficult to give detailed assignments for SiOB and BOB bridges; at higher bond angles > 150° , SiOB[4] always shows larger δ_i^{O} than SiOB[3], and it is also the case between B[4]OB[4] and B[3]OB[3]. At lower angle region < 140° , however, SiOB[4] and SiOB[3] overlap with each other, and B[4]OB[4] and B[3]OB[3] are in the reverse order from the higher angle region.

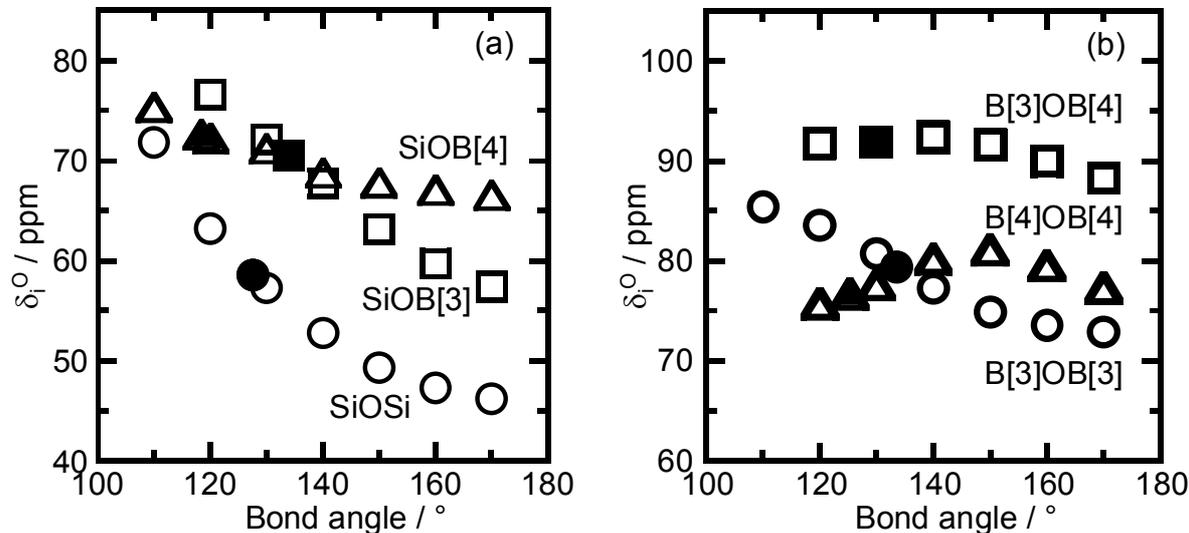


Fig. 2. The relations between the ^{17}O isotropic chemical shift δ_i^{O} and the bond angle of the central oxygen atoms in the clusters shown in Fig. 1. Solid markers indicate the clusters with full optimization.

BO_4 unit possesses a negative charge so that the clusters containing B[4], that is, SiOB[4], B[3]OB[4], and B[4]OB[4], are negatively charged. One alkali ion is required as a

charge compensator of one BO_4 unit. Then, Na ion was introduced into these clusters, examining the effect of Na ion on δ_i^{O} . It should be reminded that the atomic configurations in these clusters were fixed at those in the respective crystal structures. In NaBSi_3O_8 crystal,⁹ there are four distinct SiOB[4] sites. In $\text{Na}_2\text{B}_4\text{O}_7$ crystal,¹⁰ there present nine B[3]OB[4] sites, and the results shown in Fig. 3 were obtained from the B[3]OB[4] sites excluding the sites in B[3]B[4]B[4] trimeric ring or B[3] coordinated by NBO. It is clearly shown that the Na addition results in the 5 ~ 10 ppm decrease in δ_i^{O} . As shown in Fig. 2, SiOB[4] and SiOB[3] indicate similar δ_i^{O} , but δ_i^{O} of SiOB[4] should be quoted as reducing 5 ~ 10 ppm from the value given in Fig. 2. It is also the case for B[3]OB[4]. It is also noted that δ_i^{O} shown in Fig. 3 is widely distributed, and in the case of the optimal geometries (Fig. 2), the variation in δ_i^{O} is quite small for SiOB[4] and B[3]OB[4]. However, the average in δ_i^{O} is not so different between the results shown in Figs. 2 and 3.

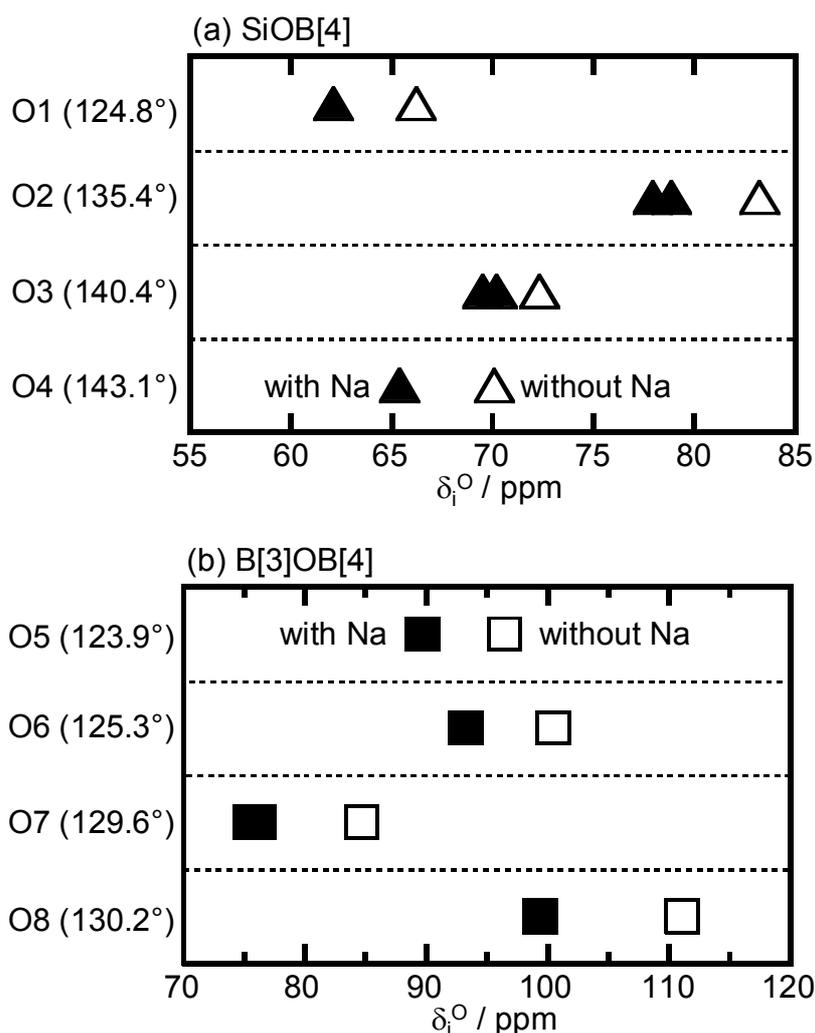


Fig. 3. The effect of Na addition on the ^{17}O isotropic chemical shift δ_i^{O} of the central oxygens in the clusters (a) SiOB[4] and (b) B[3]OB[4] constructed from the different oxygen sites in NaBSi_3O_8 and $\text{Na}_2\text{B}_4\text{O}_7$ crystals. Values in the parentheses are the bond angle of the central oxygen in the SiOB[4] and B[3]OB[4] units.

As mentioned, the optimal hydrogen positions for the B[4]OB[4] cluster were not obtained, and hence the clusters of a trimeric ring formed by BO₃ and two BO₄ units were prepared, where two Na ions were also introduced for charge compensation. Changing Na positions, two sets of calculations were carried out. As shown in Fig. 4, δ_i^O of B[4]OB[4] is smaller than that of B[3]OB[4] in the both sets. δ_i^O of B[3]OB[4] in the B[3]B[4]B[4] trimeric ring (Fig. 4) is much higher than that of B[3]OB[4] outside the ring (Fig. 3), indicating that δ_i^O is also affected by the second neighboring borons. This feature is probably prominent in borate system consisting of small rings of the structural units.

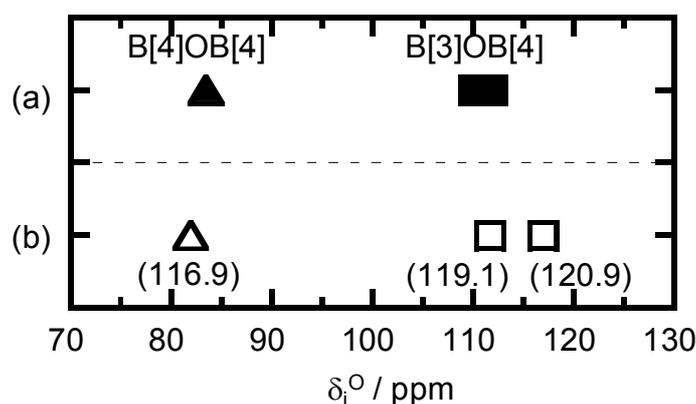


Fig. 4. The ¹⁷O isotropic chemical shift δ_i^O of the oxygen atoms in the trimeric ring formed by BO₃ and two BO₄ units present in Na₂B₄O₇ crystal. The charge of the ring was compensated by two Na ions. Changing the Na position, two sets of calculation were carried out. Values in the parentheses are the bond angle of the oxygen atoms in B[3]OB[4] and B[4]OB[4] units.

From these results, it is finally expected that δ_i^O increases in the order of SiOSi < SiOB[4] < SiOB[3] < B[4]OB[4] < B[3]OB[4] < B[3]OB[3]. It is generally assumed that B–O bond has higher covalency than Si–O bond, and B3–O bond has higher covalency than B4–O bond because B3–O is shorter than B4–O. The order of δ_i^O seems to be in accordance with the order of bond covalency.

Quadrupole coupling constant C_q

According to Xue and Kanzaki,⁷ C_q is depended on the central bond angle in silicate and aluminosilicate glasses. Then, in Fig. 5, C_q in borosilicate system are plotted against the bond angle. C_q of all the bridging oxygens increases with increasing the bond angles. In silicate and aluminosilicate glasses, C_q is different between SiOSi, SiOAl, and AlOAl,⁷ but SiOSi, SiOB, and BOB bridges have similar C_q values. It is finally concluded that it is difficult to distinguish a bridging oxygen among SiOB[3], SiOB[4], B[3]OB[3], and B[3]OB[4] because these oxygens are similar not only in C_q but also in δ_i^O .

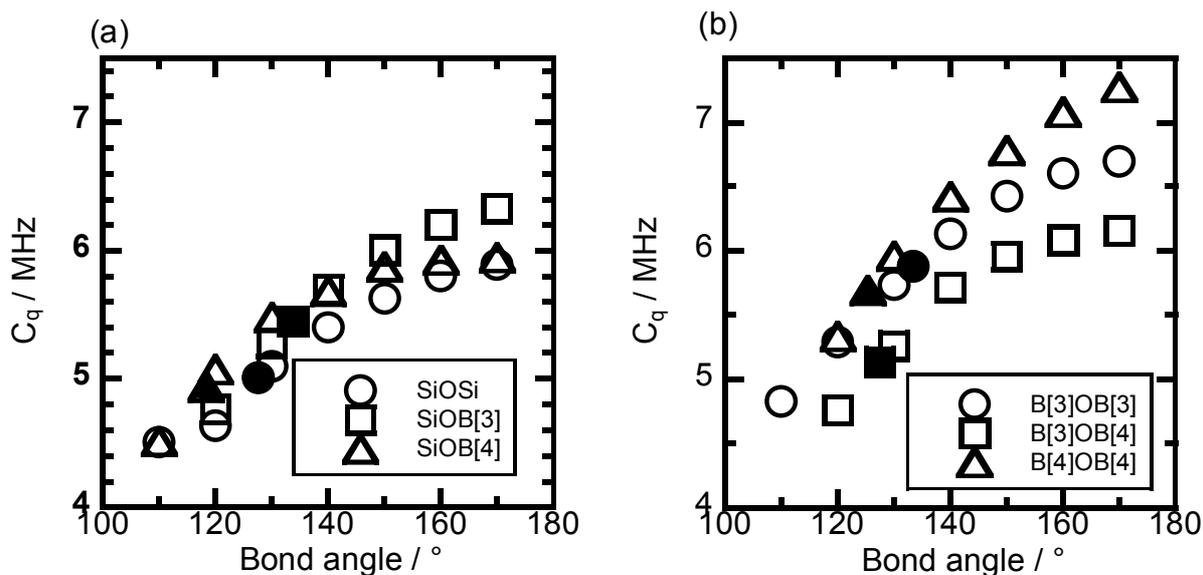


Fig.5. The relations between quadrupole coupling constant C_q and the bond angle of the central oxygen atoms in the clusters shown in Fig. 1. Solid markers indicate the clusters with full optimization.

CONCLUSION

The ^{17}O NMR parameters, isotropic chemical shifts δ_i^{O} and quadrupole coupling constant C_q , were theoretically calculated for the oxygen sites in the borosilicate system. As for the oxygen atoms in SiOSi, SiOB[3], and B[3]OB[3] bridges, δ_i^{O} decreased with increasing the bond angle. As for the oxygen atoms coordinated by B[4] as SiOB[4], B[3]OB[4], and B[4]OB[4] bridges, δ_i^{O} was weakly dependent on the bond angle, and B[4]OB[4] showed a maximum in δ_i^{O} at 150°. C_q of all the bridging oxygens increased with increasing the bond angle.

As for the oxygen atoms in SiOB[4] and B[3]OB[4] bridges, δ_i^{O} decreased by 5 ~ 10 ppm when Na ion was added to the clusters for the charge compensation. In the case of Na-associated B[4]OB[4] bridge, optimal geometries were not obtained. Then, the B[3]B[4]B[4] trimetric ring cluster associated with two Na ions was constructed. In the trimetric ring, δ_i^{O} of B[4]OB[4] was smaller than that of B[3]OB[4], and δ_i^{O} of B[3]OB[4] in the ring was much higher than that of B[3]OB[4] outside the ring, indicating that δ_i^{O} was also influenced from the second neighboring borons. It was finally expected that δ_i^{O} increased in the order of SiOSi < SiOB[4] < SiOB[3] < B[4]OB[4] < B[3]OB[4] < B[3]OB[3], which was in accordance with the order of bond covalency.

ACKNOWLEDGEMENTS

The authors would like to thank Profs. Xianyu Xue and Masami Kanzaki of Okayama University for their helpful advices in the MO calculations.

REFERENCES

- W.J. Dell, P.J. Bray, and S.Z. Xiao, " ^{11}B NMR studies and structural modeling of $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ glasses of high soda content," *J. Non-Cryst. Solids*, **58**, 1-16 (1983).
- J.W. MacKenzie, A. Bhatnagar, D. Bain, S. Bhowmik, C. Parameswar, K. Budhwani, S.A. Feller, M.L. Royle, and S.W. Martin, " ^{29}Si MAS-NMR study of the short range order in

alkali borosilicate glasses,” *J. Non-Cryst. Solids*, **177**, 269-76 (1994).

³T. Nanba and Y. Miura, “Alkali distribution in borosilicate glasses,” *Phys. Chem. Glasses*, **44**, 244-8 (2003).

⁴T. Nanba, M. Nishimura, and Y. Miura, “A Theoretical interpretation of the chemical shift of ²⁹Si NMR peaks in alkali borosilicate glasses,” *Geochim. Cosmochim. Acta*, **68**, 5103-11 (2004).

⁵P. Zhao, S. Kroeker, and J.F. Stebbins, “Non-bridging oxygen sites in barium borosilicate glasses: Results from ¹¹B and ¹⁷O NMR,” *J. Non-Cryst. Solids*, **276**, 122-31 (2000).

⁶L.-S. Du and J.F. Stebbins, “Solid-state NMR study of metastable immiscibility in alkali borosilicate glasses,” *J. Non-Cryst. Solids*, **315**, 239-55 (2003).

⁷X. Xue and M. Kanzaki, “NMR characteristics of possible oxygen sites in aluminosilicate glasses and melts: An ab initio study,” *J. Phys. Chem. B*, **103**, 10816-30 (1999).

⁸M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.J.A. Montgomery, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez and J.A. Pople, GAUSSIAN 03, Gaussian, Inc., Pittsburgh, PA (2003).

⁹D. E. Appleman and J. R. Clarl, “Crystal structure of reedmergnerite, a boron albite, and its relation to feldspar crystal chemistry,” *Am. Mineral.*, **50**, 1827-50 (1965).

¹⁰J. Krogh-Moe, “The Crystal Structure of Sodium Diborate Na₂O.2B₂O₃,” *Acta Cryst.*, **B30**, 578-82 (1974).

¹¹J. R. Cheeseman, G. W. Trucks, T. A. Keith and M. J. Frisch, “A comparison of models for calculating nuclear magnetic resonance shielding tensors,” *J.Chem. Phys.*, **104**, 5497-509 (1996).

¹²J. Verhoeven, A. Dymanus, and H. Bluysen “Hyperfine Structure of HD¹⁷O by Beam-Maser Spectroscopy,” *J. Chem. Phys.*, **15**, 3330-8 (1969).

¹³J. Krogh-Moe ”The Crystal Structure of Sodium Triborate β-Na₂O.3B₂O₃,” *Acta Cryst.*, **B28**, 1571-76 (1972).