^{29}Si MAS NMR of Na-Si-O-N Oxynitride Glasses

Hidero UNUMA, Hideki MAEKAWA*, Hajime KIYONO*, Katsuyuki KAWAMURA*,
Takashi MAEKAWA*† and Toshio YOKOKAWA*

Government Industrial Development Laboratory, Hokkaido, 2-17, Tsukisamu-Higashi, Toyohira-ku, Sapporo-shi 062

*Department of Chemistry, Faculty of Science, Hokkaido University, Kita-10 Nishi-8, Kita-ku, Sapporo-shi 060

Na-Si-O-N オキシナイトライドガラスの ^{29}Si MAS NMR

鶴沼英郎・前川英己*・清野 肇*・河村雄行*・前川 尚*†・横川敏雄*

北海道工業開発試験所, 062 札幌市豊平区月寒東2条17丁目 2-1

*北海道大学理学部化学科, 060 札幌市北区北10条西8丁目

[Received April 8, 1992; Accepted August 21, 1992]

Local structure around silicon and nitrogen atoms in Na-Si-O-N oxynitride glasses has been studied by means of ^{29}Si MAS NMR spectroscopy. The NMR spectra have been analyzed on the assumption that the resonances of singly nitrated silicate tetrahedra shift towards less shielded direction by about 15 ppm compared with those of non-nitrated ones. It has been estimated that the number of silicon atoms around nitrogen is about 2.5, suggesting that about a half of the total nitrogen atoms may be bonded to two silicon atoms.

Key-words: Oxynitride glass, Structure, ^{29}Si MAS NMR

1. Introduction

Oxynitride glasses contain nitrogen as well as oxygen as anions in glass structure. The density, viscosity, hardness, refractoriness, elastic modulus and glass transition temperature increase and the thermal expansion coefficient decreases with increasing nitrogen content in oxynitride glasses.¹⁻⁴⁾ Oxynitride glasses, therefore, have become of industrially interest as prospective materials such as reinforcing glass fibers,⁵⁾ nuclear waste glasses or joining aids of silicon nitride ceramics.⁶⁾

The change of the properties of glass on nitridation has been explained using a structural model proposed by Mulfing⁷⁾ in which a nitrogen atom is bonded to three network forming (NWF) cations, T, as shown in (1).^{2,3)}

Density and elastic modulus of Ca-Al-Si-O-N⁸⁾ and Na-Ca-Si-O-N⁹⁾ glasses, respectively, were well-explained on the assumption that all the N atoms are coordinated by three NWF atoms. Hater et al.¹⁰⁾ and

Aujla et al.¹¹⁾ deduced the same conclusion from the ^{29}Si NMR measurements on Na-Si-O-N and Y-Al-Si-O-N oxynitride glasses, respectively.

There is a possibility, however, that the following structural groups as well as that of (1) may exist in oxynitride glasses;

in which the nitrogen atom is bonded to two and one NWF cation(s), respectively. Some workers have suggested the existence of the structural groups (2) and/or (3) on the basis of the N1s and O1s XPS measurements for Na-Si-O-N,¹²⁾ Na-Ca-Si-O-N¹³⁾ and Ca-Si-O-N¹⁴⁾ oxynitride glasses and the molecular dynamics (MD) calculations on Na-Si-O-N oxynitride glasses.¹⁵⁾

When nitrogen atoms are incorporated into an oxide glass which has no non-bridging oxygen such as SiO₂ glass, all the nitrogen atoms would substitute for bridging oxygen atoms to form structural group (1) (Eq. (4)).

Little has been known, however, what would happen when nitrogen atoms substitute for non-bridging oxygen in such glasses as alkali-silicate glasses having non-bridging oxygen.

It is important to study the structure of oxynitride glasses to understand better the properties of oxynitride glasses. The purpose of the present study is to investigate the local structure around silicon and nitrogen by means of ^{29}Si MAS NMR spectroscopy.

2. Experimental

2.1 Preparation and analysis of glasses

Two series of oxynitride glasses of the compositions $30\text{Na}_2\text{O} \cdot (70-3x)\text{SiO}_2 \cdot x\text{Si}_3\text{N}_4$ and $20\text{Na}_2\text{O} \cdot (80-3x)\text{SiO}_2 \cdot x\text{Si}_3\text{N}_4$ ($x=0, 2$ and 4) have been prepared. These series will be referred to as 37- and 28-series. The compositions of the former series were

† Present affiliation: Faculty of Engineering, Ehime University, 3, Bunkyo-cho, Matsuyama-shi 790

現在: 愛媛大学工学部応用化学科, 790 松山市文京町 3

comparable with those studied by Hater et al.¹⁰⁾ by ^{29}Si MAS NMR while the nitrogen content has been made higher in the present compositions. The compositions of the latter series were chosen because they were adequate for the NMR measurement, because the peak separation of the NMR spectra could be conducted more quantitatively than in the former series, as described in Chapter 3. The compositions of both series are comparable with those studied by the MD calculations.¹⁵⁾

The oxide parts of the compositions were melted in Pt crucibles in air to prepare base glasses. The base glasses were ground to powders. The mixtures consisting of the base glass powders and calculated amounts of $\beta\text{-Si}_3\text{N}_4$ were melted in molybdenum crucibles at 1400–1500°C for 1 to 3 h under flowing dry nitrogen gas to prepare oxynitride glasses.

Spin-lattice relaxation time (T_1) for Si nucleus in silicate glasses is generally very long (from a few minutes to an hour) and can be accelerated by the spin diffusion from paramagnetic centers. Therefore, 0.05 mol% of Gd_2O_3 was added to all the glasses. It has been confirmed that the addition of this small amount of Gd_2O_3 does not cause any significant change on the NMR spectra.

The oxynitride glasses prepared were analysed for the nitrogen and sodium contents by the Kjeldahl method and the flame emission technique, respectively. The detailed procedure for the Kjeldahl method has been described elsewhere.¹⁶⁾

2.2 ^{29}Si MAS NMR measurement

The ^{29}Si NMR spectra were recorded at room temperature on a Bruker MSL-200 spectrometer operating at 4.7 T (39.76 MHz for ^{29}Si). Glass specimens were ground to powders and were stuffed into alumina or zirconia sample holders. The specimens were spun at the magic angle (54.74°) with respect to the external magnetic field. The spinning rate was 3500 Hz. A pulse width of 3 μs and dead time of 20 μs were used. Typical repetition interval was 2.5 s and spectrum was accumulated 1000 times. Tetramethylsilane (TMS) was used as a shift reference for ^{29}Si . An external chemical shift standard, Q8M8, was used as a secondary standard whose chemical shift

(M site) was 11.51 ppm from TMS.

3. Results

3.1 Analysis of glasses

The glasses obtained were free from crystalline phases as examined by the powder X-ray diffraction analysis. The analyzed compositions are shown in Table 1. The retention of nitrogen ranged from 80 to 90% of the calculated content of the batch. Sodium was slightly lost (1.2 mol% at most) during the melting under flowing nitrogen. The deviation of the sodium content from the batch was taken into account on analyzing NMR spectra as described in Chapter 4.

3.2 NMR spectra

Figure 1 shows the ^{29}Si NMR spectra of the glasses. Each spectrum was analyzed by separating it to an appropriate number of Gaussian curves (peak separation). The best fit was searched for by varying the peak position, linewidth and amplitude of the Gaussians. As indicated in Figs. 1(a) and (b), each Gaussian curve was assigned to Q_n (or Q_n') depending on the peak position. The notation Q_n represents $[\text{SiO}_4]$ silicate tetrahedral unit containing n bridging oxygen. The notation Q_n' is used for nitrated glasses to distinguish the peaks from those of non-nitrated glasses. The percentage of the Q_n' species present in the glasses, $W[Q_n']$, is obtained from the relative intensity area of each Gaussian curve.

Table 2 summarizes the analysis of the NMR spectra. The peak separation could be conducted more quantitatively for the 28-series than for the 37-series since the overlap of the peaks of Q_4' and Q_2' with the main peak of Q_3' is more extensive in the latter series, which leads to some ambiguity in peak separation. The present analysis of the non-nitrated glasses (37-0 and 28-0) is consistent with a previous study.¹⁷⁾

It is clearly recognized from Fig. 1 and Table 2 that the intensities of less shielded peaks (those of less negative chemical shifts) increase with increasing nitrogen content, that is, $W[Q_1']$ and $W[Q_2']$ increase and $W[Q_4']$ decreases. The line width of each peak slightly increases with increasing nitrogen content.

Table 1. Analyzed compositions of glasses.

Sample	Na_2O (mol%)	SiO_2 (mol%)	$\text{SiN}_{4/3}$ (mol%)	N (at%)	N (wt%)
37-0	30.0	70.0	0	0	0
37-2	29.9	65.7	4.4	2.0	1.4
37-4	28.9	62.6	8.5	3.9	2.7
28-0	20.0	80.0	0	0	0
28-2	18.8	76.5	5.2	2.3	1.6
28-4	18.9	71.7	9.4	4.3	3.0

Fig. 1. ^{29}Si MAS NMR spectra of glasses; (a) 37-0, (b) 37-2, (c) 37-4, (d) 28-0, (e) 28-2 and (f) 28-4. See Table 1 for the notations of the samples.

Table 2. Observed chemical shifts (σ (ppm)), line width (half-width at half maximum: hwhm (ppm)) and Q_n distributions ($W(\%)$) in oxynitride glasses.

Sample	Q_4			Q_3			Q_2			Q_1		
	$-\sigma$	(hwhm)	W	$-\sigma$	(hwhm)	W	$-\sigma$	(hwhm)	W	$-\sigma$	(hwhm)	W
37-0	101.5	(6.2)	19.4	90.1	(4.8)	75.2	78.9	(4.0)	5.4	-	-	-
37-2	103.0	(6.9)	16.8	89.9	(5.4)	71.8	79.0	(4.9)	8.6	71.0	(4.0)	2.7
37-4	101.2	(6.0)	13.8	89.5	(5.4)	65.0	78.5	(4.9)	16.8	70.0	(4.0)	4.4
28-0	105.6	(6.5)	50.0	92.2	(5.6)	48.0	78.0	(4.0)	3.0	-	-	-
28-2	105.4	(7.1)	44.2	91.0	(6.3)	45.9	79.5	(6.0)	8.7	67.0	(6.0)	1.2
28-4	104.7	(7.1)	38.8	89.8	(6.6)	44.7	78.5	(5.6)	12.7	67.5	(6.0)	3.9

4. Discussion

The increases in $W[Q_1']$ and $W[Q_2']$ and decrease in $W[Q_4']$ on nitridation should be caused by the substitution of oxygen by nitrogen in silicate tetrahedral units. In the present discussion, a semi-quantitative interpretation of the changes of $W[Q_n']$ on nitridation will be attempted employing the number of silicon atoms around nitrogen (referred to as M_{Si}) as a parameter.

It may be reasonably expected that the predominant silicate tetrahedral unit containing nitrogen present in the oxynitride glasses would be singly nitrated one, $[\text{SiNO}_3]$. However, the available NMR data of the silicate tetrahedral units containing nitrogen are only those of $[\text{SiN}_4]$ and $[\text{SiN}_3\text{O}]$ deter-

mined from crystalline α - and β - Si_3N_4 and $\text{Si}_2\text{N}_2\text{O}$, respectively.^{18),19)} Therefore, we introduced the following working hypotheses to analyze the present NMR spectra.

(a) The substitution of an oxygen atom in a $[\text{SiO}_4]$ tetrahedron by nitrogen atom causes a change of the chemical shift of the resonance of the tetrahedron by about +15 ppm.

This working hypothesis was withdrawn from the comparison of the chemical shifts of Si nuclei in β - Si_3N_4 (-48 ppm, $[\text{SiN}_4]$ unit), $\text{Si}_2\text{N}_2\text{O}$ (-63 ppm, $[\text{SiN}_3\text{O}]$ unit),^{18),19)} and quartz (-107 ppm, $[\text{SiO}_4]$ unit). This working hypothesis would be supported by the fact that the NMR spectra of the nitrated glasses could be successfully separated to the Gaussi-

ans located at about -105 , -90 , -77 and -67 ppm, with only a little increase in the line width. Since the change of the chemical shift by $+15$ ppm is very close to that caused by the substitution of a bridging oxygen by a non-bridging oxygen, the resonances of singly nitrated Q_n (denoted as $Q_n(1N)$) would appear in the similar positions to those of non-nitrated Q_{n-1} . Then, each observed NMR peak of the nitrated glasses, Q_n' , would be regarded to be a sum of $Q_n(0N)$ and $Q_{n+1}(1N)$, i.e., $W[Q_4'] = W[Q_4(0N)]$, $W[Q_3'] = W[Q_3(0N)] + W[Q_4(1N)]$, $W[Q_2'] = W[Q_2(0N)] + W[Q_3(1N)]$, and so on.

(b) A nitrogen atom of structural group (2), if any, accompanies a Na^+ ion as charge compensator as shown below;

This working hypothesis was withdrawn from the analogy of the charge compensation of non-bridging oxygen in oxide glasses. In other words, it was considered that the nitrogen atom of structural group (2) may be formed when nitrogen atoms substitute for non-bridging oxygen atoms (Eq. (5)).

On the bases of above working hypotheses, the distribution of $W[Q_n']$ in the nitrated glasses was calculated as described below, varying the parameter M_{Si} .

When a part of oxygen atoms are substituted by nitrogen atoms in a Na_2O - SiO_2 glass having a known distribution of $W[Q_n]$, the percentage of singly nitrated Q_n would be $N_{Si-N} \cdot W[Q_n]$, where N_{Si-N} represents the number of Si-N bonds in a unit formula. N_{Si-N} is equivalent to $(4/3) \cdot X_{SiN_{4/3}} \cdot M_{Si}$, where $X_{SiN_{4/3}}$ represents the mol% of $SiN_{4/3}$ as shown in Table 1. Then, the percentage of singly- and non-nitrated Q_n species ($W[Q_n(1N)]$ and $W[Q_n(0N)]$, respectively) would be expressed as follows;

$$W[Q_n(1N)] = W[Q_{n,ref}] \cdot (4/3) \cdot X_{SiN_{4/3}} \cdot M_{Si} \quad (6)$$

$$W[Q_n(0N)] = W[Q_{n,ref}] - W[Q_n(1N)] \quad (7)$$

where $W[Q_{n,ref}]$ represents the percentage of Q_n in a glass of the composition $(X_{Na_2O} - (3 - M_{Si}) \cdot X_{SiN_{4/3}} \cdot (4/3))Na_2O \cdot (X_{SiO_2} + X_{SiN_{4/3}})SiO_2$ (which will be referred to as "reference glass"). The reference glass has less sodium content than the corresponding non-nitrated composition of the nitrated glass by the content of the nitrogen atom of type (2), because each nitrogen atom of structural group (2) accompanies one Na^+ ion as charge compensator, based on hypothesis (b). $W[Q_{n,ref}]$ can be calculated using the equilibrium constant k_3 (0.02) for the following reaction:¹⁷⁾

When the parameter M_{Si} is set at a value not larger than 3, the corresponding distribution of $W[Q_n']$ can be calculated unequivocally from the analyzed nitrogen and Na_2O contents.

Figure 2 shows the result of the calculation of $W[Q_n']$ for the 28-series. Solid circles represent the measured values. Figure 2 indicates that the measured $W[Q_n']$ are well explained when M_{Si} is set at 2.5.

Figure 3 shows the result of the calculation of the ratio $W[Q_2']/W[Q_4']$ for the 37-series. The data of Hater et al.¹⁰⁾ are also plotted in the figure as open circles, which were measured for Na-Si-O-N oxynitride glasses having about 30 mol% of Na_2O . Since the accuracy of the peak separation of the 37-series is poorer than that of the 28-series especially when

Fig. 2. Calculation of the change of $W[Q_n']$ in the glasses of 28-series as a function of nitrogen content, in which the mean for the number of silicon atoms coordinated to a nitrogen atom is 3 (—), 2.5 (---) and 2 (— · —). Solid circles represent the measured values.

Fig. 3. Calculation of the change of $W[Q_2']/W[Q_4']$ in the glasses of 37-series as a function of nitrogen content, in which the mean for the number of silicon atoms coordinated to a nitrogen atom is 3 (—), 2.5 (---) and 2 (— · —). Solid circles represent the measured values. Open circles represent the data of Hater et al.¹⁰⁾

Fig. 4. Calculation of the change of the weighed mean of $W[Q_n]$ of the glasses, in which the mean for the number of silicon atoms coordinated to a nitrogen is 3 (—), 2.5 (---) and 2 (— · —). Solid circles represent the measured values.

the nitrogen content is low, M_{Si} is close to 2 for 37-2 while that is close to 3 for the data of Hater et al. However, for the more highly nitrated glass (37-4), the measured value is well explained when M_{Si} is set at 2.5.

Figure 4 shows the change of weighed mean for $W[Q_n]$ (mean n ; mean number of bridging oxygen atoms in a silicate tetrahedron) for the 28- and 37-series as a function of the nitrogen content. The measured values of mean n are well explained when M_{Si} is set at 2.5.

The results shown in Figs. 2 to 4 suggest that about a half of total nitrogen atoms may be those of structural group (1) and the rest may be those of structural group (2). According to Eq. (5), M_{Si} should increase with decreasing Na_2O content. The MD calculations conducted by the present authors¹⁵⁾ have shown that M_{Si} of the 37- and 28-series is ca. 2.1 and 2.3, respectively, indicating the dependence of M_{Si} on the Na_2O content. On the other hand, the dependence of M_{Si} on the Na_2O content were not clearly detected in the present study. However, the results of the MD calculations and the present NMR are in close accordance with each other on the point that a part of nitrogen atoms are of structural group (2).

N1s XPS measurements^{12),13)} on Na-Si-O-N and Na-Ca-Si-O-N oxynitride glasses indicated that there are at least two kinds of nitrogen atoms in different structural groups. These nitrogen atoms may correspond to those of structural groups (1) and (2).

The factors causing the ambiguity in the present analysis of the NMR spectra would be: (1) absence of the treatment of multiply nitrated silicate tetrahedra, (2) absence of the estimation of the difference in the shielding effects of different types of

nitrogen atoms on neighboring silicon nuclei, (3) the poor quantitativity of peak separation of Q_2' and Q_1' and (4) limited solubility of nitrogen into glass.

5. Conclusions

The local structure around silicon and nitrogen atoms in Na-Si-O-N oxynitride glasses has been investigated by ^{29}Si MAS NMR spectroscopy. The change of the NMR spectra on nitrification of the glasses have been analyzed on the assumption that the resonances of singly nitrated silicate tetrahedra shift towards less shielded direction by about 15 ppm, employing the number of silicon atoms around nitrogen as a parameter. The NMR spectra of the nitrated glasses are well explained when the parameter is set at 2.5, suggesting that about a half of total nitrogen atoms may be bonded to two silicon atoms. It has been considered that the nitrogen atoms bonded to two silicon atoms may form when nitrogen atoms substitute for non-bridging oxygen atoms.

References

- 1) S. Sakka, *Ann. Rev. Mater. Sci.*, **16**, 29-46 (1986).
- 2) S. Hampshire, R. A. L. Drew and K. H. Jack, *Phys. Chem. Glasses*, **26**, 182-86 (1985).
- 3) R. E. Loehman, *J. Non-Cryst. Solids*, **56**, 123-34 (1983).
- 4) D. R. Messier, *Rev. Chim. Miner.*, **22**, 518-33 (1985).
- 5) D. R. Messier, R. P. Gleisner and R. E. Rich, *J. Am. Ceram. Soc.*, **72**, 2183-86 (1989).
- 6) D. N. Coon, R. L. Tallman and R. M. Neilson, Jr., *Adv. Ceram. Mater.*, **3**, 154-58 (1988).
- 7) H.-O. Mulfinger, *J. Am. Ceram. Soc.*, **49**, 462-67 (1966).
- 8) S. Sakka, K. Kamiya and T. Yoko, *J. Non-Cryst. Solids*, **56**, 147-52 (1983).
- 9) C. Schrimpf and G. H. Frischat, *J. Non-Cryst. Solids*, **56**, 153-60 (1983).
- 10) W. Hater, W. Mueller-Warmuth and G. H. Frischat, *Glastech. Ber.*, **62**, 328-35 (1989).
- 11) R. S. Aujla, G. Leng-Ward, M. H. Lewis, E. F. Seymour, G. A. Styles and G. W. West, *Phil. Mag. B*, **54**, L51-56 (1986).
- 12) R. K. Brow and C. G. Pantano, *J. Am. Ceram. Soc.*, **67**, C72-74 (1984).
- 13) J. G. Clabes, R. E. Fern and G. H. Frischat, *J. Vac. Sci. Technol.*, **A4**, 1580-84 (1986).
- 14) T. Hanada, N. Ueda and N. Soga, *Seramikkusu Ronbunshi (J. Ceram. Soc. Japan)*, **96**, 284-91 (1988).
- 15) H. Unuma, K. Kawamura, N. Sawaguchi, H. Maekawa and T. Yokokawa, "Science and Technology of New Glasses", Proc. of Int'l Conf. on Sci. and Technol. of New Glasses, Tokyo, October, 1991, Ed. by S. Sakka and N. Soga, Ceramic Society of Japan, Tokyo (1991) pp. 341-46; Idem, submitted to *J. Am. Ceram. Soc.*
- 16) K. Kamiya, M. Ohta and T. Yoko, *J. Non-Cryst. Solids*, **83**, 208-22 (1986).
- 17) H. Maekawa, T. Maekawa, K. Kawamura and T. Yokokawa, *J. Non-Cryst. Solids*, **127**, 53-64 (1991).
- 18) R. Dupree, M. H. Lewis, G. Leng-Ward and D. S. Williams, *J. Mater. Sci. Lett.*, **4**, 393-95 (1985).
- 19) K. R. Carduner, C. S. Blackwell, W. B. Hammond, F. Reidinger and G. R. Hatfield, *J. Am. Chem. Soc.*, **112**, 4676-79 (1990).