

## Studies on the characterization of sulfur and coloration in borosilicate glasses

Taro Asahi<sup>a,\*</sup>, Susumu Nakayama<sup>a</sup>, Tokuro Nanba<sup>b</sup>, Hajime Kiyono<sup>c</sup>, Hiroshi Yamashita<sup>d</sup> and Takashi Maekawa<sup>d</sup>

<sup>a</sup>Niihama National College of Technology, 7-1 Yagumo-cyo Nihama-shi Ehime 792-8580, Japan

<sup>b</sup>Graduate of School of Environmental Science, Okayama University, 3-1-1, Tsushima-naka, Okayama-shi 700-8530, Japan

<sup>c</sup>Graduate of School of Engineering, Hokkaido University, N13, W8, Kita-ku, Sapporo 060-8628, Japan

<sup>d</sup>Graduate of School of Science and Engineering, Ehime University, 3, Bunkyo-cyo, Matsuyama-shi 790-8577, Japan

Ternary alkali borosilicate glasses containing sulfur were prepared by a conventional melt quenching method, and their chemical bonding states were investigated based on XPS and  $^{29}\text{Si}$ ,  $^{11}\text{B}$  MAS-NMR measurement. The glass samples changed in color from blue to reddish brown due to the state of the sulfur and their glass compositions. From S2p photoelectron spectra, it can be seen that the sulfur exists with a negative charge in the glass. The forming of non-bridging oxygen components was observed from O1s photoelectron spectra of the glasses, which colored to brown and reddish brown. Furthermore, a signal from silicon atoms coordinated to the sulfur was detected in these glasses by the  $^{29}\text{Si}$  MAS-NMR measurement. From these results, it is considered that sulfur atoms bonded silicon atoms at the forming range of the non-bridging oxygen component.

**Key word:** Sulfur, Oxyulfide glass, XPS, MAS-NMR, Coloration, Glass structure.

### Introduction

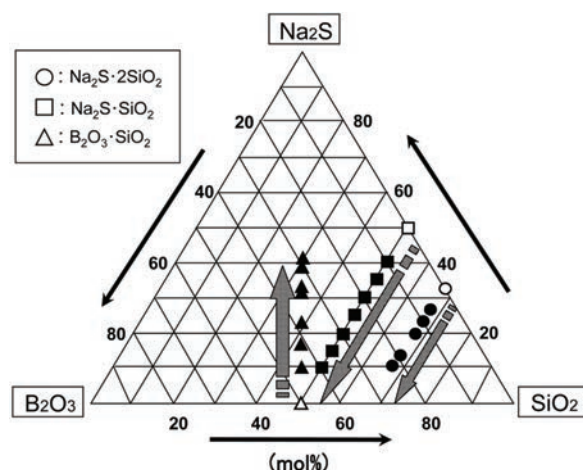
The behavior of sulfur in melts and glasses is closely related to the refining and the coloration phenomenon. Therefore, it is a very important issue to clear the chemical bonding states of sulfur for the glass industry [1, 2]. In previous studies, we have prepared binary oxyulfide system glasses, which can contain large amounts of sulfur, such as  $\text{Na}_2\text{S}$ - $\text{SiO}_2$  and  $\text{Na}_2\text{S}$ - $\text{B}_2\text{O}_3$  glasses based on the alkali sulfide by a conventional melt quenching method to confirm the glassy state and determine the glass-forming range. Additionally, the chemical state of residual sulfur in the glass system, and the effect of the sulfur on the glass structure have also been investigated mainly by XPS (X-ray Photoemission Spectroscopy) and MAS (Magic Angle Spinning)-NMR (Nuclear Magnetic Resonance) measurement [3, 4]. There are some reports which discuss the chemical bonding state of sulfur in borosilicate glasses based on the redox equilibrium in the melts [5-7]. However, there is still no report which discusses the coloration phenomenon due to the residual sulfur atoms and their chemical bonding states in the borosilicate glass, relating to their effects on the glass structure.

In this study, we prepared and determined the glass-forming range of the ternary  $\text{Na}_2\text{S}$ - $\text{B}_2\text{O}_3$ - $\text{SiO}_2$  glass system substituting alkali sulfide ( $\text{Na}_2\text{S}$ ) for the modifier oxide ( $\text{Na}_2\text{O}$ ) in the sodium borosilicate glass. Furthermore, we investigated and discussed the correlation between the

coloration due to the compositional change and the chemical bonding state of sulfur in the glass system by XPS and MAS-NMR measurements.

**Table 1.** Batch compositions of glass samples in the system of  $\text{Na}_2\text{S}$ - $\text{B}_2\text{O}_3$ - $\text{SiO}_2$

[A] (1-x)		[B] (1-x)		[C]	
$\text{Na}_2\text{S} \cdot x\text{B}_2\text{O}_3 \cdot 2\text{SiO}_2$		$\text{Na}_2\text{S} \cdot x\text{B}_2\text{O}_3 \cdot \text{SiO}_2$		$x\text{Na}_2\text{S} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$	
Sample No.	Batch	Sample No.	Batch	Sample No.	Batch
A-1	x = 0.7	B-1	x = 0.8	C-1	x = 0.2
A-2	0.6	B-2	0.7	C-2	0.4
A-3	0.4	B-3	0.6	C-3	0.6
A-4	0.3	B-4	0.5	C-4	0.9
A-5	0.2	B-5	0.4	C-5	1.0
		B-6	0.3	C-6	1.2
		B-7	0.2	C-7	1.4



\*Corresponding author:  
Tel : +81-(0)897-37-7796  
Fax: +81-(0)897-37-7796  
E-mail: asahi@mat.niihama-nct.ac.jp

## Experimental

Batch compositions of the glass samples shown in Table 1 were prepared using  $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$  and  $\text{Na}_2\text{S}$  as the starting materials. The dry-mixed batch using a mortar were melted in an alumina crucible with a lid at 1350 °C for 20 minutes in an electric furnace under a normal atmosphere. After melting, sample glasses were obtained by pouring and pressing melts onto a stainless steel plate. Compositional analysis of the glass samples was firstly done, and the analytical composition was calculated from the stoichiometric ratio of the glass composition.

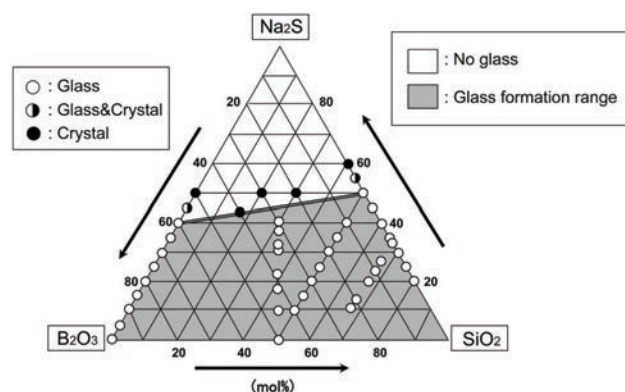
The XPS measurements were done with a Fisons Instruments S-Probe ESCA SSX-100S, following the method previously reported [8]. A JEOL JNC-CMX 300 spectrometer was employed to obtain the  $^{29}\text{Si}$  and  $^{11}\text{B}$  MAS-NMR spectrum. As for the reference materials of the chemical shift, tetramethoxy silane (TMS) and poly-dimethyl silane (−34.11 ppm) was used for  $^{29}\text{Si}$ , and  $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$  and  $\text{BPO}_4$  (−3.60 ppm) was used for  $^{11}\text{B}$ , respectively. In addition, glass samples prepared by adding 0.01–0.05 mass%  $\text{Fe}_2\text{O}_3$  against the total amount of the batch were prepared for the  $^{29}\text{Si}$  MAS-NMR measurements.

## Results and Discussion

### Composition Range of Glass Forming and Coloration

The glass forming range for the  $\text{Na}_2\text{S}$ - $\text{B}_2\text{O}_3$ - $\text{SiO}_2$  systems is shown in Fig. 1. For the glass compositions in the high alkali region which is above a tie line connected between the vitrification limit points of the  $\text{Na}_2\text{S}$ - $\text{SiO}_2$  and  $\text{Na}_2\text{S}$ - $\text{B}_2\text{O}_3$  system glass, some diffraction peaks due to crystallization were observed. Therefore, it was revealed that the glass forming range of the samples is at low alkali region below the tie line. The color of samples changed with the composition change, and sample coloration of the  $\text{Na}_2\text{S}$ - $\text{B}_2\text{O}_3$ - $\text{SiO}_2$  glass systems is summarized in Table 2.

As in the above mentioned binary system glass, the ternary glass system also showed a coloration change due to the composition change. For this reason, the chemical bonding states of sulfur in the glass may be changed



**Fig. 1.** Glassy state and glass forming range for  $\text{Na}_2\text{S}$ - $\text{B}_2\text{O}_3$ - $\text{SiO}_2$  system.

**Table 2.** Coloration of  $\text{Na}_2\text{S}$ - $\text{B}_2\text{O}_3$ - $\text{SiO}_2$  glass samples

Sample No.	Batch composition	Color of glass
	$\text{Na}_2\text{S} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$	
[A] $(1-x) \text{Na}_2\text{S} \cdot x\text{B}_2\text{O}_3 \cdot 2\text{SiO}_2$		
A-1	$x = 0.7$	Faint gray
A-2	0.6	Faint blue
A-3	0.4	Brown
A-4	0.3	Brown
A-5	0.2	Reddish brown
[B] $(1-x) \text{Na}_2\text{S} \cdot x\text{B}_2\text{O}_3 \cdot \text{SiO}_2$		
B-1	$x = 0.8$	Faint blue
B-2	0.7	Blue
B-3	0.6	Brown
B-4	0.5	Reddish brown
B-5	0.4	Reddish brown
B-6	0.3	Reddish brown
B-7	0.2	Reddish brown
[C] $x\text{Na}_2\text{S} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$		
C-1	$x = 0.2$	Faint blue
C-2	0.4	Blue
C-3	0.6	Brown
C-4	0.9	Reddish brown
C-5	1.0	Reddish brown
C-6	1.2	Reddish brown
C-7	1.4	Reddish brown

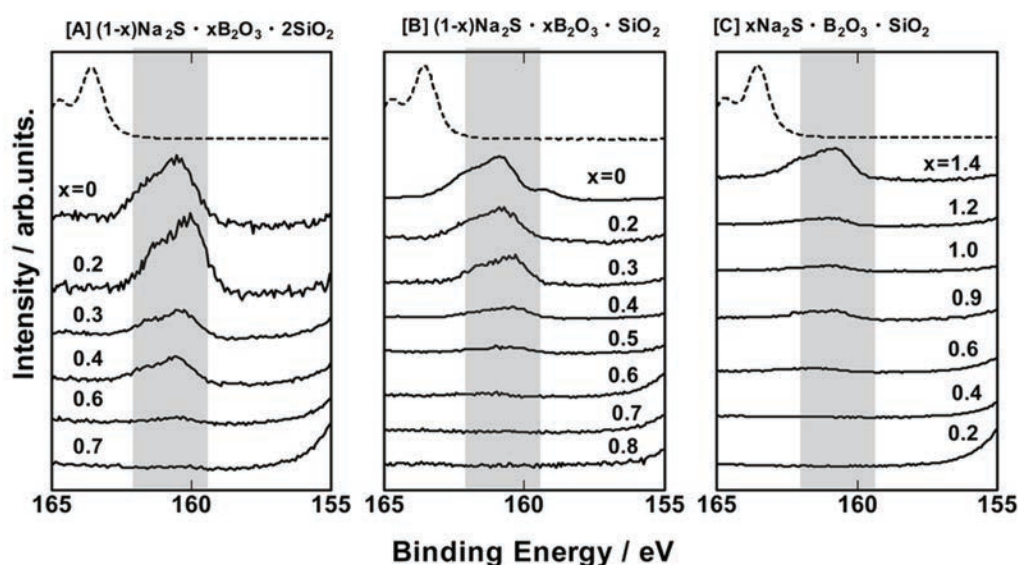
depending upon the glass structure around the sulfurs. A compositional analysis showed that the residual amount of sulfur in any of the glass systems was lower than the anticipated amount from the batch composition. It is considered that some sulfurs which were introduced into the glass system as  $\text{Na}_2\text{S}$  were volatilized, and those sites were replaced with oxygen. The batch and analytical compositions for the  $\text{Na}_2\text{S}$ - $\text{B}_2\text{O}_3$ - $\text{SiO}_2$  glass systems calculated from the stoichiometric ratio of alkali metal component and cation components are summarized in Table 3, where  $\text{Na}_2\text{S}$  is described as  $\text{Na}_2(\text{O},\text{S})$  for the pseudo-ternary system because of the volatilization of sulfur.

### XPS and MAS-NMR Measurements

$\text{S}2\text{p}$  photoelectron spectra for the  $\text{Na}_2\text{S}$ - $\text{B}_2\text{O}_3$ - $\text{SiO}_2$  glass systems are shown in Fig. 2. For the  $\text{S}2\text{p}$  signal, the peak intensity increased with an increase of the added amount of  $\text{Na}_2\text{S}$  in the batch composition, and mostly the peaks were observed around 161 eV for all of the signal detected samples. The valence of sulfur in the range from (+6) to (−2) in the glass can be variously changed depending upon the redox condition during melting. In the case of high valence sulfur such as  $\text{S}^{6+}$  and  $\text{S}^{4+}$ , along with a decrease in the density of electron charge, the photoelectron binding energy of the  $\text{S}2\text{p}$  orbit appears on the higher energy side ( $\text{S}^{6+} \approx 168.9$  eV,  $\text{S}^{4+} \approx 166.6$  eV) than that for  $\text{S}^0$  ( $\approx 164$  eV). The  $\text{S}2\text{p}$  photoelectron binding

**Table 3.** Batch and analytical composition for Na<sub>2</sub>S-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass systems (Analytical composition was calculated from the glass forming cation components ratio by chemical analysis.)

No.	Composition /molar ratio $x\text{Na}_2\text{S} \cdot y\text{B}_2\text{O}_3 \cdot z\text{SiO}_2$	Batch /mol%			Analytical /mol%		
		Na <sub>2</sub> S	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Na <sub>2</sub> (O, S)	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
A-1	$x = 0.3; y = 0.7; z = 2$	10.0	23.3	66.7	7.4	21.5	71.1
A-3	$x = 0.6; y = 0.4; z = 2$	20.0	13.3	66.7	16.5	12.7	70.8
A-5	$x = 0.8; y = 0.2; z = 2$	26.6	6.7	66.7	22.7	6.6	70.6
B-1	$x = 0.2; y = 0.8; z = 1$	10.0	40.0	50.0	8.2	38.8	53.0
B-3	$x = 0.4; y = 0.6; z = 1$	20.0	30.0	50.0	15.8	27.9	56.2
B-5	$x = 0.6; y = 0.4; z = 1$	30.0	20.0	50.0	24.8	19.0	56.2
B-7	$x = 0.8; y = 0.2; z = 1$	40.0	10.0	50.0	34.3	9.3	56.3
C-1	$x = 0.2; y = z = 1$	9.0	45.5	45.5	7.8	45.2	47.0
C-3	$x = 0.6; y = z = 1$	23.0	38.5	38.5	19.7	36.7	43.6
C-5	$x = 1.0; y = z = 1$	33.4	33.3	33.3	27.9	33.2	38.9
C-7	$x = 1.4; y = z = 1$	41.2	29.4	29.4	34.4	30.3	35.2

**Fig. 2.** S2p photoelectron spectra for Na<sub>2</sub>S-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass systems. (The broken line in figure is the S2p photoelectron spectrum for orthorhombic sulfur.)

energy for the Na<sub>2</sub>S-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass systems appeared on the lower energy side than for orthorhombic sulfur, and it was close to the value ( $\approx 161.7$  eV) observed for sodium sulfide. Accordingly the valence of sulfur in the present glass systems is not in such a high valence state as S<sup>6+</sup> and S<sup>4+</sup>, and it exists as a lower valence anion species with a higher density of electron charge than for elemental sulfur. O1s photoelectron spectra for the Na<sub>2</sub>S-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass systems are shown in Fig. 3. Curve fitting for the spectra was done using a Gauss-Lorentz symmetry function (Gaussian: 85%) to get an appropriate half bandwidth. These peaks can be separated into two components, which are attributable to bridging oxygen (BO) and non-bridging oxygen (NBO) viewed from the high binding energy side. (The peak around 535 eV is attributable to Na Auger.) From the results of our previous research, it was found that the NBO component was observed when alkali sulfide Na<sub>2</sub>S was added to silica similar to the

Na<sub>2</sub>O-SiO<sub>2</sub> binary system glass. Also the NBO components increased with an increase of the amount of Na<sub>2</sub>S added [3]. Similarly, in the present experiments it was seen that the area intensity of the NBO component in the O1s spectra decreased along with a sequential substitution of B<sub>2</sub>O<sub>3</sub> for the Na<sub>2</sub>S in the Na<sub>2</sub>S·2SiO<sub>2</sub> and Na<sub>2</sub>S·SiO<sub>2</sub> binary systems. The NBO generated due to the addition of Na<sub>2</sub>S to SiO<sub>2</sub> was used to transform the substituted B<sub>2</sub>O<sub>3</sub> from a [BO<sub>3</sub>] planar triangular unit to a [BO<sub>4</sub>] tetrahedral unit.

<sup>11</sup>B MAS-NMR spectra for the Na<sub>2</sub>S-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass systems are shown in Fig. 4. The spectra consisted of two types of peaks; sharp peaks around 0 ppm which are attributable to four coordinated boron, and broad peaks around -20 - +20 ppm which are attributable to three coordinated boron. Peak separation in these spectra was done by consideration of the asymmetry of the nuclear quadrupole, and then the ratio of four coordinated boron (N<sub>4</sub>) was calculated. It was found that the N<sub>4</sub> value was

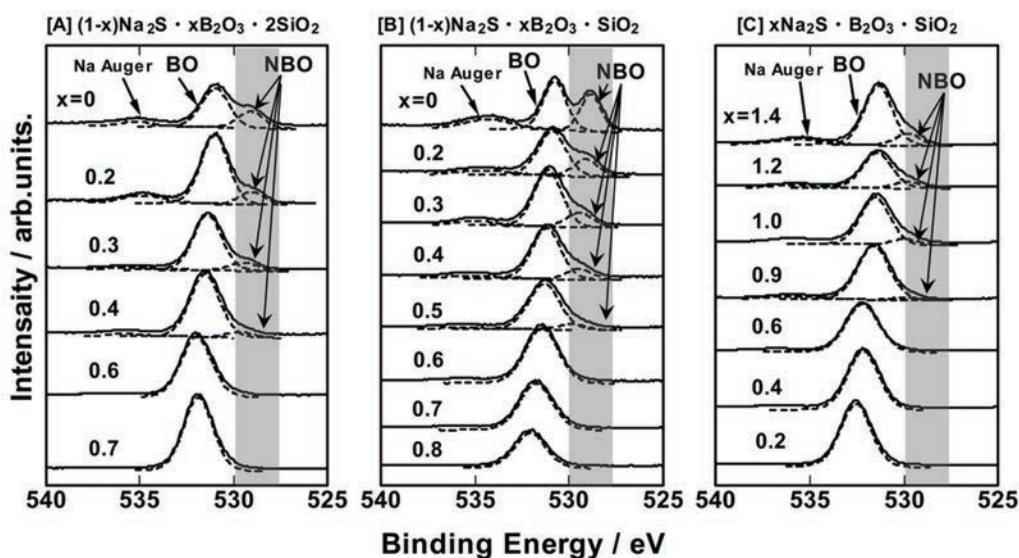


Fig. 3. O1s photoelectron spectra for  $\text{Na}_2\text{S}-\text{B}_2\text{O}_3-\text{SiO}_2$  glass systems.

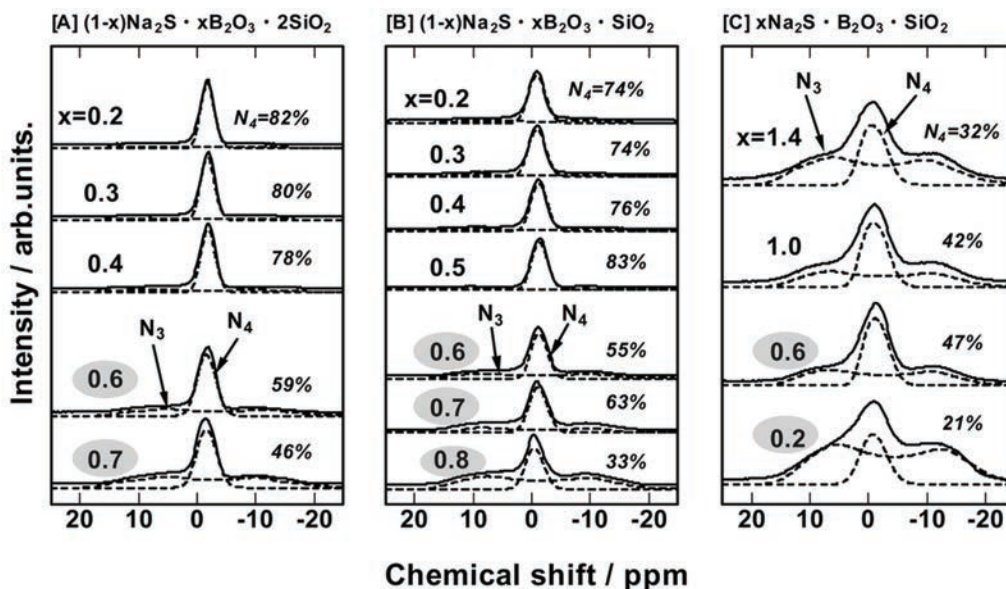


Fig. 4.  $^{11}\text{B}$  MAS-NMR spectra for  $\text{Na}_2\text{S}-\text{B}_2\text{O}_3-\text{SiO}_2$  glass systems. (The mesh circles represent the samples containing an NBO component.)

larger for the samples with a smaller amount of  $\text{B}_2\text{O}_3$  substitution, and this suggested that a number of the  $[\text{BO}_4]$  tetrahedral units were generated in the glass systems. In addition, the NBO components were decreased with an increase of the amount of  $\text{B}_2\text{O}_3$  substitution in the O1s spectra. Therefore, it is suggested that the NBO in the glass system was used to transform the substituted  $\text{B}_2\text{O}_3$  from a  $[\text{BO}_3]$  planar triangular unit to a  $[\text{BO}_4]$  tetrahedral unit, and the observed NBO components were equivalent to the  $\text{NBO}(\text{Si}-\text{O}^- \bullet \bullet \text{Na}^+)$  generated due to the breakage of  $\text{Si}-\text{O}-\text{Si}$  bonding.  $^{29}\text{Si}$  MAS-NMR spectra for the  $\text{Na}_2\text{S}-\text{B}_2\text{O}_3-\text{SiO}_2$  glass systems are shown in Fig. 5. As for the binary  $\text{Na}_2\text{S}-\text{SiO}_2$  system glass formed by substituting the modifier oxygen in the oxide system glass ( $\text{Na}_2\text{O}-\text{SiO}_2$ ) with sulfide, the peaks ( $Q_n$  in the figure,  $n$ : number of bridging oxygens) attributable to the silicon in the tetrahedral

$\text{SiO}_4$  unit were observed together with the new peaks (black circle in the figure) at a lower magnetic field. These peaks were already confirmed as the signals which belong to the silicon bonding to oxygen and sulfur at the same time [9-12]. The peak intensity of the signal increased with the amount of  $\text{Na}_2\text{S}$  added, and it is suggested that the number of the silicons coordinated to sulfur was on the increase in the glass system. For the glass samples only BO components were observed in the O1s spectra, and only the signals which have a chemical shift around  $-100$  -  $-110$  ppm attributable to  $Q_4$  were observed. On the other hand, for the samples where both BO and NBO component were observed, new peaks were observed in the lower magnetic field region where  $Q_4$  appears. From these results, it is suggested that the continuous  $\text{SiO}_2$  network structure consisting of  $Q_4$  has changed into an open network structure



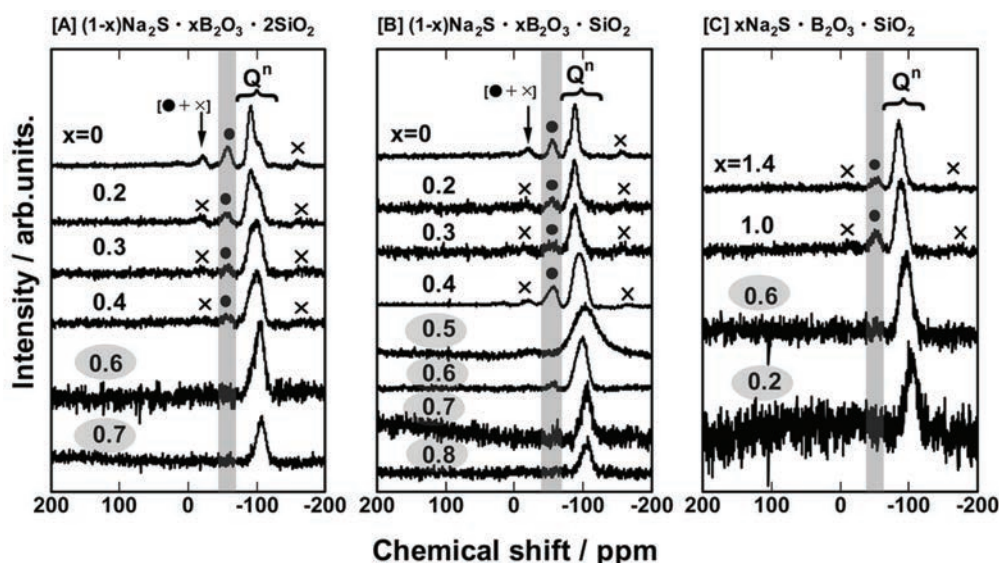


Fig. 5.  $^{29}\text{Si}$  MAS-NMR spectra for  $\text{Na}_2\text{S}$ - $\text{B}_2\text{O}_3$ - $\text{SiO}_2$  glass systems. (X marks in figure represent spinning side band.)

consisting of  $\text{SiO}_4$  tetrahedra with NBO along with the addition of  $\text{Na}_2\text{S}$ .

### Correlation between Glass Structure and Coloration

Correlation between the forming range of the NBO components and sample coloration due to the composition change is shown in Fig. 6. The color of the samples in which only the BO components were observed was colorless, faint blue, blue, and brown. For the samples observed with both BO and NBO components, brown to reddish brown colors were observed. It is shown that the coloration of the samples depended upon the existence of NBO components in the glasses. Furthermore, as for the samples (white triangles in the figure) in the composition range in which NBO components were observed from the  $^{29}\text{Si}$  MAS-NMR measurements, signals which belong to the silicon bonded to sulfur were observed. However, for the samples (white circles in the figure) in the composition range in which only BO components were observed, a signal which belongs to the silicon bonding to sulfur was not observed. According to the above mentioned results, the bonding

of silicon and sulfur in glass can be formed where the glass structure is loose, and it was considered that the bonding of silicon and sulfur in the glass greatly affected the coloration of glass samples.

### Conclusions

The ternary  $\text{Na}_2\text{S}$ - $\text{B}_2\text{O}_3$ - $\text{SiO}_2$  glass systems were prepared by a conventional melt quenching method using an alkali sulfide as a starting material, and their glass forming ranges were also determined. A chemical analysis showed that sulfurs remained in the prepared glass samples, and thus the residual amount of the sulfur and a systematic change of coloration corresponding to a glass composition was observed in this research. From the  $\text{S}2\text{p}$  photoelectron spectra, it was found that the sulfur exists as an anion species having a high ionic bonding character. Also from the  $\text{O}1\text{s}$  photoelectron spectra, it was found that the samples in the composition range in which the non-bridging oxygen components were observed showed a systematic color change as compared to the samples in the composition range in which only the bridging oxygen components were observed. In addition, from the  $^{29}\text{Si}$  MAS-NMR measurements, it was also confirmed that the peak which belong to the silicon coordinated to the sulfur in the glass can be observed for the sample in the composition range in which the non-bridging oxygen is formed. From these results, it can be concluded that the residual sulfur exists without coordinating with the cation, component of the glass network structure, in the case of the composition range in which the amount of  $\text{Na}_2\text{S}$  added was low. However, for the composition range with a larger amount of  $\text{Na}_2\text{S}$ , the glass structure becomes loose and a non-bridging oxygen site is formed in the glass. Therefore, the residual sulfur coordinated with the cation as a component of the glass network structure. It may be considered that the presence of the bonding of

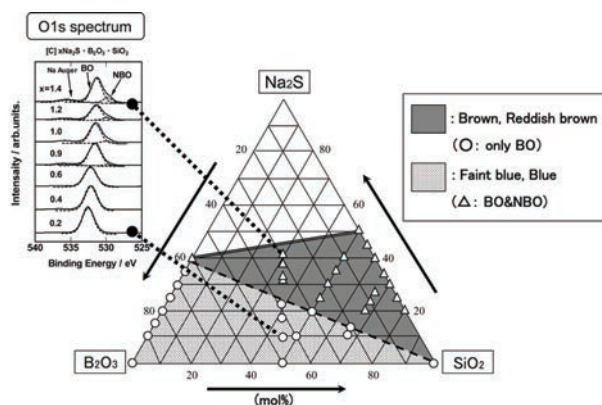


Fig. 6. Correlation between coloration and non-bridging oxygen forming range for  $\text{Na}_2\text{S}$ - $\text{B}_2\text{O}_3$ - $\text{SiO}_2$  glass systems.

the residual sulfur and glass network component cation is closely related to the systematic change in color of the glass samples.

### References

1. P.M. DiBello, *Glass Tech.* 30 (1989) 160-165.
2. Haya, Müller-Simon, *Glass Sci. Technol.* 67 (1994) 297-303.
3. T. Asahi, T. Ino, Y. Miura, T. Nanba and H. Yamashita, *J. Ceram. Soc. Japan.* 106[2] (1998) 150-154.
4. T. Asahi, Y. Miura, H. Yamashita, T. Maekawa, *J. Ceram. Soc. Japan.* 110[6] (2002) 576-582.
5. H.D. Schreiber, S.K. Kozak, P.G. Leonhard and K.K. McManus, *Glastech. Ber.* 60[12] (1987) 389-398.
6. H.D. Schreiber, S.K. Kozak, P.G. Leonhard, K.K. McManus and C.W. Schreiber, *Glastech. Ber.* 61[1] (1988) 5-11.
7. H.D. Schreiber, S.K. Kozak, C.W. Schreiber, D.G. Wetmore and M.W. Riethmiller, *Glastech. Ber.* 63[3] (1990) 49-60.
8. S. Matsumoto, Y. Miura, T. Nanba and A. Osaka, *Proc. 17<sup>th</sup> Int. Congr. Glass.* 3 (1995) 72-77.
9. H. Eckert, Z. Zhang and J.H. Kennedy, *J. Non-Cryst. Solids.* 107 (1989) 271-282.
10. H. Eckert and J.H. Kennedy, *J. Non-Cryst. Solids.* 113 (1989) 287-293.
11. A. Pradel, G. Taillades, M. Ribes and H. Eckert, *J. Non-Cryst. Solids.* 188 (1995) 75-86.
12. K. Hirai, M. Tatsumisago, M. Takahashi and T. Minami, *J. Am. Ceramic. Soc.* 79 (1996) 349-352.