

A theoretical interpretation of the chemical shift of ^{29}Si NMR peaks in alkali borosilicate glasses

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Abstract—In ^{29}Si -NMR, it has so far been accepted that the chemical shifts of Q^n species (SiO_4 units containing n bridging oxygens) were equivalent between alkali borosilicate and boron-free alkali silicate glasses. In the sodium borosilicate glasses with low sodium content, however, a contradiction was confirmed in the estimation of alkali distribution; ^{11}B NMR suggested that Na ions were entirely distributed to borate groups to form BO_4 units, whereas a -90 ppm component was also observed in ^{29}Si -NMR spectra, which has been attributed to Q^3 species associated with a nonbridging oxygen (NBO). Then, cluster molecular orbital calculations were performed to interpret the -90 ppm component in the borosilicate glasses. It was found that a silicon atom which had two tetrahedral borons (B4) as its second nearest neighbors was similar in atomic charge and $\text{Si}2p$ energy to the Q^3 species in boron-free alkali silicates. Unequal distribution of electrons in Si-O-B4 bridging bonds was also found, where much electrons were localized on the Si-O bonds. It was finally concluded that the Si-O-B4 bridges with narrow bond angle were responsible for the -90 ppm ^{29}Si component in the borosilicate glasses. There still remained another interpretation; the Q^3 species were actually present in the glasses, and NBOs in the Q^3 species were derived from the tricluster groups, such as $(\text{O}_3\text{Si})\text{O}(\text{BO}_3)_2$. In the glasses with low sodium content, however, it was concluded that the tricluster groups were not so abundant to contribute to the -90 ppm component. Copyright © 2004 Elsevier Ltd

1. INTRODUCTION

In oxide glasses such as silicate glass, oxide ions are generally classified into bridging oxygen (BO) and nonbridging oxygen (NBO). When an alkali oxide, R_2O is added to silica, SiO_2 , Si-O-Si bridging networks were dissociated to form NBOs, where each alkali ion is adjoined by an NBO for valence compensation. It is widely known that the addition of Al_2O_3 or B_2O_3 is effective in improving chemical durability and mechanical strength of the glass. With increasing Al_2O_3 content, NBO decreases along with the alternative formation of tetrahedral AlO_4 units, and NBO disappears at $\text{R}_2\text{O}/\text{Al}_2\text{O}_3$ ratio = 1, where alkali ions compensate the negative charge of AlO_4 units (Scholze, 1991). In case of the B_2O_3 addition, however, the situation is quite different; Yun and Bray (1978) revealed from ^{11}B nuclear magnetic resonance (NMR) studies of $\text{RN}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{KSiO}_2$ glasses that NBO is present even at $R = 1$. It is due to the difference in preferential coordination structure between B and Al; in glassy state part of borons always occupy the trigonal BO_3 site, and the fraction of four-fold coordinated borons (N_4) is less than 1.

From the viewpoint of valence compensation, alkali ions are distributed to the following negatively charged structural species: BO_4 units and NBOs in SiO_4 and BO_3 units. Various alkali distribution models have been proposed by Dell et al. (1983) and Zhong et al. (1988) from ^{11}B NMR, MacKenzie et al. (1994) from ^{29}Si magic angle spinning (MAS) NMR, and Miura et al. (2001) from X-ray photoelectron spectroscopy (XPS). However, these models have been applied only to their own experimental results and have not been tested using the experimental data collected from the different spectrometries.

Recently, Nanba and Miura (2003) examined the alkali distribution in combining ^{11}B and ^{29}Si -NMR data for $\text{RN}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{KSiO}_2$ glasses, where the relative amounts of Na ions distributed to the structural units, f_{Na} were estimated from the simple assumptions. Firstly, it has been commonly accepted that oxygen atoms in BO_4 units consisted entirely of BOs in B-O-B or B-O-Si bridges. In this case, the BO_4 units possess a unit charge as $[\text{BO}_{4/2}]^-$. NBOs in $\equiv\text{Si-O}^-\cdot\text{Na}^+$ and $=\text{B-O}^-\cdot\text{Na}^+$ units also carry a negative charge of -1 . Hence, the equivalent amount of Na^+ ions is distributed to the $[\text{BO}_{4/2}]^-$ units and NBOs for charge compensation. In an $\text{RN}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{KSiO}_2$ glass, the amount of $[\text{BO}_{4/2}]^-$ units is given by $2N_4$, where N_4 is determined from ^{11}B NMR. Then, the fraction of Na ions distributed to the BO_4 units, $f_{\text{Na}}(\text{B4})$ is expected as

$$f_{\text{Na}}(\text{B4}) = 2N_4/2R = N_4/R. \quad (1)$$

It is generally accepted that Si atoms in alkali borosilicate glasses prefer tetrahedral sites, and they are classified into Q^n species which are associated with n BOs in Si-O-Si or Si-O-B bridges and $(4 - n)$ NBOs in $\equiv\text{Si-O}^-\cdot\text{Na}^+$ units. In the $\text{RN}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{KSiO}_2$ glass, the total amount of NBOs in a Q^n species is expressed as $f(Q^n) \times (4 - n) \times K$ by using the fraction of Q^n species, $f(Q^n)$ determined from ^{29}Si -NMR. Consequently, the total fraction of Na^+ ions compensating the negative charge of NBOs in SiO_4 units, $f_{\text{Na}}(\text{Si})$ can be estimated by

$$f_{\text{Na}}(\text{Si}) = \sum f(Q^n) \times (4 - n) \times K/2R. \quad (2)$$

It is finally expected that the residual Na^+ ions are associated with the NBOs in BO_3 units, because it has been commonly accepted that NBOs are preferentially formed in BO_3 units rather than BO_4 units (Scholze, 1991). Then, we obtain

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$$f_{\text{Na}}(\text{B3}) = 1 - f_{\text{Na}}(\text{B4}) - f_{\text{Na}}(\text{Si}). \quad (3)$$

Even if NBOs are present in BO_4 units, Eqn. 3 is valid. In such a case, $f_{\text{Na}}(\text{B3})$ represents the fraction of Na^+ ions distributed to the NBOs in borate ($\text{BO}_3 + \text{BO}_4$) groups. In the alkali distribution estimated in this way (Nanba and Miura, 2003), it was found a strange result that $f_{\text{Na}}(\text{B3})$ was negative at the small R region (see open markers in Fig. 4b), indicating that the amount of fourfold coordinated boron, B4 and/or the amount of NBO in SiO_4 units were overestimated in the NMR analyses.

Such a contradiction in NMR has been already reported by Zhao et al. (2000). In barium borosilicate glass, different amounts of NBO were estimated from ^{11}B and ^{17}O NMR. It was concluded that the contradiction was due to the tricluster unit sharing one oxygen by three-tetrahedral SiO_4 and BO_4 units. For example, when two BO_4 units are present in a tricluster $(\text{O}_{3/2}\text{Si})\text{O}(\text{BO}_{3/2})_2$, the charge of the tricluster unit is identified as -1 , and hence only one Na is required to compensate its negative charge. As a result, $f_{\text{Na}}(\text{B4})$ is overestimated.

On the other hand, Nanba and Miura (2003) proposed the following interpretation. When an NBO is formed in an SiO_4 unit, the NBO in the SiO_4 unit donates its lone pair electrons to the vacant $\text{B}2p_z$ orbital in the neighboring BO_3 unit, and the NBO turns into BO forming an Si-O-B4 bridge. The electronic delocalization through the B4-O bond is much less than that through the B3-O bond due to the lower π -bonding character of B4-O, and it is therefore expected that BOs in the Si-O-B4 bridges formed in this way possess many electrons similar to the NBOs in $\equiv\text{Si}-\text{O}^-\cdot\text{Na}^+$ units, and they have been assigned to NBO in Si-NMR. Bhasin et al. (1998) performed the deconvolution of ^{29}Si MAS NMR spectra of ternary sodium borosilicate glasses, assuming the same chemical shifts of the Q^n species in binary sodium silicate glasses (Maekawa et al., 1991). The $f_{\text{Na}}(\text{Si})$ given in the previous investigation (Nanba and Miura, 2003) was based on the Q^n fractions reported by Bhasin et al. (1998). If the interpretation by Nanba and Miura (2003) is appropriate, the ^{29}Si chemical shifts of the Q^n species in borosilicate glasses should be revised. In practice, it was confirmed in aluminosilicates that the chemical shift of ^{29}Si in Q^4 species ranges over $-86 \sim -110$ ppm and the chemical shift depends on the number of Al atoms at the second neighboring sites (Lippmaa et al., 1981). According to Maekawa et al. (1991), ^{29}Si chemical shift is proportional to the optical basicity of glass matrix; in $\text{Na}_2\text{O}-\text{SiO}_2$ glasses, Na_2O addition results in the increase in basicity and ^{29}Si shift to the smaller Q^n side. Based on the theoretical expression (Duffy and Ingram, 1976), the optical basicities of B_2O_3 , SiO_2 , and Al_2O_3 are estimated as 0.42, 0.48, and 0.59, respectively. It is hence expected that the addition of Al_2O_3 into SiO_2 results in the increase in basicity, and in the case of B_2O_3 addition, however, the basicity decreases slightly. Actually, the ^{29}Si chemical shifts of alkali-free borosilicate glasses are almost constant at -110 ppm (Martin et al., 1992; Martens and Müller-Warmuth, 2000), which is the same as alkali-free silica glass. This is probably the reason why the assumption by Bhasin et al. (1998) has been accepted.

Recently, Du and Stebbins (2003) applied ^{11}B and ^{17}O triple quantum magic angle spinning (3QMAS) NMR to sodium borosilicate glasses, indicating the absence of NBOs in the glasses with

low Na_2O content. This absence indicates the exclusive presence of Q^4 species at small R regions, and hence the ^{29}Si chemical shift in the NBO-free glasses should be attributed to Si-O-B bridges. In the alkali-free borosilicate glasses, tetrahedral borons are not present and ^{29}Si peaks are commonly observed at around -110 ppm (Martens and Müller-Warmuth, 2000). It is therefore supposed that not Si-O-B3 but Si-O-B4 bridges are responsible for the ^{29}Si chemical shift in the small R regions. Furthermore, it was also noted that the presence of tricluster oxygens was negligible in the low alkali glasses, because tricluster oxygens were always accompanied by NBOs.

In the previous investigation (Nanba and Miura, 2003), the NMR data used were given by the different researchers (^{11}B NMR by Yun and Bray, 1978; Dell et al., 1983, and ^{29}Si MAS NMR by Bhasin et al., 1998). Therefore, NMR measurements using the same specimens were desired to confirm the contradiction in the alkali distribution. Then, in the present study, ^{11}B and ^{29}Si MAS NMR measurements were performed using the specimens prepared in the same manner, and the alkali distribution was reexamined according to the N_4 and $f(Q^n)$ data derived from the conventional procedures. Furthermore, molecular orbital theoretical calculations were performed to interpret the origin of the unexpected ^{29}Si chemical shift in the sodium borosilicate glasses. As for aluminosilicates, ab initio studies by Xue and Kanzaki (1998, 1999) offer valuable insights for the NMR characteristics. In the case of borosilicates, however, little was published, and Lee et al. (2001) just discussed topological disorder and reactivity. Furthermore, little was discussed concerning the electronic states and chemical bonding character based on theoretical calculations. In the present study, the electronic states of borosilicate glass were also investigated on the basis of a cluster molecular orbital (MO) calculation for the purpose of obtaining the theoretical prediction of ^{29}Si chemical shift. The cluster models were constructed based on a sodium borosilicate mineral, reedmergnerite NaBSi_3O_8 . A structural group, $\text{B}(\text{SiO}_4)_4$ in which a BO_4 unit is surrounded by four SiO_4 units, is present in the borosilicate mineral, and according to Yun and Bray (1978), the group is commonly present in borosilicate glasses. The alkali distribution model proposed by Dell et al. (1983), which has been most widely accepted, is based on this structural group. This mineral is also suitable for the present investigation. Neither NBO nor BO_3 unit is present in the structure, but Si-O-Si bridges are present other than B4—O—Si bridges (Table 2b). Therefore, the electronic states and chemical bonding characters can be compared between the bridging bonds, B4-O-Si and Si-O-Si with the different atomic combinations.

2. EXPERIMENTAL

Glasses with the chemical composition, $R\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot K\text{SiO}_2$ ($K = 0.5$ and 2.0) were prepared by a conventional melt-quenching method. For Si-NMR measurements, 0.2 mol.% Fe_2O_3 was also added to the batches for reducing the spin lattice relaxation time. The 10 -g batches were melted in a platinum crucible at 1000°C for 30 min to remove carbonates and were melted for 30 more min at $1000 \sim 1300^\circ\text{C}$ with the lid of alumina, where the melts were stirred several times to obtain homogeneous specimens. Postannealing was not done in order to avoid phase separation. Inductively coupled plasma analysis was done for some glasses prepared, and the compositional deviation of the cations was less than 5 atomic%.

NMR measurements were carried out at 7.05 T on a Varian UNITY-I-

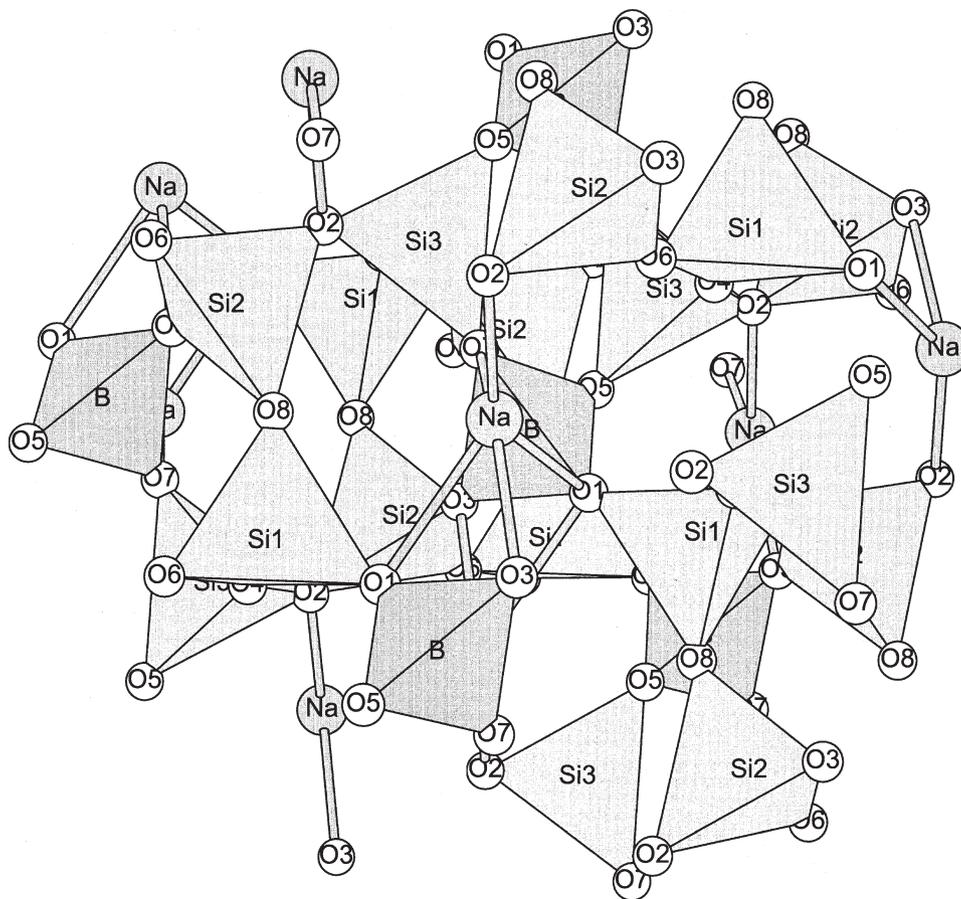


Fig. 1. An example of the cluster models. Boron-centered $(\text{Na}_9\text{B}_5\text{Si}_{17}\text{O}_{64})^{36-}$ cluster. The symbols with numbers, Si1~3 and O1~8 represent the crystallographic sites in reedmergerite (Appleman and Clark, 1965).

NOVA300 spectrometer. The sample spinning speed at the magic angle to external field was 4.5 kHz. ^{11}B MAS NMR spectra were collected at 96.3 MHz with 1.0- μs pulses and 1.0-s recycle delays, and ^{29}Si MAS NMR spectra were obtained at 59.6 MHz with 5.0- μs pulses and 1.0-s recycle delays. The chemical shift standards used were BPO_4 for ^{11}B and poly (dimethyl siloxane) (PDMS) for ^{29}Si .

First-principle MO calculations were performed with the self-consistent-charge discrete-variational $X\alpha$ method (Adachi et al., 1978) using a Hartree-Fock-Slater approximation. Cluster models were constructed on the basis of the crystal structure of reedmergerite, NaBSi_3O_8 (Appleman and Clark, 1965). The clusters were embedded in a Madelung potential to reduce the termination effects. The atomic orbitals used in the calculations are Si 1s–3d, O 1s–2p, and Na 1s–3d. Chemical bonding character was estimated from net charge and bond overlap population on the basis of the Mulliken population analysis (Mulliken, 1955). In our experience for the silicate crystals (Nanba et al., 2003), atoms near the cluster surface have a tendency to possess unrealistic charges even in applying Madelung potentials, and hence for evaluating the electronic state of an atom, it should be surrounded by at least two layers of SiO_4 tetrahedra. In reedmergerite crystal, there are 13 distinct crystallographic sites. If a cluster model were constructed in which each site had the second neighboring SiO_4 or BO_4 tetrahedra, the cluster would become too huge to perform the MO calculation. Then, 13 cluster models were constructed in which the atoms at the respective crystallographic sites were located at the center of the clusters and the central atoms were covered by at least two layers of SiO_4 or BO_4 tetrahedra. The radius of the clusters is 0.75 nm for Na (central atom), 0.7 nm for B and Si, and 0.6 nm for O. The B-centered cluster model, $(\text{Na}_9\text{B}_5\text{Si}_{17}\text{O}_{64})^{36-}$ is illustrated in Figure 1. The population analyses were done only for the central atom and the bonds including the central atom.

3. RESULTS

3.1. NMR Spectrometry and Alkali Distribution

Figure 2 shows ^{11}B and ^{29}Si MAS NMR spectra for $R\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot K\text{SiO}_2$ ($K = 0.5$) glasses. In ^{11}B MAS NMR spectra (Fig. 2a), the symmetric sharp peak at around 5 ppm is attributed to B4 in BO_4 unit, and the asymmetric broad peak at 20 ~ -20 ppm is assigned to B3 in BO_3 unit. In ^{29}Si MAS NMR spectra (Fig. 2b), the peak shifts to the higher relative frequency side with increasing R , indicating the increase of NBO in SiO_4 unit according to the conventional interpretation. The spectra were deconvoluted into the structural components, $\text{B}n$ and Q^n species (Fig. 3), obtaining N_4 and Q^n distribution. In the deconvolution of ^{29}Si MAS NMR spectra, the position of the Q^n components was settled on the basis of the results for sodium silicate glasses (Maekawa et al., 1991). The N_4 and Q^n distribution obtained (Table 1) have margins of error of 3% and 5%, respectively.

Alkali distribution estimated from Eqns. 1–3 is shown in Table 1 and Figure 4. In the glasses at $K = 0.5$, $f_{\text{Na}}(\text{B4})$ exceeds 100% at $R = 0.2$ and 0.4, which probably resulted from the compositional deviation. During the melting process, B_2O_3 volatilizes slightly, and the relative amount of Na_2O increases. Hence, the actual Na_2O content, R , in the products should be larger than the nominal content. There-

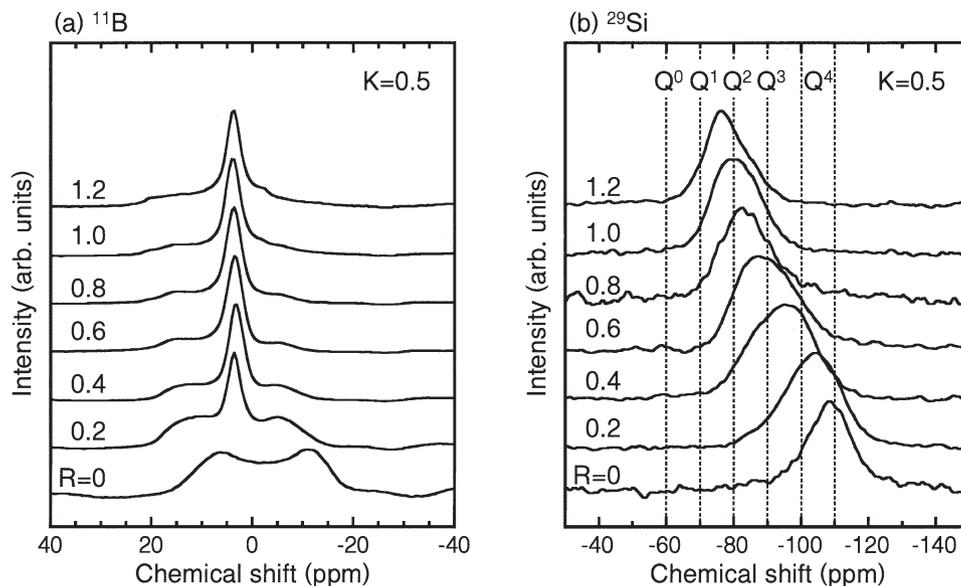


Fig. 2. ^{11}B and ^{29}Si MAS NMR spectra at 7.05 T for $R\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{KSiO}_2$ glasses ($K = 0.5$). The vertical lines indicate the general position of ^{29}Si chemical shifts in sodium silicate glasses (Maekawa et al., 1991).

fore, the $f_{\text{Na}}(\text{B4})$ values at the nominal compositions should be smaller than the observation. $f_{\text{Na}}(\text{B4})$ is given by the division of N_4 by R , and it is hence expected that $f_{\text{Na}}(\text{B4})$ at smaller R region has larger numerical error (10% at a maximum) due to the compositional deviation. In the glasses indicating $f_{\text{Na}}(\text{B4}) > 100\%$, the actual R must be 0.21 and 0.42, expecting $f_{\text{Na}}(\text{B4}) = 100\%$.

As shown in Figure 4b by the open markers, the alkali distributions were also estimated from the NMR data reported by Dell et al. (1983), Yun and Bray (1978), and Bhasin et al. (1998). The agreement in $f_{\text{Na}}(\text{B4})$ between the present and previous results is a satisfactory level. The

$f_{\text{Na}}(\text{Si})$ data are also consistent, with an exception at $R = 1.0$. In both K -series, $f_{\text{Na}}(\text{B3})$ shows negative value at small R regions. As mentioned, $f_{\text{Na}}(\text{B4})$ is overestimated in observation due to the compositional deviation, and it is also the case in $f_{\text{Na}}(\text{Si})$. However, $f_{\text{Na}}(\text{B3})$ values smaller than -10% are out of the margin of error. As also described, the glasses with $f_{\text{Na}}(\text{B4}) > 100\%$ should be 100% in the actual $f_{\text{Na}}(\text{B4})$ value, which means that $f_{\text{Na}}(\text{Si})$ as well as $f_{\text{Na}}(\text{B3})$ should be 0% in these glasses. As shown in Table 1 and Figure 4a, however, $f_{\text{Na}}(\text{Si})$ in these glasses is much larger than 0%, that is, $f_{\text{Na}}(\text{Si}) = 9\%$ and 16% at $R = 0.2$ and 0.4 , respectively. As shown in Figure 3b, the ^{29}Si MAS NMR spectrum

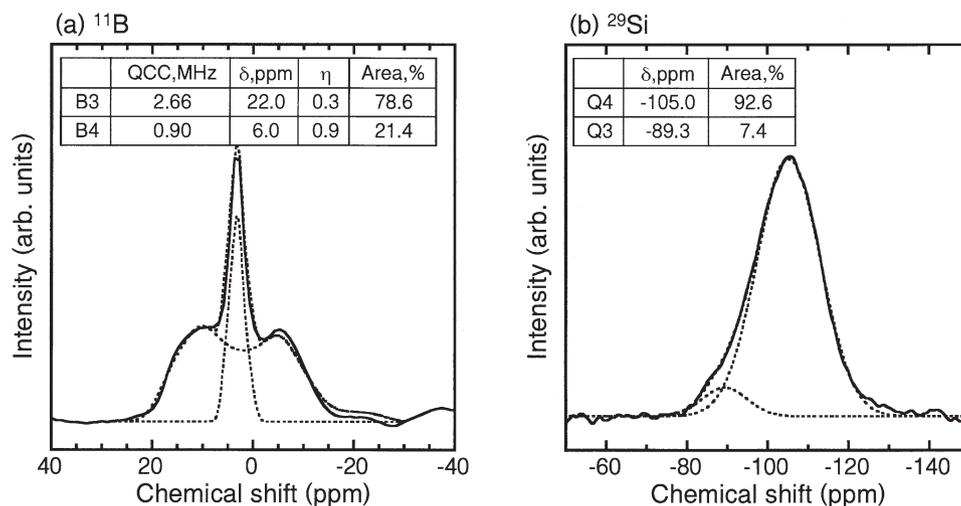


Fig. 3. Examples of spectral deconvolution of ^{11}B and ^{29}Si MAS NMR spectra for an $R\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{KSiO}_2$ glass ($R = 0.2$, $K = 0.5$). The simulated components and total curves are shown by dotted lines. The fitting parameters used in the spectral simulation are also shown (QCC: quadrupolar coupling constant; δ : isotropic chemical shift; η : asymmetry parameter).

Table 1. Fraction of 4-fold boron, N_4 obtained from ^{11}B MAS NMR, Q^n distribution from ^{29}Si MAS NMR, and alkali distribution from Eqns. 1~3 for $R\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{KSiO}_2$ glasses.

Composition		Q^n distribution (%)				Alkali distribution (%)			
K	R	N_4 (%)	$f(Q^4)$	$f(Q^3)$	$f(Q^2)$	$f(Q^1)$	$f_{\text{Na}}(\text{B4})$	$f_{\text{Na}}(\text{B3})$	$f_{\text{Na}}(\text{Si})$
0.5	0	0	100	0	0	0			
	0.2	21	93	7	0	0	107	-16	9
	0.4	42	74	26	0	0	105	-21	16
	0.6	50	67	28	5	0	83	1	16
	0.8	49	16	68	16	0	61	8	31
	1.0	47	3	46	49	3	47	15	38
2.0	1.2	39	0	28	69	3	33	31	36
	0.45	38	86	14	0	0	84	-17	32
	0.6	45	78	22	0	0	75	-12	37
	1.0	60	57	43	0	0	60	-3	43
	2.0	45	0	71	29	0	23	13	64
	2.5	33	0	41	54	5	13	21	66
	3.0	22	0	31	53	16	7	31	62

at $R = 0.2$ consists of two components located at -105 and -90 ppm, which have been conventionally assigned to Q^4 and Q^3 species, respectively. In sodium silicate glasses, the chemical shift of ^{29}Si ranges over $-96 \sim -110$ ppm for Q^4 and $-85 \sim -92$ ppm for Q^3 species (Maekawa et al., 1991). Therefore, it is tentatively concluded from Figure 3b that a measurable amount of NBO is present in the glass. This conclusion obtained from ^{29}Si -NMR is, however, inconsistent with the conclusion from ^{11}B NMR, that is, the amount of NBO is negligible from ^{11}B NMR and not negligible from ^{29}Si -NMR. It should be emphasized that the contradiction between ^{11}B and ^{29}Si -NMR is confirmed even in the glass specimens prepared in the same way. It is also noted that the contradiction is significant only when the -90 ppm component is attributable to the Q^3 species even in the borosilicate glasses.

3.2. Atomic Charge

It is commonly accepted that atomic charge is different between BO and NBO. If the chemical bonding character is completely ionic, both BO and NBO carry the same charge of -2 . According to the formal charge assuming 100% covalency, however, the formal charge of NBO becomes -1 , while BO is neutral. In practice, their charges are intermediate between -2 and 0 , and it is expected that NBO possesses more electrons than BO. Then, the net charge, Z_n of oxygen atoms was examined from MO calculations (Table 2a and Fig. 5a).

As expected, NBO in sodium disilicate ($\text{Na}_2\text{Si}_2\text{O}_5$) has smaller net charge (higher electronic population) than BO (Nanba et al., 2003). In reedmergerite (NaBSi_3O_8), there are eight oxygen sites; four sites in the B-O-Si bridge and

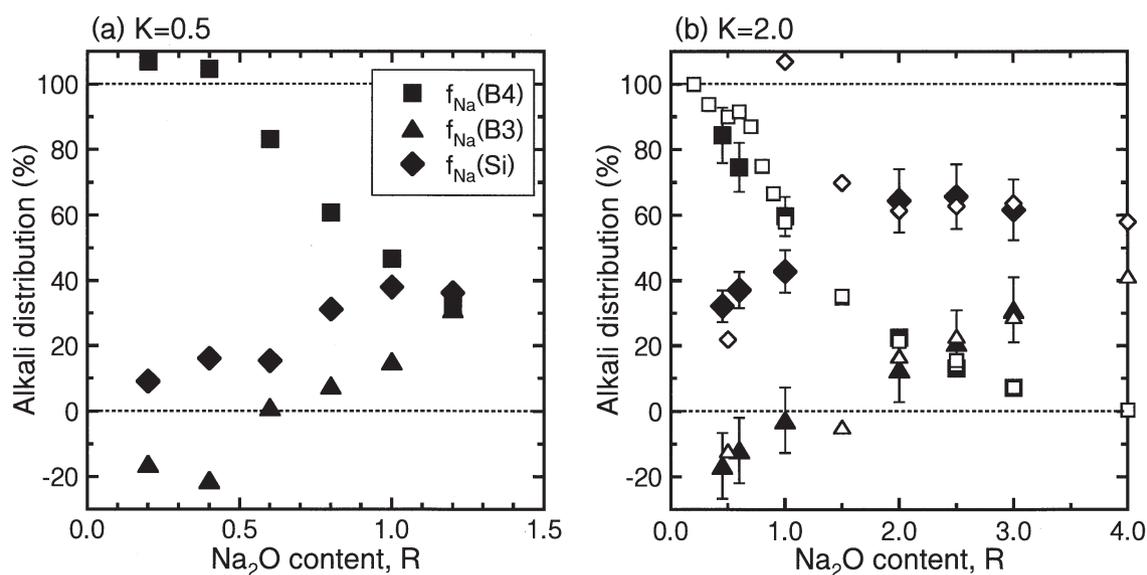


Fig. 4. Relative amount of Na ions distributed to BO_4 units, $f_{\text{Na}}(\text{B4})$, NBO in BO_3 units, $f_{\text{Na}}(\text{B3})$, and NBO in SiO_4 units, $f_{\text{Na}}(\text{Si})$ for $R\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{KSiO}_2$ glasses. Closed markers: present study; open markers: estimation from the NMR data given by Dell et al. (1983), Yun and Bray (1978), and Bhasin et al. (1998).

Table 2. Summary of the MO calculations and local structures around oxygen.

(a) Net charge Z_n , and atomic orbital energy E_{AO} (Ols, Bls, Si2p and Nals)

Site	Z_n	E_{AO} (eV)	Site	Z_n	E_{AO} (eV)
O(1)	-0.990	-504.38	B	1.399	-172.92
O(2)	-1.018	-505.03	Si(1)	2.034	-91.15
O(3)	-1.030	-504.19	Si(2)	1.985	-90.96
O(4)	-1.004	-505.30	Si(3)	1.935	-90.35
O(5)	-1.013	-503.35	Na	0.861	-1022.02
O(6)	-1.061	-504.62			
O(7)	-1.042	-504.29			
O(8)	-1.051	-505.31			

(b) Bond distance r , bond overlap population BOP, and bond angle $\angle(B, Si) - O - Si$

Bond	r (nm)	BOP	\angle ($^\circ$)
O(1)	—B	0.480	143.1
	—Si(1)	0.1595	
	—Na	0.2464	
	—Na	0.2498	
O(2)	—Si(2)	0.652	128.4
	—Si(3)	0.1648	
	—Na	0.2412	
O(3)	—B	0.481	140.7
	—Si(2)	0.1592	
	—Na	0.2410	
O(4)	—Si(1)	0.676	158.2
	—Si(3)	0.1626	
O(5)	—B	0.538	124.7
	—Si(3)	0.1612	
O(6)	—Si(1)	0.625	135.8
	—Si(2)	0.1630	
	—Na	0.2817	
O(7)	—B	0.501	135.4
	—Si(3)	0.1614	
	—Na	0.2382	
O(8)	—Si(1)	0.633	146.3
	—Si(2)	0.1613	
	—Na	0.2862	

another four sites in Si-O-Si, indicating broad Z_n distribution. The average $Z_n(O)$ of the borosilicate is higher than that of the silicate. Furthermore, the average $Z_n(O)$ in the B-O-Si bridge is slightly higher than that in the Si-O-Si bridge in the borosilicate. This result is disappointing, compared to the original expectation that some oxygens in the B-O-Si bridge possess higher electronic population than those in the Si-O-Si bridge.

The net charge of silicon, $Z_n(Si)$, is also shown in Figure 5b. In the sodium silicates, $Z_n(Si)$ decreases with increasing the number of NBO in SiO_4 units (in the order of Q^4 , Q^3 , and Q^2). In the sodium borosilicate, $Z_n(Si)$ is distributed between 2.05 and 1.95. It is noted that silicons in the sodium borosilicate have closer charge of Q^3 silicon rather than Q^4 silicon in the sodium silicates.

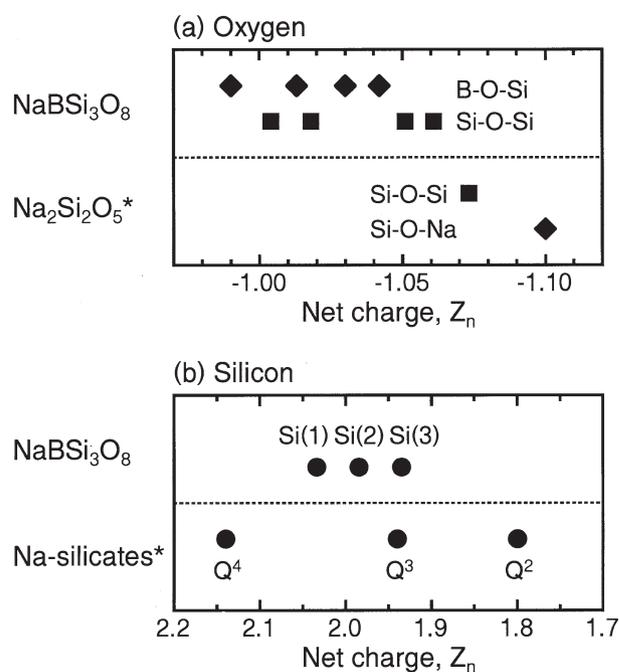


Fig. 5. Net charge, Z_n obtained from the MO calculations. *Nanba et al. (2003).

3.3. Chemical Shift in Energy Level

According to Grunthaner and Grunthaner (1986), the chemical shift in NMR is proportional to the chemical shift in XPS, that is, the energy shift in the core-level atomic orbitals. As is generally known, BO and NBO give different O1s binding energy in XPS. Then, O1s and Si2p orbital energies were examined (Table 2a). However, the absolute value of the orbital energies is not given in the MO calculation used in the present study, and hence the orbital energies between the different clusters are not compared directly. Next, the energy correction was done as follows. A cluster in which O(1) was the central atom (designated as O(1) cluster) was chosen for the energy correction, and the central O(1) and its nearest neighbors, B and Si(1) in the O(1) cluster were used as the energy standards; O(1)1s = -504.4 eV, B1s = -172.9 eV, and Si(1)2s = -133.7 eV. Si(1)2p was not chosen as the energy standard, because it split into three levels. As listed in Table 2b, B has another three ligand oxygens, O(3), O(5), and O(7). Next, the orbital energies in O(3), O(5), and O(7) clusters were corrected as B1s of borons bound to the central oxygens to be -172.9 eV. The orbital energies of O(4), O(6), and O(8) clusters including Si(1) as the nearest neighbor of the central oxygens were also corrected using Si(1)2s. The orbital energies of the O(2) cluster were corrected by Si(2)2s averaging over the clusters, O(3), O(6), and O(8). Finally, the Si2p orbital energies of Si(1), Si(2), and Si(3) were estimated with the average energies among the oxygen-centered clusters.

Figure 6 shows the electronic density of states (DOS) of the atomic orbitals, O1s and Si2p. The partial density of states (PDOS) of oxygens in the Si-O-Si bridge is situated at a lower energy side than that in the B-O-Si bridge, from which it is generally interpreted that oxygens in the Si-O-Si bridge have

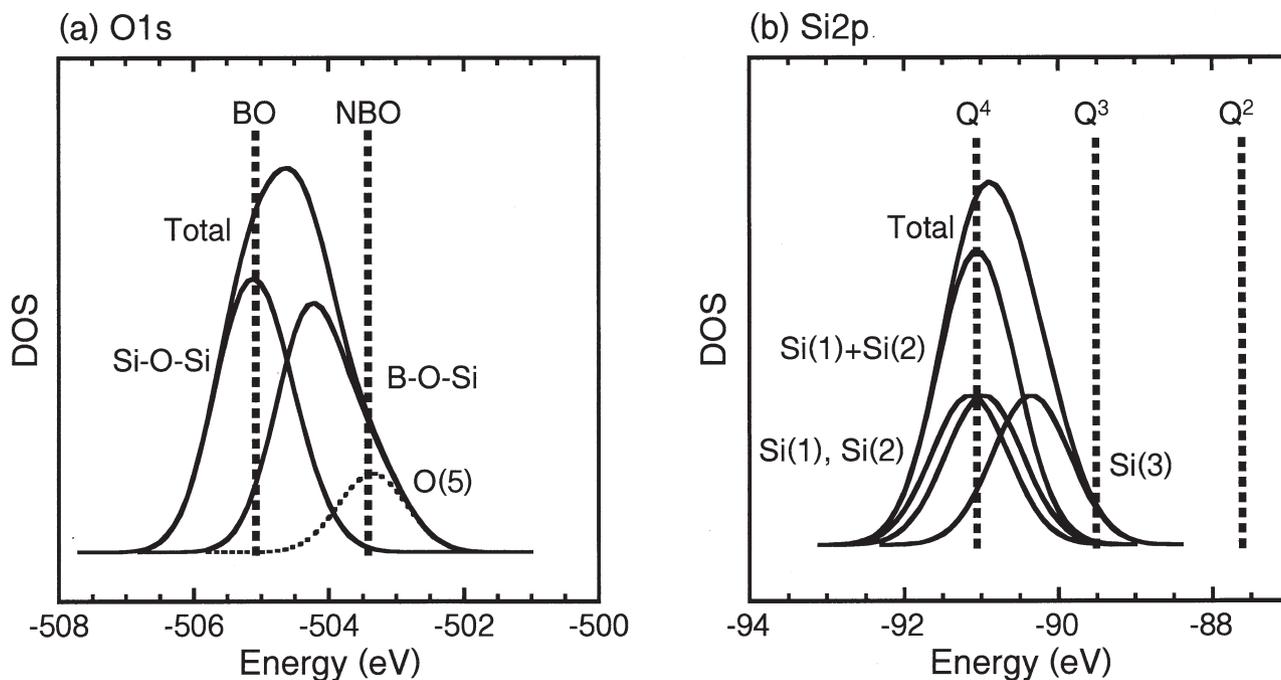


Fig. 6. Density of states (DOS) of the atomic orbitals obtained from the MO calculations. Curves were obtained assuming a gaussian profile with a 1.0-eV full width at the half maximum. The vertical lines are the energy levels in sodium silicates (Nanba et al., 2003).

smaller electronic population, that is, less negative charge, than those in the B-O-Si bridge. The electronic population expected is inconsistent with the results of net charge indicated in Table 2a and Figure 5a.

The shape of total DOS of O1s (Fig. 6a) is asymmetric, which is due to the outlying O(5) component. In Figure 6a, the O1s energies of BO and NBO in sodium disilicate (Nanba et al., 2003) are also shown as vertical lines. It is noteworthy that the energy difference between BO and NBO in the silicate is almost the same as the difference between the average in Si-O-Si and O(5) in B-O-Si. Supposing that O1s XPS spectrum were measured, the shoulder due to O(5), if present, would be assigned as NBO.

Figure 6b shows DOS of Si2p. As mentioned, Si2p splits into three distinct levels in MO calculation. From the average values listed in Table 2a, PDOS values shown in Figure 6b were obtained. In the case of net charge, three silicons are at even intervals (Fig. 5b). In DOS, however, Si(1) and Si(2) are located at almost the same energy, but Si(3) is ~ 0.7 eV away from the other ones. It is notable that the energy difference is almost half of the difference between Q⁴ and Q³ silicons. It is therefore expected that Si(3) gives a peak at higher relative frequency side in ²⁹Si-NMR.

Geisinger et al. (1988) reported the ²⁹Si MAS NMR data of reedmergerite. Three well-resolved peaks are observed at -95.5 , -98.4 , and -107.1 ppm, and the chemical shifts are within the region of Q⁴ silicon ($-96 \sim -110$ ppm) in sodium silicate glasses (Maekawa et al., 1991). The ²⁹Si peak at -95.5 ppm is attributable to Si(3), because similarities between Si(3) in reedmergerite and Q³ silicon in sodium disilicate are found both in net charge and Si2p orbital energy obtained from the MO calculations. Additionally, O(5) which shows the highest O1s energy is bound to Si(3) (Table 2b). The other peaks at -98.4 and -107.1 ppm probably

originate in Si(2) and Si(1), respectively. If Si2p energy of Si(2) estimated from the MO calculations were much closer to that of Si(3) instead of Si(1), this assignment would be more reliable.

4. DISCUSSION

4.1. Chemical Bonding Character

It was found in the present MO calculations that Si(3) in reedmergerite had higher electronic population and higher Si2p energy than the other silicons, and it was also suggested that the electronic state of Si(3) was quite similar to that of Q³ silicon in sodium silicate. Then, chemical bonding character was examined based on the bond overlap population (BOP) for clarifying the origin of the specific properties of Si(3). The physical meaning of BOP is the population of electrons shared between two atoms (Mulliken, 1955), and it is often associated with bond order and bond modulus.

Figure 7 shows BOPs in the borosilicate crystal together with the data for the silicate and borate crystals. It is noted that Si-O bonds show different BOP between Si-O-Si and Si-O-B4 bridges, and B4-O bond shows smaller BOP compared with the Si-O bonds. B4-O bond in the borate crystal also shows smaller BOP than the other B-O bonds, and BOP in the B4-O-B4 bridge is, however, almost the same with that in the B3-O-B3 bridge. The relation of BOP in magnitude between the bonds, B4-O and B3-O in a B4-O-B3 bridge is quite similar to the relation between the bonds, B4-O and Si-O in the B4-O-Si bridges. In the heterogeneous combinations, such as B4-O-Si and B4-O-B3 bridges, B4-O bonds always show much smaller BOP (~ 0.5), whereas the opponent Si-O and B3-O bonds indicate higher BOP (~ 0.7) as compared with the homogeneous combinations, Si-O-Si,

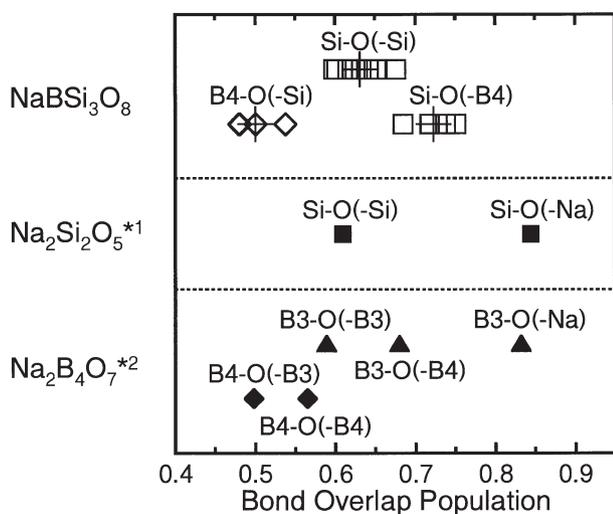


Fig. 7. Bond overlap population, BOP, obtained from the MO calculations. For instance, B4-O(-Si) represents BOP of B4-O bond in B4-O-Si bridge. Cross markers in NaBSi₃O₈ indicate the average of open markers. *1: Nanba et al. (2003); *2: unpublished data.

B3-O-B3, and B4-O-B4 (~0.6). It is also notable that the homogeneous combinations indicate almost the same BOP (~0.6) even in the different crystals. It is therefore concluded that electrons are evenly distributed between the bonds in the homogeneous combinations, and in the heterogeneous combinations such as Si-O-B4 and B3-O-B4 bridges; however, the electron distribution is unequal and many electrons are localized on Si-O and B3-O bonds. Moreover, the difference in BOP between Si-O and B4-O bonds in Si-O-B4 bridges (~0.2) is close to the difference between Si-O and Si-NBO bonds in the silicate crystal. Certainly, the absolute value of BOP of Si-O in Si-O-B4 bridges (0.72) is much less than that of Si-NBO (0.84). In reedmergerite, Si(3) has two B4 borons as the second nearest neighbors, whereas Si(1) and Si(2) have one second-neighboring B4. The difference in BOP indicates that the electronic population around Si(3) is higher than Si(1) and Si(2), and it is probably the reason for the higher net charge and Si2p energy of Si(3).

4.2. Interpretation of the -90 ppm Component in ²⁹Si-NMR

The contradiction in alkali distribution was confirmed from the experiments; ¹¹B NMR suggests that Na ions are exclusively distributed to BO₄ units and NBO is not present in the low alkali content glasses, whereas ²⁹Si-NMR indicates that the negligible amount of Na ions are distributed to SiO₄ units forming NBOs in the glasses. However, this conclusion is based on the two hypotheses. It has been assumed that the -90 ppm component observed in ²⁹Si-NMR (Fig. 3b) was attributable to the Q³ unit even in the case of borosilicate glasses. As for the Q⁴ species in aluminosilicates, the ²⁹Si-NMR peak shifts to the higher relative frequency side with increasing the number of second neighboring Al, and the ²⁹Si chemical shift of Si surrounded by three Al is around -90 ppm (Lippmaa et al., 1981), which overlaps with the region for the Q³ species in sodium silicate glasses (Maekawa et al., 1991). As mentioned, the situation in aluminosilicates is apparently similar to the borosilicate glass. According to the basicity concept proposed

by Duffy and Ingram (1976), the basicities of oxygens in Si-O-Si, Si-O-B4, and Si-O-Al bridges are estimated as 0.48, 0.52, and 0.59, respectively. If ²⁹Si-NMR chemical shift is proportional to the basicity of surrounding oxygens, the chemical shift in borosilicates should be much smaller than that in aluminosilicates. In practice, however, the chemical shift is affected by other factors, such as bond strength and bond angle of Si-O-T bridges (Stebbins, 1995). In any case, the results obtained in this paper suggest that the -90 ppm component in ²⁹Si-NMR should be assigned not only to Q³ species with one NBO but also to Q⁴ species associated with abundant B4 as second neighbors. Direct estimation of the NMR parameters, such as the theoretical elucidation by Xue and Kanzaki (1998, 1999) should be required for further discussion.

Another hypothesis is that a BO₄ unit possesses a negative charge of -1, and one Na ion is distributed around the BO₄ unit as a charge compensator. This hypothesis is valid, when all four oxygens are usual BOs in the bridges, such as B-O-B and B-O-Si. However, if tricluster oxygen such as B4-O-M₂ (M = Si or B4) is present, the negative charge of the BO₄ unit is reduced. As mentioned, the charge of a tricluster, (O_{3/2}Si)O(BO_{3/2})₂ including two BO₄ units is -1, and hence only one Na is required for the charge neutrality. The atoms left over in this way, Na and 1/2O are used for the formation of NBO elsewhere in the material. Zhao et al. (2000) proposed this model to interpret the contradiction between ¹¹B and ¹⁷O NMR in barium borosilicate glasses, and they also stated that the experimental observation of the tricluster oxygens is quite difficult even in ¹⁷O NMR. Lee et al. (2001) examined the stability of a tricluster based on the theoretical calculations, inferring small fractions of the tricluster. According to the latest ¹⁷O 3QMAS NMR analyses for sodium borosilicate glasses (Du and Stebbins, 2003), no NBO peaks were observed in the glasses with low Na₂O content, suggesting that the effects due to the tricluster oxygens and NBOs on the ²⁹Si chemical shifts were negligible in the low Na₂O glasses.

At this moment, these hypotheses are not denied or confirmed. A tentative conclusion should be drawn as follows. The triclusters and NBOs derived from the triclusters are present in borosilicate glass but not so abundant as to compensate the fictitious Q³ component at -90 ppm in ²⁹Si-NMR spectra on their own. Another compensator for the -90 ppm component is BOs in B4-O-Si bridges which are in a similar electronic state to NBOs. In the NBO-free glasses (*K* = 0.5, *R* = 0.2 and 0.4), the amount of the fictitious NBOs per Si is estimated as 0.07 and 0.26 at *R* = 0.2 and 0.4, respectively. If the Q⁴ silicons associated with two tetrahedral borons are assigned as the fictitious Q³ silicons, the amount of tetrahedral borons next to the fictitious Q³ silicons is expected as 0.14 (0.07 × 2) and 0.52 at the maximum, which is much less than the total amount of tetrahedral borons present in the glasses, 0.85 (2 × 0.21/0.5) and 1.68 at *R* = 0.2 and 0.4, respectively. Furthermore, according to Du and Stebbins (2003), tetrahedral borons are preferentially associated with silicons to form B4-O-Si bridges. It is therefore concluded that there are enough tetrahedral borons to compensate the -90 ppm component.

Before beginning MO calculations, it was expected that O(1) in reedmergerite would show a similar character to NBO because it had two neighboring Na (Table 2b). As shown in Table 2a and Figure 6a, however, O(5) showed the highest O1s energy which was close to NBO in sodium silicate. As theoretically elucidated by Xue and Kanzaki (1998, 1999), the chemical shifts in ²⁹Si and

^{17}O NMR depend on the bond angle of the Si-O-T bridge (T = Si, Al); the chemical shifts commonly move to the higher relative frequency side with decreasing the bond angle. Among B-O-Si bridges in reedmergnerite, the B-O(5)-Si(3) bridge is narrowest (Table 2b). The narrow bond angle is probably the reason for the distinctive characteristics in O(5) and Si(3). It is finally expected that some B4-O-Si bridges in borosilicate glass are in a narrow bond angle, and Si atoms in the narrow B4-O-Si bridges appear in the -90 ppm component, which has been attributed to Q^3 species according to the conventional assignments.

5. CONCLUSIONS

^{11}B and ^{29}Si MAS NMR spectra were measured for $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glasses. For the glasses with low Na_2O content, ^{11}B NMR suggested that Na ions were exclusively distributed to borate groups forming BO_4 units, whereas a -90 ppm component was extracted from ^{29}Si -NMR spectra, which had so far been attributed to Q^3 species in accordance with the conventional assignments. To clarify the origin of the fictitious Q^3 component in ^{29}Si -NMR, MO calculations were performed to evaluate the electronic states of Si and O atoms, where cluster models were constructed on the basis of a borosilicate crystal, reedmergnerite NaBSi_3O_8 . Among the three Si sites in the borosilicate crystal, Si(3) which was Q^4 species in the conventional notation was similar in net charge and Si2p energy to Q^3 species in sodium silicates. The results led to a conclusion that the Q^4 species which were in a similar environment to Si(3) were responsible for the fictitious Q^3 species in ^{29}Si -NMR spectra. There still remained a possibility that the triclusters such as $(\text{O}_{3/2}\text{Si})\text{O}(\text{BO}_{3/2})_2$ were present in borosilicate glasses, but the triclusters were probably not so abundant to contribute to the -90 ppm component.

The chemical bonding character was also estimated on the basis of the bond overlap population. It was found that electrons were unequally distributed around oxygens in Si-O-B4 bridges, and many electrons were localized on Si-O bonds, suggesting that the Q^4 species associated with abundant B4 atoms as the second neighbors were responsible for the fictitious Q^3 species. It was also suggested that Si-O-B4 bridges with narrow bond angle contributed to the -90 ppm component in ^{29}Si -NMR spectra. In any case, theoretical predictions of the NMR parameters are required to clarify the chemical shifts of the Q^n species in borosilicates.

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