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STUDIES ON THE STRUCTURE AND PROPERTIES OF OXYNITRIDE GLASSES

HIDERO UNUMA

1992

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CONTENTS

GENERAL INTRODUCTION

This thesis presents a series of studies on the structure
and properties of oxynitride glasses. Oxynitride glasses
contain nitrogen as well as oxygen as anions in glass structure.
In other words, oxynitride glasses are formed when a part of
oxygen atoms in oxide glasses are substituted by nitrogen atoms.

In oxide glasses, most properties such as chemical
durability, electrical conductivity. crystallization behavior and
mechanical properties vary with a change of the cationic
composition. So far, the properties of oxide glasses have been
designed by the proper selection of cationic species.

The substitution of oxygen atoms by another anion is an
alternative method to change the properties of oxide glasses.
The substitution of fluorine for a part of oxygen promotes the
phase separation[1] and reduces the refractive index of the oxide
glass. The substitution of chalcogens for all the oxygen may
induce the electronic conductivity. Both the elements, however,
weaken the glass networks. It is interesting to see that, in
contrast to halogens and chalcogens, nitrogen strengthens the
glass when it is incorporated in the glass network.

Elmer and Nordberg[2] and Mulfinger et al.[3, 4] attempted
the nitridation of oxide glasses for the first time. Elmer and
Nordberg heat-treated a porous silica glass in ammonia, producing
nitrided silica glasses. The resultant glasses showed an
increased stability to devitrification. Mulfinger et al. melted
$Na_2O\text{-}CaO\text{-}SiO_2$ glasses in ammonia, producing nitrogen-containing
soda-lime-silica glasses. For melting a batch of the
composition $2La_2O_3 \cdot SiO_2 \cdot Si_3N_4$. Makishima et al.[5] used high
nitrogen pressure to prevent the thermal decomposition of Si_3N_4.
The resultant La-Si-O-N oxynitride glass containing 18.2 at%

nitrogen showed an excellent chemical durability and transmittance. Kamiya et al.[6] heat-treated silica gel fibers derived from methyltriethoxysilane, $CH_3Si(OC_2H_5)_3$, under a flow of ammonia and obtained Si-O-N glass fibers containing 6 wt% nitrogen, which exhibited an improved chemical durability to alkaline solution.

The glass transition temperature, density, elastic modulus and refractive index increase and the thermal expansion coefficient decreases on incorporation of nitrogen in oxide glasses[7]. Therefore, oxynitride glasses are attracting much attention as prospective materials for industrial use, such as fibers for reinforcing plastics, protective coatings on metals, materials for hermetic sealing of electronic circuits and glasses for solidification of nuclear waste.

The nitrogen atoms incorporated in the glass network form Si-N bonds[5, 8, 9]. It is generally believed that nitrogen atoms may be bonded to three network forming cations. The change of properties, such as the increased density and hardness on nitridation, has been interpreted by the formation of the nitrogen atoms bonded to three network forming cations. Murakami and Sakka[10] have shown on the basis of the ab initio molecular orbital calculation that the Si-N bonds have more covalent nature than Si-O bonds and the bending force constant for the $N[Si(-O-)_3]_3$ is much higher than that of Si-O-Si bonds, to which an increased elastic modulus of oxynitride glasses has been attributed.

In order to apply oxynitride glasses as industrial materials, it is essential to investigate the physical and chemical properties of oxynitride glasses which still remain unclear. In addition, it is essential to understand the effect of nitrogen on the properties of glass from the structure of

glass and the nature of the bonds between nitrogen and other elements.

In this thesis, results of investigations on the structure and properties of oxynitride glasses are described. The structure of oxynitride glasses is discussed in relation to the composition. Effects of addition of nitrogen on the electrical and chemical properties, liquid-liquid phase separation and crystallization are described. Also, the interaction of an oxynitride glass with metals is discussed to find the applicability of oxynitride glasses to preparation of glass-metal composites.

In Chapter 1, molecular dynamics studies on the structure of Na-Si-O-N oxynitride glasses are described. A special attention is focused on the local structure around the nitrogen atoms in relation to the composition. The dependences of the density, bulk modulus and bulk thermal expansion coefficient on the composition are also studied and compared with those observed in the real glasses.

In Chapter 2, ^{29}Si nuclear magnetic resonance (NMR) investigations on the structure of Na-Si-O-N oxynitride glasses are described. The results are compared with those described in Chapter 1.

In Chapter 3, the electrical conductivity of Na-Si-O-N and Li-Si-O-N oxynitride glasses are described. The effect of nitrogen on the conductivity and activation energy for conduction is discussed from the viewpoint of the change of the covalency of the bonds in the glass network on nitridation.

In Chapter 4, the chemical durability of Na-Si-O-N and Li-Si-O-N oxynitride glasses is described. The effect of nitrogen on the chemical durability is discussed in relation to the change of the covalency of the bonds in the glass network and the diffusivity of ions in the glasses on nitridation.

In Chapter 5, the liquid-liquid phase separation in Li-Si-O-N oxynitride glasses are described. The effect of nitrogen on the phase separation is discussed in relation to the change of the covalency of the bonds in the glass network.

In Chapter 6, the crystallization of Li-Si-O-N and Li-Al-Si-O-N oxynitride glasses is described. The effect of nitrogen on the crystallization temperature, precipitated crystalline phases and nucleation mechanism is discussed. The properties of the resultant Li-Al-Si-O-N glass-ceramics including the density, hardness and thermal expansion coefficient are also described.

In Chapter 7, the interaction of a Na-Si-O-N oxynitride glass with nickel, iron and chromium metals is described. The reactivity of the oxynitride glass with the metals is discussed on the basis of the thermodynamics of the reactions between silicon nitride and the metals.

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CHAPTER 1   Molecular Dynamics Study on the Structure of Na-Si-O-N Oxynitride Glasses

INTRODUCTION

Substitution of a part of oxygen atoms in oxide glasses by nitrogen atoms changes the physical and chemical properties of the glasses to a considerable extent[1-3].   The density, hardness, elastic modulus, viscosity and glass transition temperature increase with increasing nitrogen content, and the thermal expansion coefficient decreases.   The chemical durability to acidic and alkaline solutions is drastically improved by the incorporation of nitrogen[4].   These changes of the properties suggest that the network of glass is strengthened and tightened by the incorporation of nitrogen.

The properties of oxynitride glasses have been interpreted by many authors[1-8] using a structural model proposed by Mulfinger[9], in which each nitrogen atom is bonded to three network forming (NWF) cations as shown in (1);

$$\equiv T-N-T\equiv$$
$$|$$
$$T$$
$$|||$$
(1)

In silicate oxynitride glasses, for example, this structural model means that a nitrogen atom makes three silicate tetrahedra, $[SiO_{4-m}N_m]$, connected with each other at the corners.   When such a structural group is formed, the glass network would become compact and the bonds between Si and the anions would be strengthened on the average.

The structural group (1) has been proved to exist in oxynitride glasses by means of IR[10, 11], ^{29}Si NMR[12, 13] and N_{1s} XPS[11, 14] spectroscopies and the analyses of the structure

from the data of density[6] and Young's modulus[7].

On the other hand, recent studies on the coordination state of nitrogen atoms by ^{15}N MAS NMR[15] and XPS[11, 14, 16, 17] spectroscopies and the neutron diffraction technique[18] have shown that, in addition to structural group (1), the following structural groups (2) and (3) may also exist in oxynitride glasses, in which a nitrogen atom is bonded to two or one NWF cation(s), respectively.

$$\equiv T-N^{-}-T\equiv \tag{2}$$

$$\equiv T-N^{2-} \tag{3}$$

The studies cited above were carried out on the glasses of various cationic compositions. The structure of oxynitride glasses may vary depending on the composition. In order to understand better the properties of oxynitride glasses, it is essential to investigate the structure in relation to the composition.

The molecular dynamics (MD) calculaitons have been employed to study the structure of inorganic glasses[19, 20], melts[21, 22] and crystals[23, 24], which give numerous informations on the structure such as bond angle distribution and pair correlation function. The advantage of the MD calculations is that the dynamic properties such as elastic behavior, viscosity and diffusion phenomena can also be simulated[25, 26].

In the present chapter, the local structure around nitrogen atoms in Na-Si-O-N oxynitride glasses studied by the MD calculations has been described with respect to its dependence on the composition. The dependences of the properties such as the density, bulk thermal expansion coefficient and bulk modulus on the nitrogen content have been compared with those observed in

the real system to examine the validity of the calculations.

MOLECULAR DYNAMICS CALCULATION

Two series of glasses were studied.   The compositions were
$30Na_2O \cdot (70-3x)SiO_2 \cdot xSi_3N_4$ (x=0, 2, 5 and 10) for one series and
$yNa_2O \cdot (85-y)SiO_2 \cdot 5Si_3N_4$ (y=30, 20 and 15) for the other series.
These two series of compositions were selected to examine the
effects of the nitrogen and sodium contents, respectively.
The pair potential used was the Busing approximation of
Born-Mayer-Huggins form (4)[19, 21, 22, 25].

$$\Phi_{ij} = f_0(b_i+b_j)\exp\{(a_i+a_j-r)/(b_i+b_j)\} + Z_iZ_je^2/4\pi\varepsilon_0 r \qquad (4)$$

where r is the distance between atoms, ε_0 is the dielectric
constant, e is the electron charge (unit:C), Z_i is the valence of
ith atom, and $f_0 = 6.9472 \times 10^{-11}$ N. a_i and b_i are the
potential parameters which are related to the size and softness
of ith atom, respectively.   The potential parameters of each
atom were empirically determined to reproduce two or more crystal
structures comprising each atom such as quartz, cristobalite,
$Na_2Si_2O_5$, Na_2SiO_3, Si_2N_2O and Si_3N_4.   The values of the
parameters are shown in Table 1.   Three dimensional periodic
boundary conditions were applied to the basic cells containing
1260 to 1350 atoms.   The computations were initiated from a
random distribution of the atoms in the basic cells.   The
equation of motion was integrated at the time intervals of 1.5 to
2.5 fs.   A constant pressure of 0.0001 GPa and constant
temperatures of 4000, 3000, 2500, 2000, 1500 and 1000 K were
achieved and the systems were kept at each temperature for 20 to
100 ps.   The structural data were accumulated at 1000 K.

Table 1   The parameter set used

in the present calculations.

	Z	a (Å)	b (Å)
Si	4	1.012	0.080
Na	1	1.260	0.080
O	-2	1.626	0.085
N	-3	1.713	0.080

The bulk thermal expansion coefficient between 1000 and 2000 K, β, was calculated from the change of the cell volume using equation (5).

$$\beta \quad = \quad (dV/V_0 dT)_{T,P} \tag{5}$$

The bulk modulus, K, was calculated from the change of the cell volume between 0.0001 and 1.0 GPa using equation (6).

$$K \quad = \quad 1/(-dV/V_0 dP)_{T,P} \tag{6}$$

RESULTS

(1) Local structure around nitrogen atoms

Table 2 shows the distribution of the number of silicon atoms bonded to a nitrogen atom together with the mean value (M_{Si}). Nitrogen atoms bonded to n silicon atoms will be denoted as $N_{(n)}$. $N_{(3)}$, $N_{(2)}$ and $N_{(1)}$ correspond to structural groups (1), (2) and (3), respectively. As can be seen from Table 2, $N_{(2)}$ is the predominant species in all the glasses, and $N_{(3)}$ being the second major species. $N_{(1)}$ is the minor species. The ratio of $N_{(2)}$ atoms to the total nitrogen atoms ranges from 59 to 78%. M_{Si} ranges from 2.4 to 2.1, decreasing with increasing Na_2O content.

Fig. 1 shows the distribution of the bond angles of <Si-O-Si and <Si-N-Si in $30Na_2O \cdot 40SiO_2 \cdot 10Si_3N_4$ glass. The <Si-O-Si bond angle distributes from 130 to 180 degree (solid line). On the other hand, the <Si-N-Si bond angle exhibits a bimodal distribution around 105-135 degree and 140-170 degree (broken line), roughly corresponding to $N_{(3)}$ and $N_{(2)}$, respectively.

Fig. 2 shows the pair correlation functions of the pairs of constituting atoms of $30Na_2O \cdot 70SiO_2$ and $30Na_2O \cdot 40SiO_2O \cdot 10Si_3N_4$

Table 2   Distribution of the nitrogen atoms bonded to one, two and three silicon atoms ($N_{(1)}$, $N_{(2)}$ and $N_{(3)}$, respectively) and the mean of the number of silicon atoms bonded to a nitrogen atom (M_{Si}).

glass	$N_{(1)}$ (%)	$N_{(2)}$ (%)	$N_{(3)}$ (%)	M_{Si}
\multicolumn				

glass	$N_{(1)}$ (%)	$N_{(2)}$ (%)	$N_{(3)}$ (%)	M_{Si}
\multicolumn: $30Na_2O.(70-3x)SiO_2.xSi_3N_4$ series				
x=2	2.8	77.8	19.4	2.17
x=5	13.5	61.8	24.7	2.11
x=10	6.2	64.7	29.1	2.23
$yNa_2O.(85-y)SiO_2.5Si_3N_4$ series				
y=30	13.5	61.8	24.7	2.11
y=20	0.0	74.0	26.0	2.26
y=15	0.0	58.7	40.3	2.41
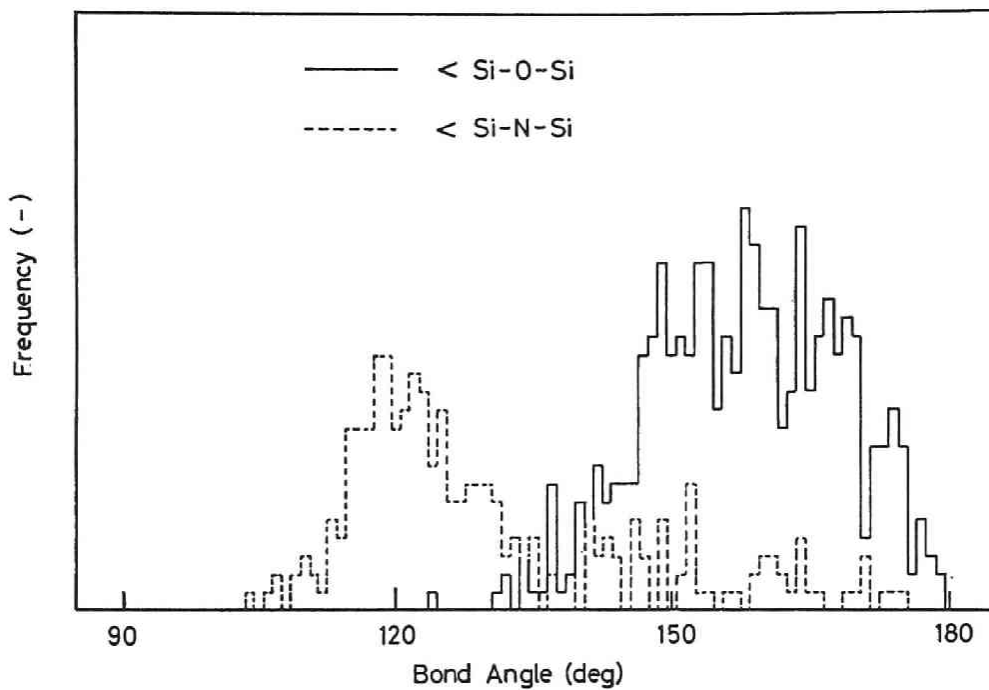
Fig. 1   The bond anlge distribution of <Si-O-Si (solid
         line) and <Si-N-Si (broken line) in
         $30Na_2O \cdot 40SiO_2 \cdot 10Si_3N_4$ glass.
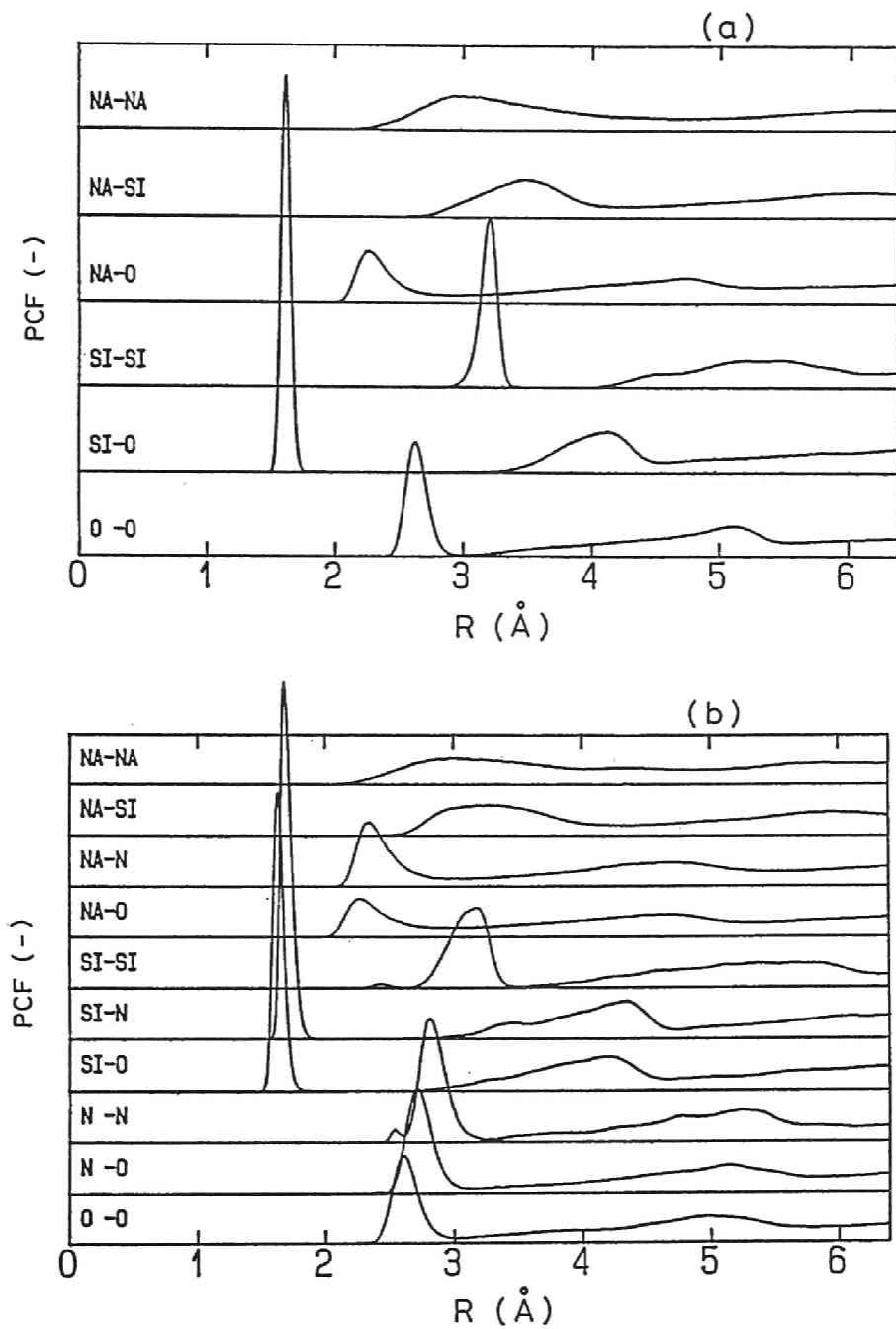
Fig. 2　The pair correlation functions for (a) $30Na_2O \cdot 70SiO_2$ and (b) $30Na_2O \cdot 40SiO_2 \cdot 10Si_3N_4$ glasses.

glasses.   The bond lengths of Si-O and Si-N are about 1.63 and
1.70 Å, respectively.   The Si-Si distance in the latter glass
is shortened compared with that in the former glass.

(2) Density

Fig. 3 shows the change of the calculated density of
$30Na_2O \cdot (70-3x)SiO_2 \cdot xSi_3N_4$ glasses as a function of temperature.
At any given temperature, the density increases with increasing
nitrogen content.

The density slowly decreases with increasing temperature in
the temperature region lower than about 2000 K, and then it
decreases a little more rapidly with increasing temperature in
the temperature region higher than about 2000 K.

(3) Bulk thermal expansion coefficient

Fig. 4 shows the variation of the bulk thermal expansion
coefficient, β, of $30Na_2 \cdot (70-3x)SiO_2 \cdot xSi_3N_4$ glasses with
nitrogen content.   The values of β measured at room temperature
in the real glasses are also plotted in the figure.   The
calculated β at first decreases, showing a minimun at about 7
at%, and then increases with increasing nitrogen content.   The
decrease in the calculated β with increasing nitrogen content
for the glasses of low nitrogen contents is consistent with that
measured in the real glasses.

(4) Bulk modulus

Fig. 5 shows the change of the bulk modulus, K, as a
function of the nitrogen content.   K increases almost linearly
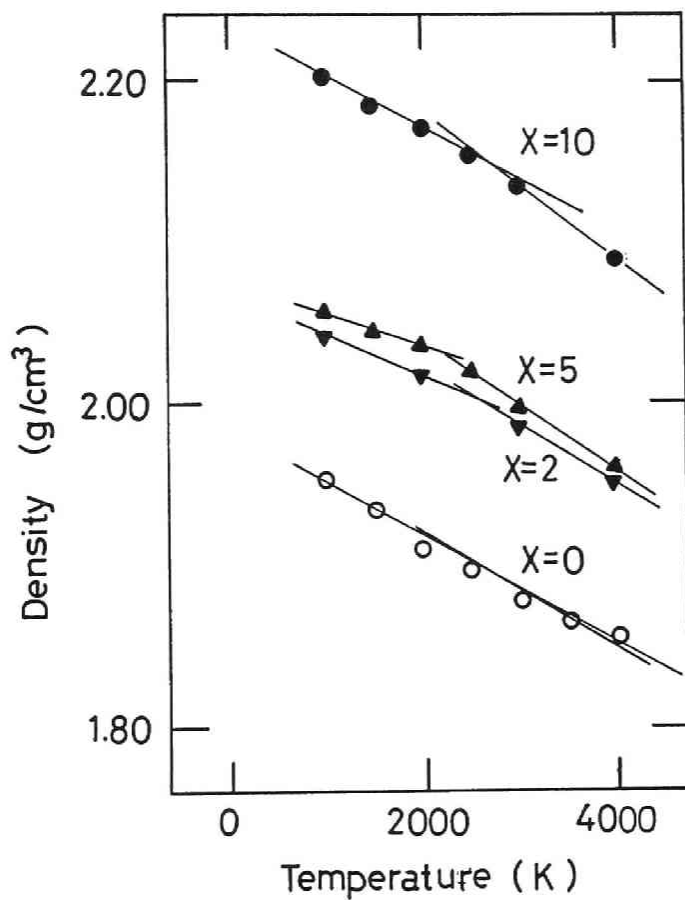with increasing nitrogen content.

Fig. 3   Change of the calculated density of
30Na$_2$O·(70-3x)SiO$_2$·xSi$_3$N$_4$ glasses as a function of
temperature.
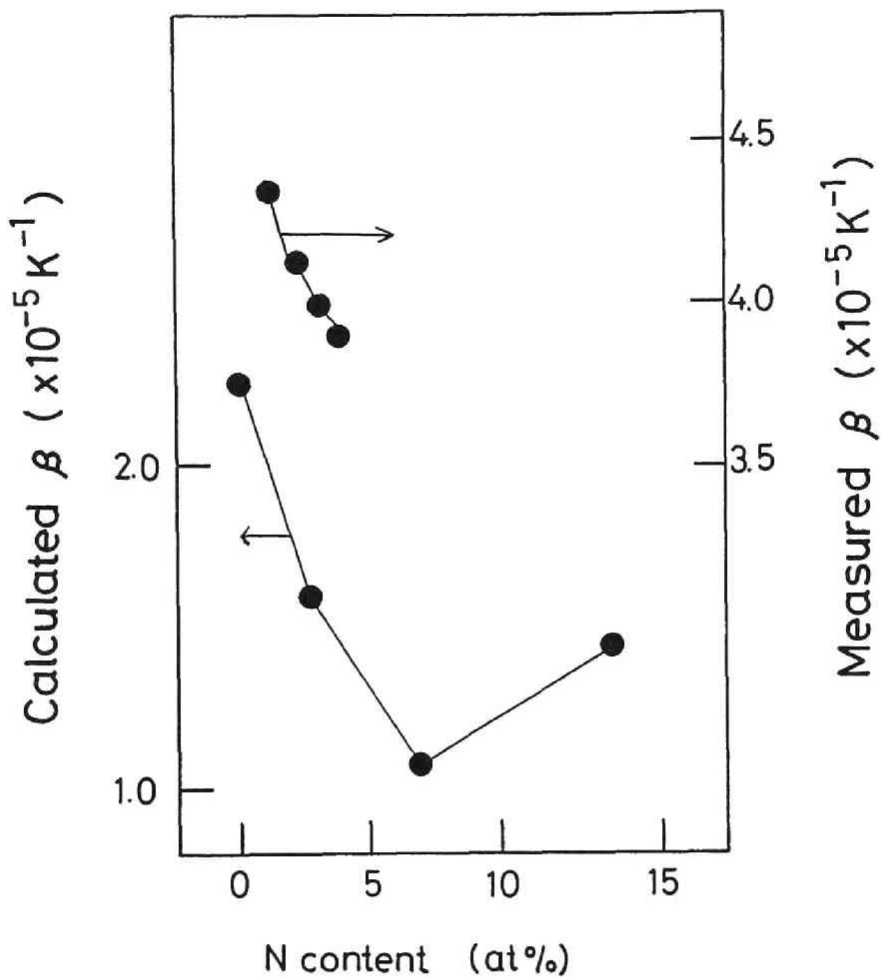
Fig. 4　Variation of the calculated bulk thermal expansion
coefficient, β, of $30Na_2O \cdot (70-3x)SiO_2 \cdot xSi_3N_4$
glasses with the nitrogen content.　Measured
values are also plotted in the figure.

Fig. 5   Change of the calculated bulk modulus, K, of
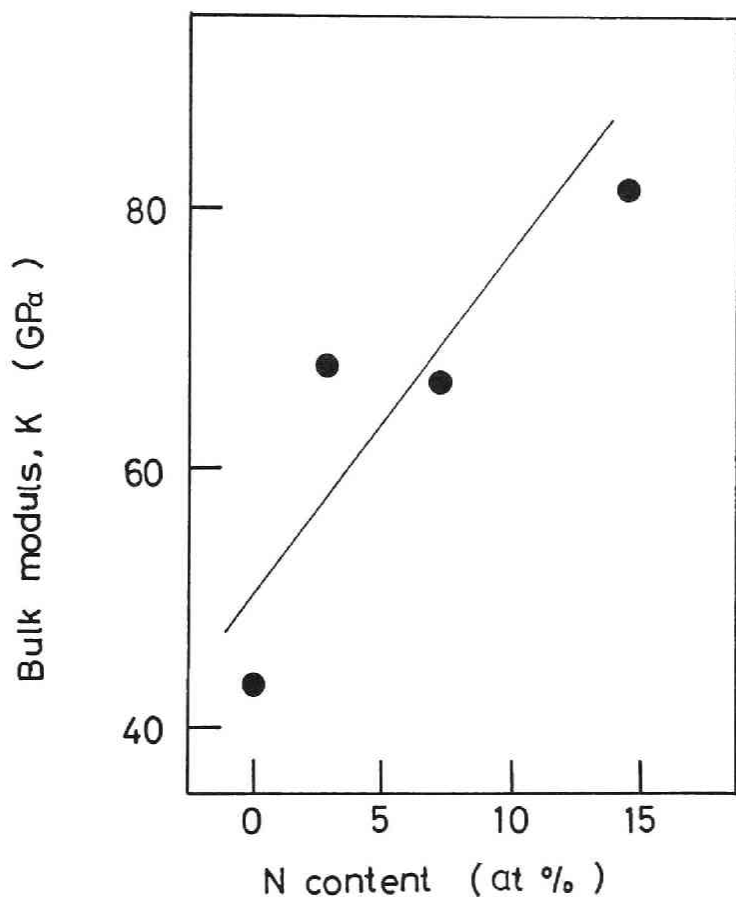$30Na_2O \cdot (70-3x)SiO_2 \cdot xSi_3N_4$ glasses as a function of
the nitrogen content.

DISCUSSION

(1) Local Structure around nitrogen atoms

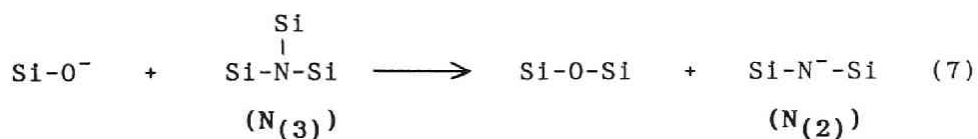It is well known that the bond angle of <Si-O-Si distributes
in a wide range between 120 and 180 degree and the length of Si-O
bond is about 1.62 Å in SiO_2 glass[27].   The MD calculation
using the present pair potential can reproduce the pair
distribution function and the interference function for the
neutron scattering for $Na_2O \cdot 2SiO_2$ glass[25].   Hence, the present
results on the bond length of Si-O and the angle distribution of
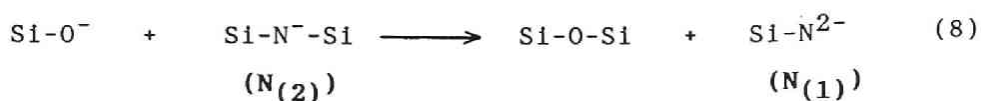<Si-O-Si appears to be reasonable.

The local structure around nitrogen atoms may be compared
with the result of the _ab initio_ molecular orbital (MO)
calculations on model molecules quarried from the framework
structure of silicon oxynitride glass conducted by Murakami and
Sakka[28].   They used the molecules $N[Si(OH)_3]_3$ and
$(OH)_3SiNHSi(OH)_3$ to represent the nitrogen atoms bonded to three
and two silicon atoms, respectively.   The nitrogen atoms in
these molecules can be compared with $N_{(3)}$ and $N_{(2)}$ in the present
study. respectively.   The MO calculaitons showed that the bond
lengths of Si-$N_{(3)}$ and Si-$N_{(2)}$ are 1.69 and 1.72 Å, and that the
bond angles of <Si-$N_{(3)}$-Si and <Si-$N_{(2)}$-Si are 120 and 131
degree, respectively.   The bond length of Si-N and the bond
angle distribution of <Si-$N_{(3)}$-Si cauculated in the present study
are consistent with those of the MO calculations.   It is
noteworthy that the directionality in the angle of <Si-N-Si
bonds, which would arise from the covalent nature in the real
system, could be well reproduced in the present calculations.
Taking into account that the Si-$N_{(2)}$-Si bonds would be more
flexible for bending than Si-$N_{(3)}$-Si bonds, the calculated angle
distribution of <Si-$N_{(2)}$-Si would be also reasonable.

As can be seen in Fig. 2, the distance between Si-Si in nitrided glasses is shortened compared with that in non-nitrided glasses. The shortened Si-Si distance would correspond to that in $Si-N_{(3)}-Si$ group, in which the bond angle around $N_{(3)}$ is smaller than that of Si-O-Si.

There are a number of studies on the coordination state of nitrogen atoms in Na-Si-O-N oxynitride glasses. In an early ^{29}Si MAS NMR study[12], it was reported that all the nitrogen atoms are bonded to three silicon atoms in Na-Si-O-N oxynitride glasses in which the ratio of Na:Si is about 6:7. On the other hand, N_{1s} XPS measurements on Na-Si-O-N and Na-Ca-Si-O-N oxynitride glasses[11, 14] have shown that there are at least two kinds of sites for nitrogen atoms which may be related to those bonded to three and two silicon atoms. Jin et al.[18] estimated on the basis of the neutron diffraction analysis on a $20Na_2O \cdot 68SiO_2 \cdot 4Si_3N_4$ oxynitride glass that about 66 % of the total nitrogen atoms are of structural group (2) and the rest are those of (1). and the mean of the number of silicon atoms bonded to a nitrogen atom is 2.3. The present results, showing that M_{Si} for $20Na_2O \cdot 65SiO_2 \cdot 5Si_3N_4$ glass is 2.26, coincide well with the result of the neutron diffraction. Therefore, it is assumed that not all the nitrogen atoms in Na-Si-O-N oxynitride glasses are bonded to three silicon atoms but a part of nitrogen atoms may be bonded to two or less silicon atoms.

The formation of the nitrogen atoms bonded to two or less silicon atoms may be explained on the assumption that nitrogen atoms may substitute for non-bridging oxygen atoms as shown in equations (7) and (8).

$$Si-O^- \quad + \quad \overset{\overset{\textstyle Si}{|}}{Si-N-Si} \quad \longrightarrow \quad Si-O-Si \quad + \quad Si-N^--Si \quad (7)$$
$$(N_{(3)}) \qquad\qquad\qquad\qquad\qquad (N_{(2)})$$

$$\text{Si-O}^- \quad + \quad \text{Si-N}^-\text{-Si} \quad \longrightarrow \quad \text{Si-O-Si} \quad + \quad \text{Si-N}^{2-} \quad (8)$$

$$(N_{(2)}) \qquad\qquad\qquad\qquad (N_{(1)})$$

These equations imply that the number of silicon atoms bonded to a nitrogen atom decreases with increasing number of non-bridging oxygen atoms. That is consistent with the present calculations that M_{Si} decreases with increasing Na_2O content since the number of non-bridging oxygen atoms increases with increasing Na_2O content.

The present idea of the formation of structural groups (2) and (3) is analogous to the formation of non-bridging oxygen atoms on addition of alkali oxides to silicate glasses, and $N_{(2)}$ and $N_{(1)}$ atoms would accompany one and two charge compensating cations (Na^+), respectively. It is noteworthy that a part of nitrogen atoms are bonded only to two silicon atoms in $LaSi_3N_5$ crystal[29] while all the nitrogen atoms are bonded to three silicon atoms in Si_3N_4 crystal. Further, each silicon atom in $Na_2Si_2O_5$ crystal is of Q_3 type whereas the dissociation of Q_3 to Q_4 and Q_2 occurs in the glass of the same composition[30], which may suggest that the disproportionation of silicate anions would occur and the positively charged alkali ions would be accompanied by different types of silicate anions in glass. Therefore, it may be plausible to assume that the reactions (7) and (8) would actually proceed in oxynitride glasses containing non-bridging oxygen atoms.

(2) Density, bulk thermal expansion coefficient and bulk modulus

The dependence of the calculated density on the nitrogen content is consistent with that observed in the real Na-Si-O-N oxynitride glasses[4]. Even when three oxygen atoms are substituted by two nitrogen atoms, the "average atomic weight", as expressed by the sum of the atomic weight devided by the

number of the atoms in a composition formula, does not increase. The increase in the density with increasing nitrogen content, therefore, should be attributed to the change of the glass structure.   The increase in the density would be mainly caused by the formation of structural group (1) since one nitrogen atom makes three silicate tetrahedra connected with each other at the corners[5].   This idea is consistent with the shortened Si-Si distance as shown in Fig. 2.

In general, the density of glass decreases with increasing temperature due to thermal expansion, and it desreases more rapidly above the glass transition temperature.   The present calculation exhibits a similar dependence of density on temperature as shown in Fig. 3; the decrease in the density becomes more rapidly above ca. 2000 K.   This temperature range around 2000 K may correspond to the glass transition region of the present MD system.

The dependence of β on the nitrogen content was reproduced by the present calculations as shown in Fig. 4 for the glasses with low nitrogen contents, although the increase in β on further increase in the nitrogen content can not be compared with the real system.

It has been reported that Young's modulus of Na-Ca-Si-O-N[7], Ca-Si-O-N[16] and Ca-Al-Si-O-N[6] oxynitride glasses increases with increasing nitrogen content.   Hence, it would not be misleading to assume that the bulk modulus of real Na-Si-O-N oxynitride glasses would increase with increasing nitrogen content, being consistent with the present calculations.

The calculated dependences of β and K on the nitrogen content would arise from the increased steepness of Si-N potential curve.   This may imply that the changes of these properties of the real glasses on addition of nitrogen would

arise from the formation of Si-N bonds which are stronger than
Si-O bonds.

SUMMARY OF CHAPTER 1

The molecular dynamics calculations based on a pair
potential have shown that the nitrogen atoms bonded to one, two
and three silicon atoms coexist in the structure of Na-Si-O-N
oxynitride glasses. It has been assumed that the nitrogen atoms
bonded to two or less silicon atoms would be formed when nitrogen
atoms substitute for non-bridging oxygen atoms. The mean of the
number of silicon atoms bonded to a nitrogen atom ranges from 2.4
to 2.1, decreasing with increasing Na_2O content. The bond angle
of <Si-N-Si exhibits a bimodal distribution around 105-135 degree
and 140-170 degree, roughly corresponding to the nitrogen atoms
bonded three and two silicon atoms. The dependences of the
density, bulk thermal expansion coefficient and bulk modulus on
the nitrogen content are consistent with those observed in the
real system. It has been assumed that the increase in the
density on nitridation would be caused mainly by the formation of
the nitrogen atoms bonded to three silicon atoms which shortens
the Si-Si distance, and that the dependences of the bulk thermal
expansion coefficient and bulk modulus on the nitrogen content
would arise from the formation of Si-N bonds which are stronger
than Si-O bonds.

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CHAPTER 2 ^{29}Si MAS NMR Study on the Structure of Na-Si-O-N Oxynitride Glasses

INTRODUCTION

In the previous chapter, the structure of Na-Si-O-N oxynitride glasses studied by the molecular dynamics (MD) calculations has been described. The MD calculations showed that the nitrogen atoms bonded to one or two silicon atoms as well as those bonded to three silicon atoms coexist in the structure of glasses. The dependence of properties of glasses on the composition has been successfully reproduced. It would be necessary, however, to reconfirm experimentally the structure deduced by the MD calculations.

The structure of oxynitride glasses has been studied by IR and N_{1s} XPS spectroscopies[1-4], but these measurements do not give a clear picture of the structural groups present in oxynitride glasses. IR spectroscopy shows only the presence of Si-N bonds in glass structure. In XPS, the intensity of N_{1s} photoelectron is not always high enough to give the information on the structure because the nitrogen content of glass is not high in general, and so the S/N ratio of the spectra is low. ^{29}Si NMR spectroscopy would give better information on the structural groups in glass than the above methods because it gives information on the connectivity of silicate tetrahedra in glass.

Hater et al.[5] measured ^{29}Si MAS NMR spectra of Na-Si-O-N oxynitride glasses, deducing that all the nitrogen atoms are bonded to three silicon atoms. However, the analysis of the NMR spectra involved a considerable uncertainty due to an extensive

overlap of the resonances from different types of silicate tetrahedral units present in the base oxide glass $30Na_2O \cdot 70SiO_2$ and the low nitrogen contents.

In the present chapter, the structure of Na-Si-O-N oxynitride glasses determined by ^{29}Si MAS NMR measurement has been described. Compositions of oxynitride glasses have been selected so as to make the analysis of NMR spectra more quantitative than the previous study[5]. The results of NMR has been compared with those of the MD calculations.

EXPERIMENTAL

(1) Preparation and analysis of glasses

Two series of oxynitride glasses of the compositions $30Na_2O \cdot (70-3x)SiO_2 \cdot xSi_3N_4$ and $20Na_2O \cdot (80-3x)SiO_2 \cdot xSi_3N_4$ (x=0, 2 and 4) have been prepared. These series will be referred to as 37- and 28-series, respectively. The compositions of the former series correspond to those studied by Hater et al.[5], but the nitrogen content is higher in the present glasses. The compositions glass of the latter series are assumed to be adequate for the NMR measurement. The compositions of both series are comparable with those studied by the MD calculations.

The oxide parts of the compositions were melted in Pt crucibles in air atmosphere to prepare base glasses. The base glasses were ground to powders. The mixture of the base glass powder and a calculated amount of β-Si_3N_4 was melted in a molybdenum crucible at 1400 to 1500 $^\circ C$ for 1 to 3 hours under flowing dry nitrogen gas to prepare oxynitride glass.

Spin-lattice relaxation time (T_1) for Si nucleus in silicate glasses is generally very long in the durations from a few

minutes to an hour.   Therefore, 0.05 mol% of Gd_2O_3 was added to all the glasses in order to accelerate the relaxation by the spin diffusion from the paramagnetic centers.   It has been confirmed that the addition of this small amount of Gd_2O_3 does not cause any significant change of NMR spectra.

The oxynitride glasses prepared were analyzed for the nitrogen and sodium contents by the Kjeldahl method and the flame emission technique, respectively.   In order to determine the nitrogen content, a pulverized specimen of about 100 mg was dissolved in 6 ml of $HF-H_2SO_4$ mixed acid to produce NH_4^+ ions from nitrogen.   The ammonia evolving from the solution upon addition of NaOH was introduced into a diluted H_2SO_4 solution and back titrated with a standard NaOH solution.   The schematic arrangement of the apparatus is shown in Fig. 1.   In order to determine the soduim content, the glass was decomposed in the same manner as above and the mixed acids was subsequently evaporated to obtain dry sodium sulfate.   The sodium sulfate was dissolved into an appropriate amount of ion-exchanged water and was analyzed with a flame emission spectrometer.

(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 placed in alumina or zirconia sample holders.   The specimens were spun at the magic angle (54.74 degree) with respect to the external magnetic field.   The spinning rate was 3500 Hz.   A pulse width of 3 μs and a dead time of 20 μs were used.   Typical repetition interval was 2.5 sec 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
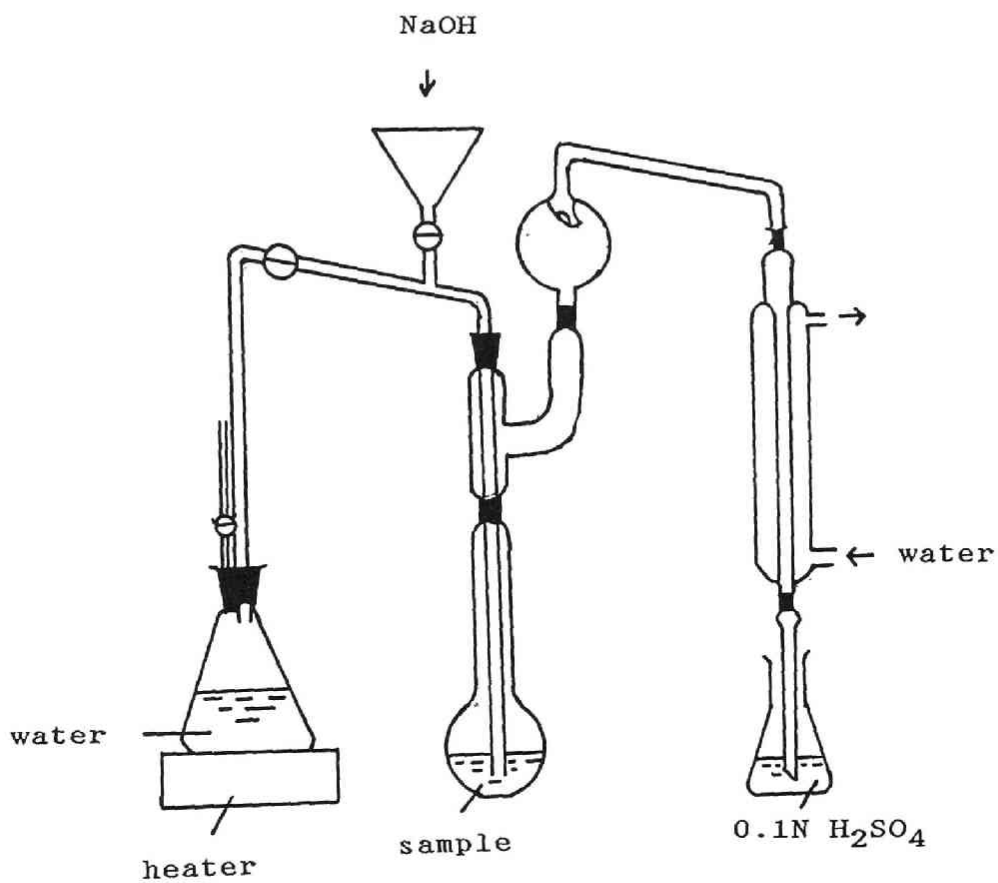
Fig. 1   A schematic arrangement of the apparatus for the determination of the nitrogen content.

from TMS.

RESULTS

(1) Analysis of glasses

The glasses obtained were free from crystalline phases as examined by 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 were 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 DISCUSSION.

(2) NMR spectra

Fig. 2 shows the ^{29}Si MAS NMR spectra of the glasses. Each spectrum was analyzed by separating to an appropriate number of Gaussian curves. The best fit was searched for by varying the peak position, linewidth and amplitude of the Gaussians. As indicated in Fig. 2 (a) and (b), each resonance peak expressed by a Gaussian curve was assigned to Q_n (or Q_n') depending on the peak position. Q_n represents $[SiO_4]$ silicate tetrahedral unit containing n bridging oxygens. Q_n' is used for nitrided glasses to distinguish their peaks from those of non-nitrided glasses. The percentage of the Q_n and Q_n' species present in the glasses, $W[Q_n]$ and $W[Q_n']$, is estimated from the relative intensity obtained as the area of each Gaussian curve.

Table 2 summarizes the result of the analysis of NMR spectra. The peak separation could be made more quantitatively for 28-series than for 37-series. The overlap of the peaks of

Table 1 Analyzed compositions of glasses

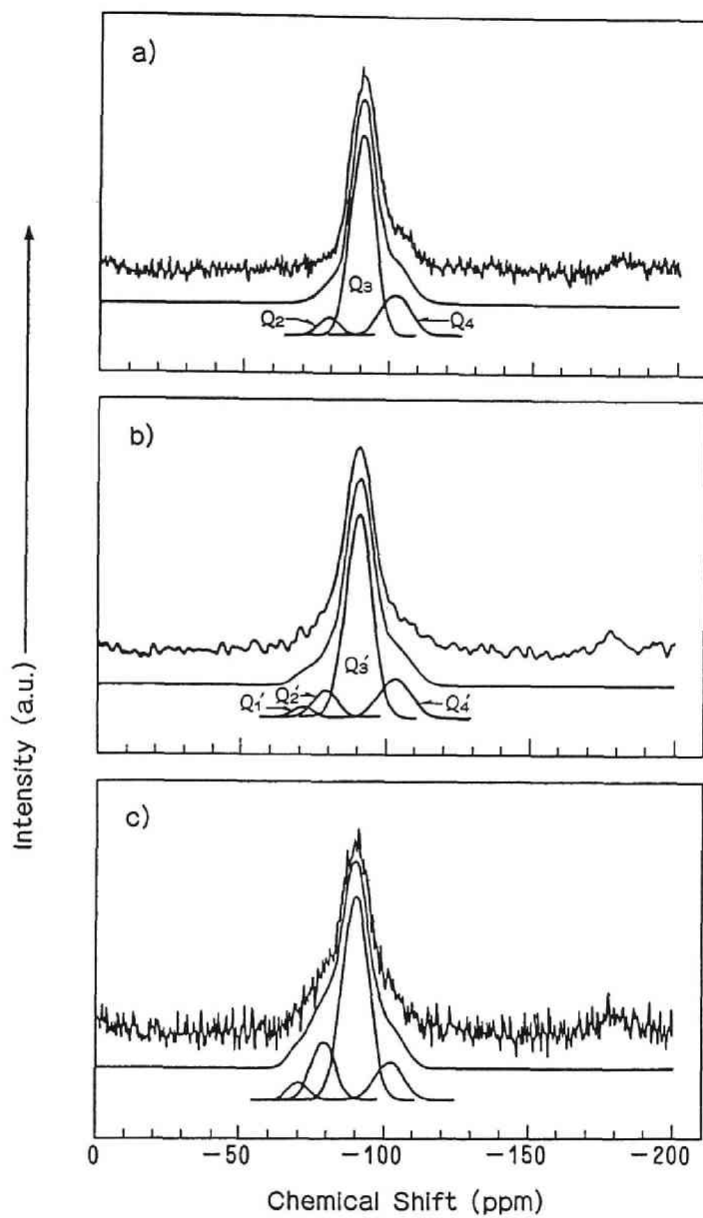| Sample	Na_2O (mol%)	SiO_2 (mol%)	$SiN_{4/3}$ (mol%)	N (at%)	N (wt%)
37-0	30.0	70.0	0	0	0
37-2	29.9	65.7	4.4	2.0	1.4
37-4	28.9	62.6	8.5	3.9	2.7
28-0	20.0	80.0	0	0	0
28-2	18.8	76.5	5.2	2.3	1.6
28-4	18.9	71.7	9.4	4.3	3.0

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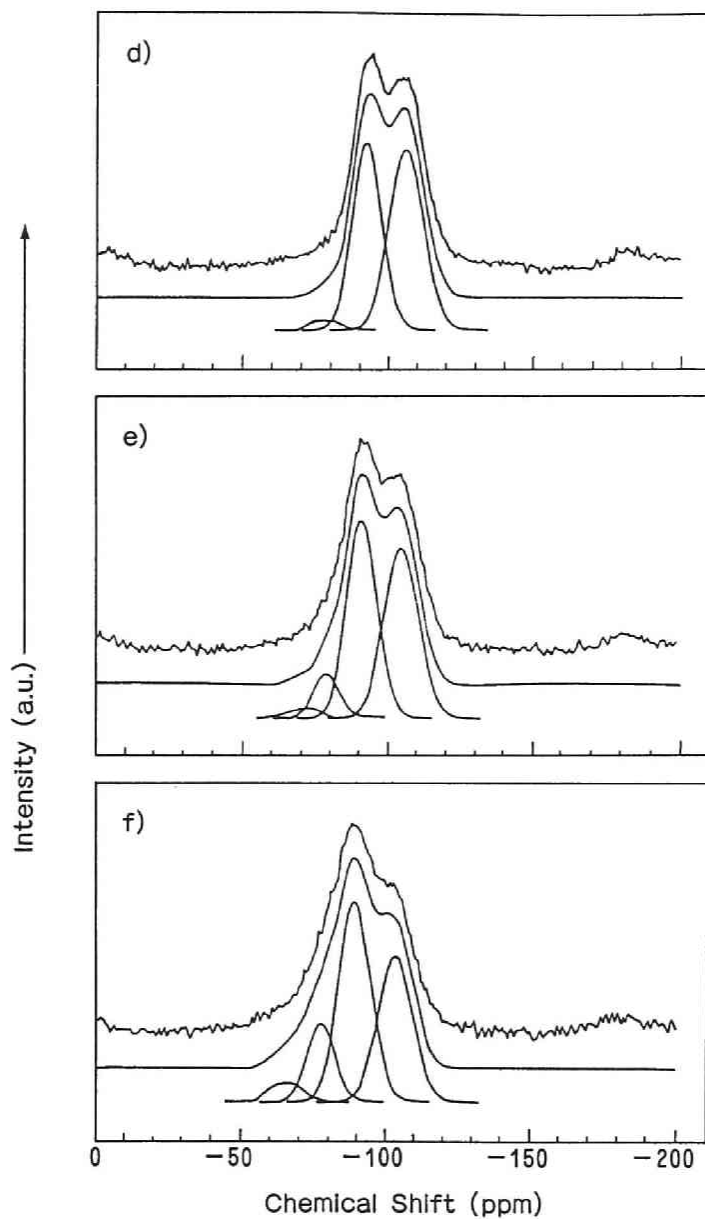(c)37-4.   See Table 1 for the notations of the
samples.

Fig. 2 ^{29}Si MAS NMR spectra of glasses; (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

Q_4 (Q_4') and Q_2 (Q_2') with the main peak of Q_3 (Q_3') is more extensive in the latter series, which leads to a certain ambiguity in peak separation. The results of the present analysis on non-nitrided glasses (37-0 and 28-0) are consistent with those of the previous study[6].

It is clearly recognized from Fig. 2 and Table 2 that the intensities of the peaks corresponding to less shielded silicon nuclei, which are those of less negative chemical shifts, increase with increasing nitrogen content. That is, $W[Q_2']$ and $W[Q_1']$ increase and $W[Q_4']$ decreases. The line width of the peaks slightly increases with increasing nitrogen content.

DISCUSSION

The increases in $W[Q_2']$ and $W[Q_1']$ and the decrease in $W[Q_4']$ on nitridation may be caused by the substitution of oxygen by nitrogen in silicate tetrahedral units. In the present discussion, a semi-quantitative interpretation of the change of $W[Q_n']$ on nitridation is attempted, in order to estimate the mean of the number of silicon atoms bonded to a nitrogen atom, referred to as M_{Si}.

Since the nitrogen concentration is relatively low, it is expected that the predominant silicate tetrahedral unit containing nitrogen in the oxynitride glasses might be singly nitrided one, $[SiNO_3]$. The only available NMR data of silicate tetrahedral units containing nitrogen, however, are those of $[SiN_4]$ and $[SiN_3O]$ determined from crystalline α- and β-Si_3N_4 and Si_2N_2O, respectively[7, 8]. Therefore, the following assumptions are introduced to analyze the present NMR spectra.

(a) The substitution of an oxygen in a $[SiO_4]$ tetrahedron by a nitrogen atom causes a change of the chemical shift of the

resonance by about + 15ppm. This assumption was drawn from the comparison of the chemical shifts of Si nuclei in β-Si_3N_4 (-48 ppm, [SiN_4] unit), Si_2N_2O (-63 ppm, [SiN_3O] unit)[7, 8] and quartz (-107 ppm, [SiO_4] unit). This assumption is supported by the fact that the NMR spectra of nitrided glasses could be successfully separated to the Gaussian curves 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 + 15ppm is very close to that caused by the substitution of a bridging oxygen by non-bridging oxygen, the resonance of singly nitrided Q_n (denoted as $Q_n(1N)$) would appear in the similar position to that of non-nitrided Q_{n-1}. Accordingly, each observed NMR peak of nitrided glasses, Q_n', is considered to be a sum of $Q_n(0N)$ and $Q_{n+1}(1N)$, that is, $W[Q_4'] = W[Q_4(0N)]$, $W[Q_3'] = W[Q_3(0N)]$ + $W[Q_4(1N)]$, $W[Q_2'] = W[Q_2(0N)] + W[Q_3(1N)]$, and so on.

(b) A nitrogen atom bonded to two silicon atoms, $N_{(2)}$, if any, accompanies a Na^+ ion as charge compensator as shown below;

$$Si\text{-}N^{\bar{}}\text{......}Na^+ \tag{1}$$
$$|$$
$$Si$$

This assumption was drawn from the analogy of the charge compensation of non-bridging oxygen in oxide glasses. The nitrogen atoms bonded to two silicon atoms are formed when non-bridging oxygen atoms are substituted by nitrogen atoms (equation (2)).

$$Si\text{-}O^- \ + \ Si\text{-}N\text{-}Si \ \longrightarrow \ Si\text{-}O\text{-}Si \ + \ Si\text{-}N^-\text{-}Si \tag{2}$$
$$|$$
$$Si$$
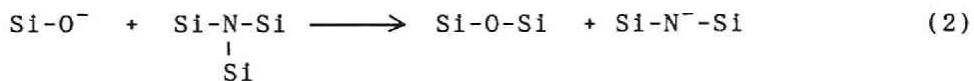
(c) The extent of the effect of shielding of nitrogen on neighboring silicon nuclei does not vary regardless of whether the nitrogen atom is bonded to two silicon atoms or three.

On the basis of the above assumptions, the distribution of $W[Q_n']$ in nitrided glasses was calculated employing M_{Si} as variable as described below. In this connection, however, multiply-nitrided silicate tetrahedral units ($[SiN_mO_{4-m}]$, $m \geq 2$) were not taken into account because the probability of the formation of such units would be very small due to the low atomic ratio of nitrogen to oxygen.

When a part of oxygen atoms are substituted by nitrogen atoms in a Na_2O-SiO_2 glass having a known distribution of $W[Q_n]$ so that the number of Si-N bonds in a unit formula might be N_{Si-N}, the percentage of singly-nitrided Q_n would be $N_{Si-N} \cdot W[Q_n]$. N_{Si-N} is equivalent to $(4/3) \cdot X_{SiN4/3} \cdot M_{Si}$, where $X_{SiN4/3}$ represents the mol% of $SiN_{4/3}$. Then, the percentage of singly-nitrided and non-nitrided Q_n species ($W[Q_n(1N)]$ and $W[Q_n(0N)]$, respectively) would be expressed as follows;

$$W[Q_n(1N)] = W[Q_{n,ref}] \cdot (4/3) \cdot X_{SiN4/3} \cdot M_{Si} \qquad (3)$$

$$W[Q_n(0N)] = W[Q_{n,ref}] - W[Q_n(1N)] \qquad (4)$$

where $W[Q_{n,ref}]$ represents the percentage of Q_n in a glass of the composition $(X_{Na2O} - (3-M_{Si}) \cdot (4/3) \cdot X_{SiN4/3})Na_2O \cdot (X_{SiO2} + X_{SiN4/3})SiO_2$ which will be referred to as "reference glass". The sodium content of the reference glass is lower than that of the corresponding non-nitrided composition of the nitrided glass by the content of the nitrogen atoms coordinated by two silicon atoms, because such nitrogen atoms accompany Na^+ ions as charge compensator, according to assumption (b). $W[Q_{n,ref}]$ can be calculated using the equilibrium constant k_3 (0.02) for the following reaction[6];

$$2Q_3 \rightleftharpoons Q_4 + Q_2 \qquad (5)$$

The distribution of $W[Q_n']$ corresponding to an assumed value of M_{Si} can be calculated unequivocally from the analyzed nitrogen

and sodium contents.

The result of the calculation of $W[Q_n']$ for 28-series is shown in Fig. 3. Solid circles in the figure represent the values obtained from the NMR spectra. Fig. 3 indicates that the values of $W[Q_n']$ obtained from the NMR spectra agree well with those calculated by assuming that M_{Si} is 2.5.

The result of the calculation of the ratio $W[Q_2']/W[Q_4']$ for 37-series is shown in Fig. 4. Solid circles represent the values obtained from the NMR spectra. The data of Hater et al.[5] 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. M_{Si} is close to 2 for 37-2 while that is close to 3 for the data of Hater et al. This discrepancy may be attributed to the lower accuracy of peak separation in 37-series than that of 28-series especially when the nitrogen content is low. For the more highly nitrided glass (37-4), the value of $W[Q_2']/W[Q_4']$ obtained from the NMR spectra agree well with that calculated by assuming that M_{Si} is 2.5.

Fig. 5 shows the change of the weighed mean for $W[Q_n(')]$, mean n, which is the mean of the number of bridging oxygen atoms in a silicate tetrahedron, for 28- and 37-series as a function of the nitrogen content. Solid circles in the figure represent the values obtained from the NMR spectra. The values of mean n obtained from the NMR spectra agree well with those calculated by assuming that M_{Si} is 2.5.

The above results suggesting that the nitrogen atoms are bonded to 2.5 silicon atoms on the average indicate that about a half of the total nitrogen atoms are bonded to three silicon atoms and the rest are bonded to two silicon atoms. Equation (2) suggests that the value of M_{Si} might increase with decreasing Na_2O content, that is, M_{Si} of 28-series might be larger than that of 37-series. In the present analysis, however, the dependence
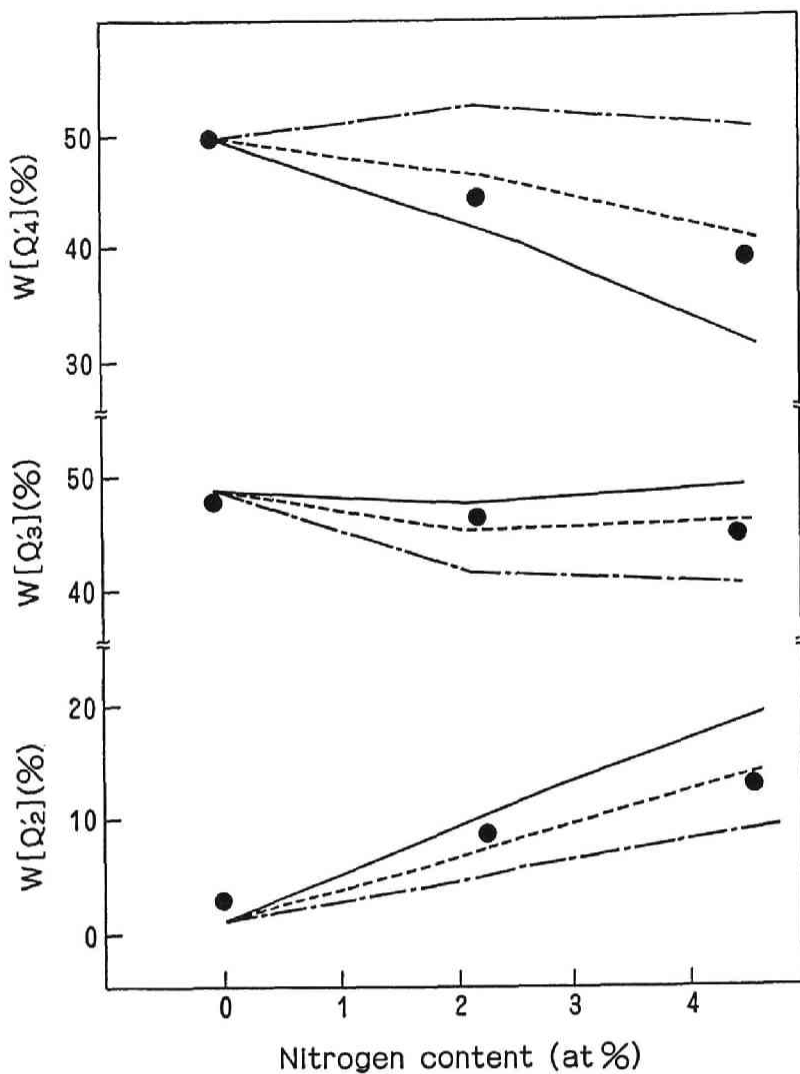
Fig. 3. Calculation of the change of $W[Q_n']$ in the glasses of 28-series as a function of nitrogen content. The mean of the number of silicon atoms bonded to a nitrogen atom is 3(——), 2.5(-----) and 2(—·—). Solid circles represent the values obtained from the NMR spectra.
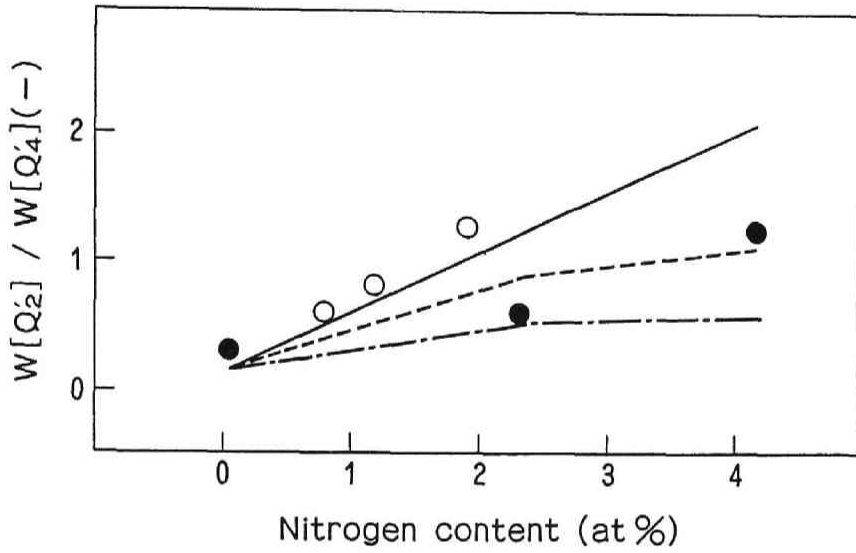
Fig. 4.   Calculation of the change of $W[Q_2']/W[Q_4']$ in the
glasses of 37-series as a function of nitrogen content.
The mean of the number of silicon atoms bonded to
a nitrogen atom is 3(——), 2.5(-·····) and 2(—·—).
Solid circles represent the values obtained from the
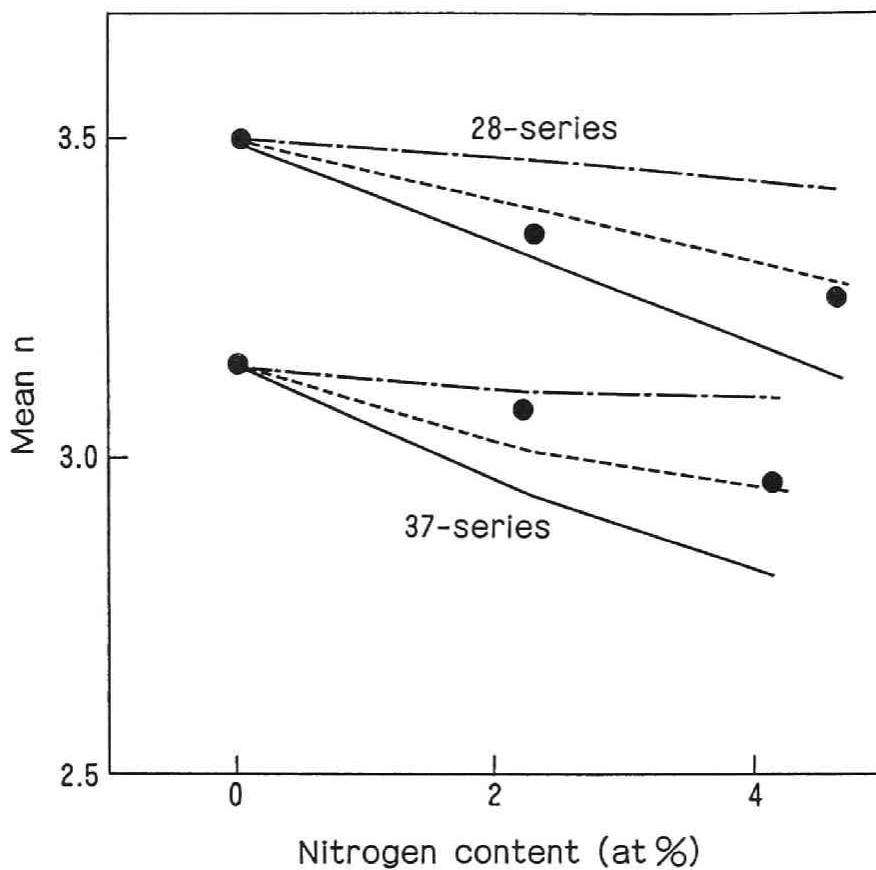NMR spectra.   Open circles represent the data of
Haller et al[5].

Fig. 5.   Calculation of the change of the weighed mean of $W[Q_n']$
(Mean n) of the glasses.   The mean of the number of
silicon atoms bonded to a nitrogen atom is 3(———),
2.5(-----) and 2(— ·—).   Solid circles represent the
values obtained from the NMR spectra.

of M_{Si} on the Na_2O content were not clearly detected.

The MD calculations in CHAPTER 1 have shown that the mean values of the number of silicon atoms bonded to a nitrogen atom are 2.1 and 2.4 for 37- and 28-series, respectively. The results of the MD calculations and the present NMR coinside with each other on the point that not all the nitrogen atoms are bonded to three silicon atoms.

N_{1s} XPS measurements on Na-Si-O-N[3] and Na-Ca-Si-O-N[4] oxynitride glasses indicated that there are at least two kinds of nitrogen atoms in different structural groups. These nitrogen atoms would be those bonded to three and two silicon atoms.

SUMMARY OF CHAPTER 2

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 NMR spectra on nitridation has been well explained by assuming that the nitrogen atoms are bonded to about 2.5 silicon atoms on the average, indicating that about a half of the total nitrogen atoms are bonded to two silicon atoms. It has been assumed that the nitrogen atoms bonded to two silicon atoms may be formed when non-bridging oxygen atoms are substituted by nitrogen atoms as shown below.

$$Si-O^- \; + \; Si\underset{\underset{Si}{|}}{-}N-Si \; \longrightarrow \; Si-O-Si \; + \; Si-N^--Si$$

The present results are consistent with those of the molecular dynamics calculations described in CHAPTER 1.

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CHAPTER 3   Electrical Conductivity of
Alkali-Silicate Oxynitride Glasses

INTRODUCTION

Mechanical, thermal and chemical properties of oxynitride glasses have been extensively studied by many workers.   The microhardness, fracture toughness and stability to devitrification increase with increaseing nitrogen content[1]. Electrical properties of oxynitride glasses, however, have been studied by only a few workers[2-4].   Elmer and Nordberg[2] reported that the incorporation of nitrogen into silica glasses increases the electrical resistivity.   Leedecke and Loehman[3] investigated the electrical properties of Y-Al-Si-O-N oxynitride glasses and found that the dc conductivity increases when nitrogen atoms are incorporated into an oxide glass.   Thorp and Kenmuir[4] studied dielectric properties of Mg-Al-Si-O-N and Ca-Al-Si-O-N oxynitride glasses and showed that the dielectric constant and ac conductivity increase with increasing nitrogen content.   In the above studies, however, the charge carriers in the glasses are not clear.

It has been well established that the charge carriers are alkali ions in alkali-containing glasses.   The transport of alkali ions in glasses are very important when the glass is employed as insulator in electronic circuit.   Further, it is assumed that the transport of alkali ions may control the chemical durability of the glass.   There is no systematic studies of the effect of nitrogen on the ionic conduction in oxynitride glasses.

In this chapter, the effect of incorporation of nitrogen on the electrical conductivity as a probe of ionic transport is

described for Li-Si-O-N and Na-Si-O-N oxynitride glasses.

EXPERIMENTAL

(1) Preparation and analysis of glasses

Oxynitride glasses of the compositions $30R_2O \cdot (70-3x) \cdot SiO_2 \cdot xSi_3N_4$ (R=Li and Na, x=0 to 3 and 4 for Li- and Na-glasses, respectively), in which the ratio of alkali to silicon is kept constant at 6 to 7, have been prepared. The glasses were prepared in the same manner as that described in CHAPTER 2. Two kinds of non-nitrided glasses containing different amounts of water were prepared to check the effect of water on the electrical conductivity. These non-nitrided glasses were prepared by melting the batch in air or under flowing nitrogen.

Oxynitride glasses thus prepared were analyzed for the nitrogen and alkali contents by the Kjeldahl method and the flame emission technique, respectively. The detailed procedure for the analyses are described in CHAPTER 2.

The water content of glasses was determined with polished plate specimens from the infrared absorption band around 3600 cm^{-1} on the basis of Beer-Lambert law. The values of 70 and 63 $liter \cdot mol^{-1} \cdot cm^{-1}$ were used as the molar extinction coefficient for Na- and Li-glasses, respectively[6, 7]. The density was measured by the Archimedes method using liquid paraffin as substituting liquid. The glass transition temperature was determined with a Shimadzu TM-30 dilatometer at a heating rate of 10 $^{\circ}C/min$. The fractured surface of the glasses was observed with a scanning electron microscope (SEM).

(2) Electrical measurement

Glasses were cut into discs and were polished with #2000 grade alumina abrasive powder to the thickness of about 1 mm. Gold electrodes and a guard ring were sputter-deposited. The ac conductivity and dielectric constant were measured in the frequency range from 30 Hz to 1 MHz at temperatures from room temperature to about 100 $^{\circ}$C with an Ando Electric Company TRS-B capacitance bridge. The cell for the electrical measurement is schematically shown in Fig. 1. The dc conductivity was determined as the reciprocal value of the intercept of the abcissa of the complex-impedance plot as shown in Fig. 2. The reproducibility of the measurement was within the error range of 5 %.

RESULTS

(1) Chemical analysis and properties

Analyzed compositions and properties of the glasses are listed in Table 1. The nitrided glasses (L1 to L3 and N1 to N4) were translucent with gray in color and visually homogeneous. All the specimens were free from crystalline phases, according to X-ray diffraction.

Table 1 shows that the nitrogen content of the glasses ranges from 70 to 95 % of the content calculated from the batch composition. The nitrogen retention is larger in the Li-glasses than in the Na-glasses. Alkali components are not seriously lost during preparation of oxynitride glasses. The water content of nitrided glasses is less than 1×10^{-4} wt%. The glass transition temperature drastically increases and the density slightly increases with increasing nitrogen content. Inclusions are not observed except for N3 and N4 which contain a small
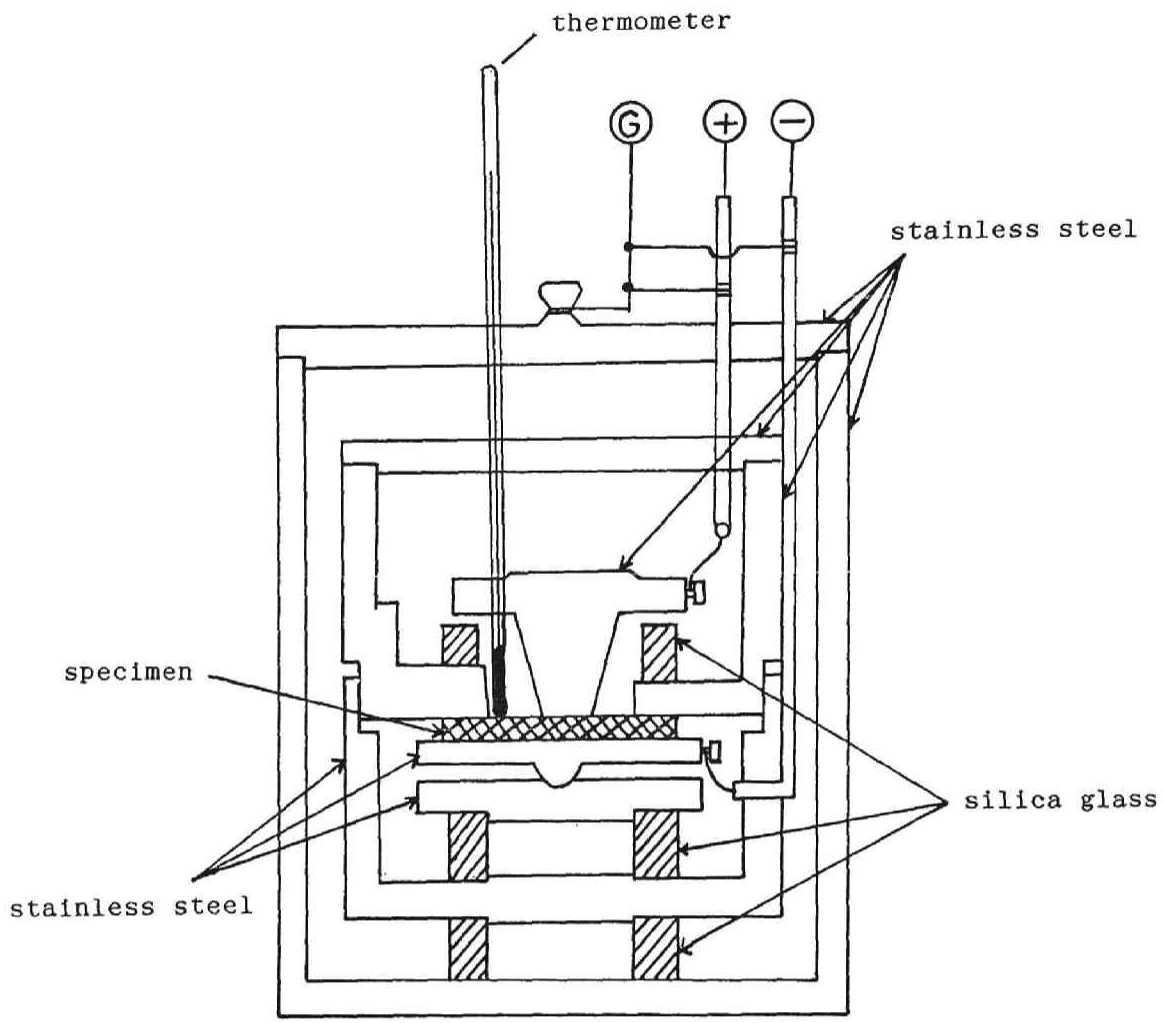
Fig. 1.   Schematic arrangement of the cell for the
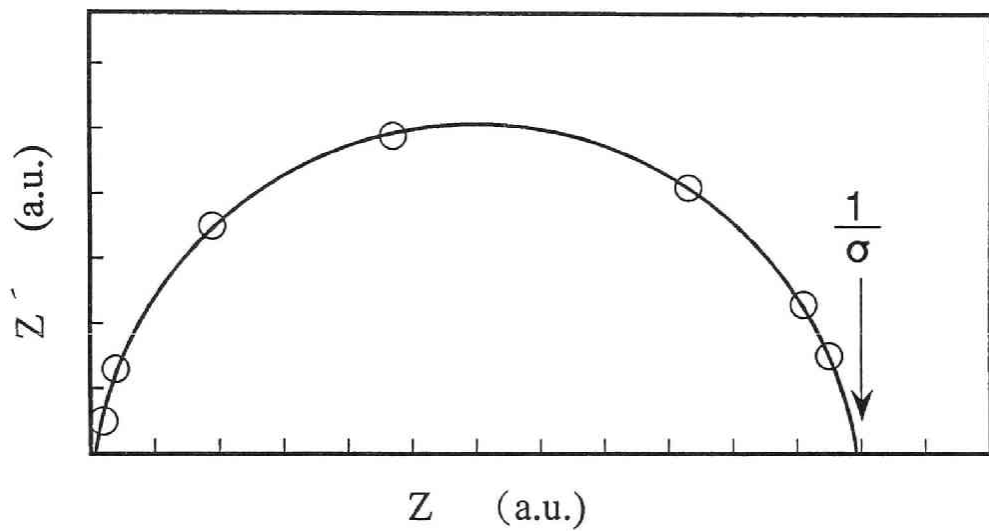electrical measurement.

Fig. 2.   An example of the complex-impedance plot.

Table 1   Analytical compositions and properties of oxynitride glasses

Sample No. (x value)	N calc. (wt%)	N anal. (wt%)	Alkali (wt%)	Density (gcm^{-3})	T_g (°C)	Water cont. (wt%)	ε (1MHz, 27 °C)
$30Na_2O\cdot(70-3x)SiO_2\cdot xSi_3N_4$ glasses							
N1	0.93	0.89	23.0	2.474	502	$<1\times10^{-4}$	12.0
N2	1.87	1.69	21.8	2.474	524	$<1\times10^{-4}$	12.2
N3	2.83	2.24	22.6	2.494	540	$<1\times10^{-4}$	13.2
N4	3.80	2.71	22.4	2.499	550	$<1\times10^{-4}$	13.7
NON*	0	0	23.0	2.470	470	3×10^{-4}	11.1
NOA**	0	0	22.9	2.470	468	5×10^{-3}	11.1
$30Li_2O\cdot(70-3x)SiO_2\cdot xSi_3N_4$ glasses							
L1	1.11	1.06	8.23	2.321	475	$<1\times10^{-4}$	12.1
L2	2.23	1.97	8.17	2.337	504	$<1\times10^{-4}$	12.5
L3	3.37	3.13	8.24	2.371	522	$<1\times10^{-4}$	12.7
LON*	0	0	8.25	2.289	463	1×10^{-3}	10.7
LOA**	0	0	8.16	2.300	460	9×10^{-3}	10.7

* Melted in N_2 atmosphere at 1400 °C for 1h.

**Melted in air at 1500 °C for 2h.

amount of inclusions at less than 0.01% in volume, as seen from
the SEM pictures, shown in Fig. 3.

(2) Electrical conductivity

The electrical conductivities versus the reciprocal
temperature are shown in Figs. 4 and 5 for Li-glasses and Na-
glasses, respectively.   It is seen that the conductivity
behavior is of the Arrhenius type in both Li- and Na-glasses.
Fig. 6 shows the dc conductivity at 40 $^{\circ}C$ as a function of the
nitrogen content.   The data of glasses containing 10 to 20 %
more alkali ions than nitrided glasses are also plotted in these
figures for comparison.   For both Li- and Na-glasses, the
conductivity increases with increasing nitrogen content.
Oxynitride glasses with relatively high nitrogen content (L2, L3,
N3 and N4) can compete with the 10 to 20 % increase in alkali
ions in terms of conductivity.

The activation energy for conduction are plotted in Fig. 7.
The values of the activation energy of the non-nitrided glasses
are in close accordance with those previously reported[8, 9].
It is seen that the activation energy for conduction decreases
progressively as the nitrogen content increases.   The extent of
the changes in the conductivity and the activation energy for
conduction appears more pronounced for the Li-glasses than for
the Na-glasses.

DISCUSSION

(1) Effect of densification and water content on electrical
conductivity

It is known that the incorporation of nitrogen results in a
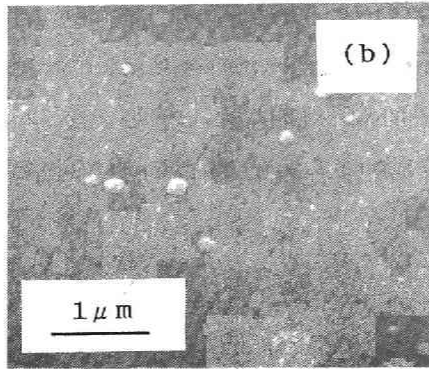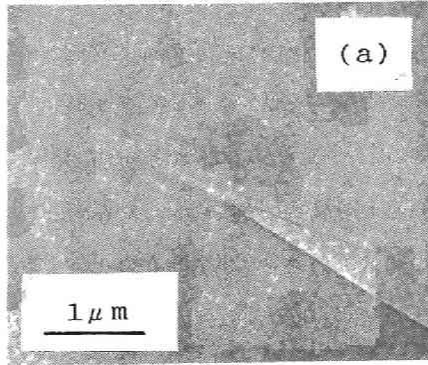
Fig. 3.   Scanning electron micrographs of fractured surfaces of
           oxynitride glasses. (a)N1 No inclusions are seen.   A
           crack is included in the picture to show the validity
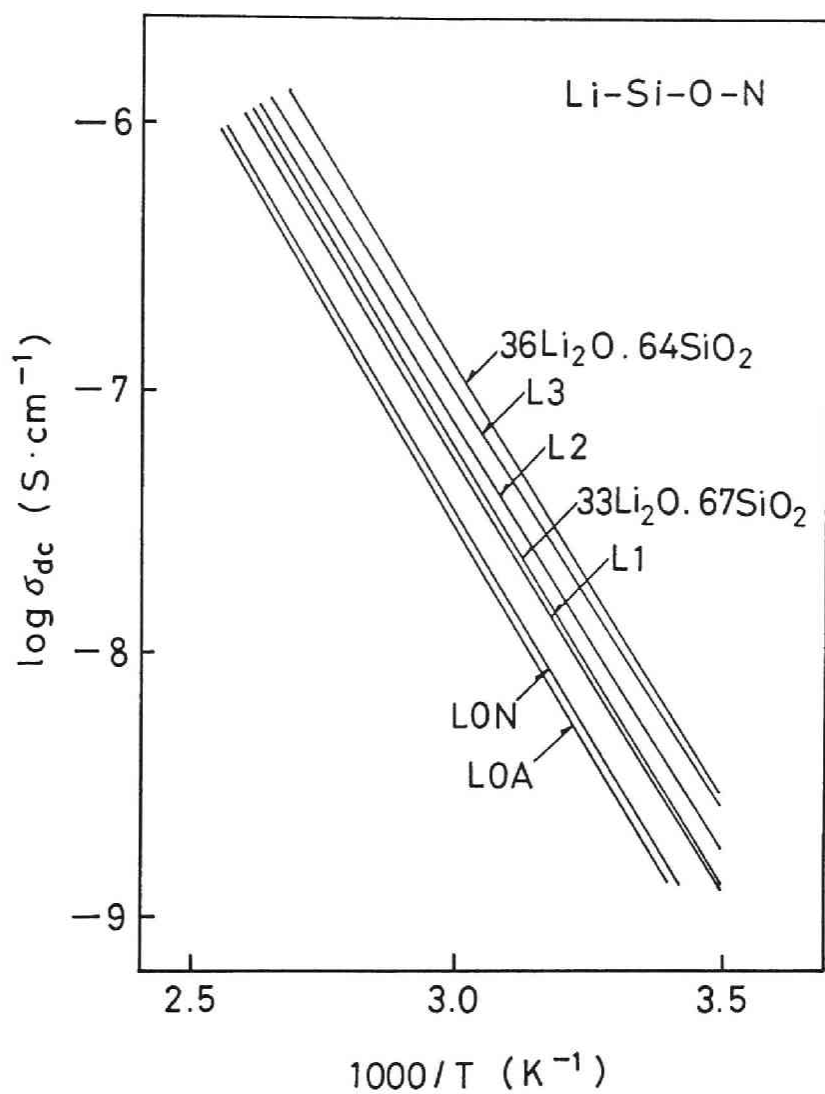   of focusing.   (b)N3 Fine particles are seen.

Fig. 4. Temperature dependence of the dc conductivity of
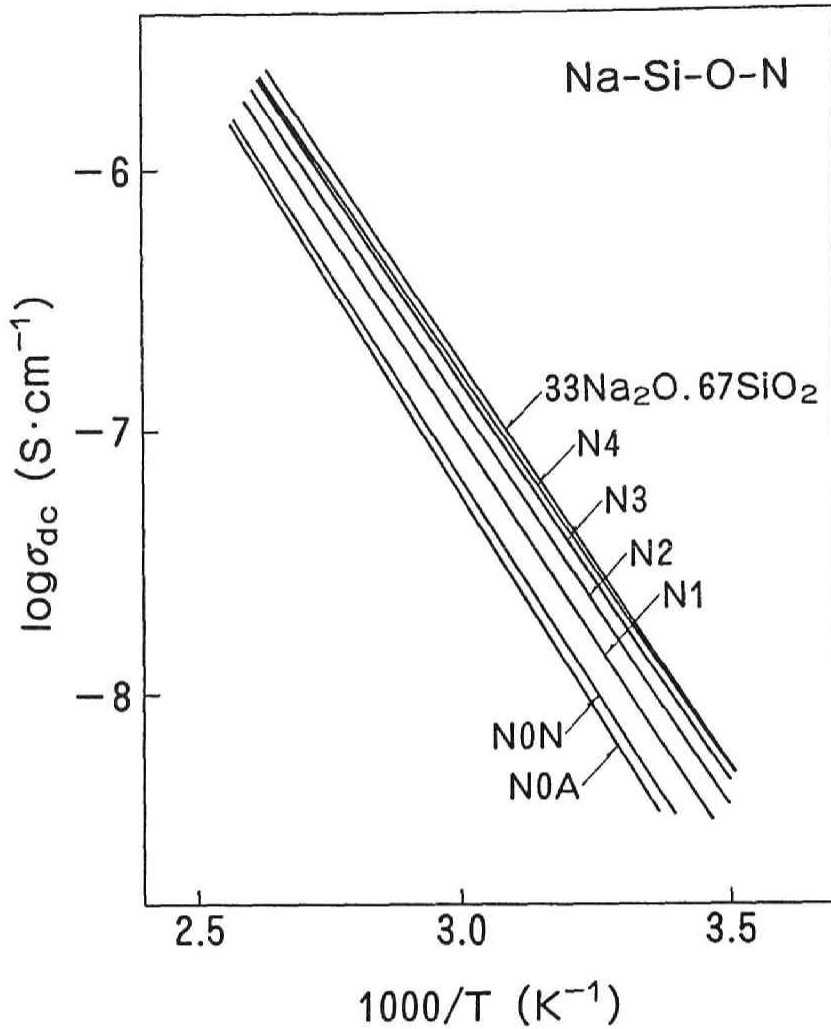the Li-Si-O-N glasses. See Table 1 for the symbols
attached to the lines.

Fig. 5.   Temperature dependence of the dc conductivity of
          the Na-Si-O-N glasses.   See Table 1 for the symbols
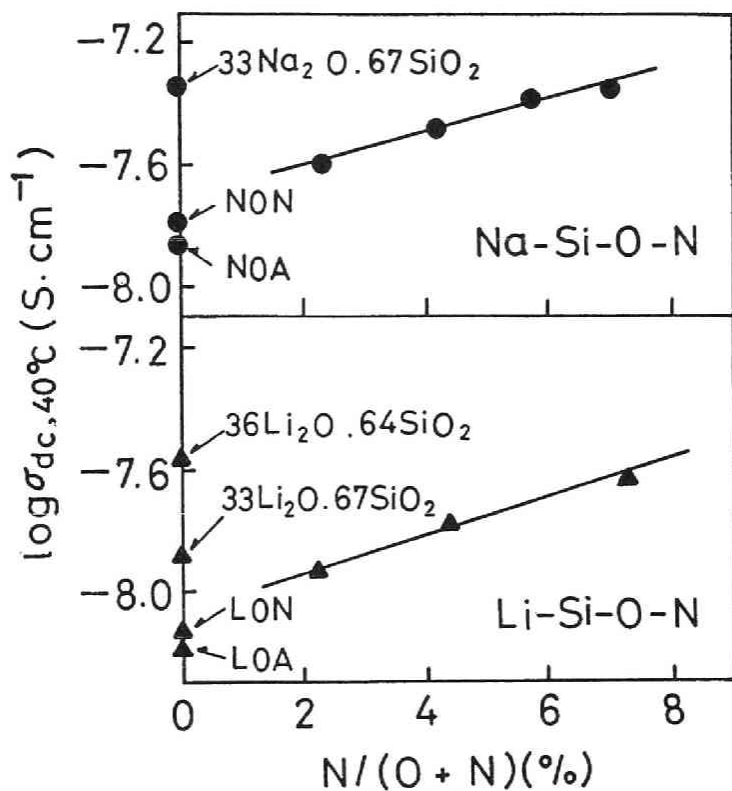   attached to the lines.

Fig. 6. Change of the dc conductivity of the Na-Si-O-N and the Li-Si-O-N glasses at 40 $^{\circ}$C as a function of the nitrogen content.
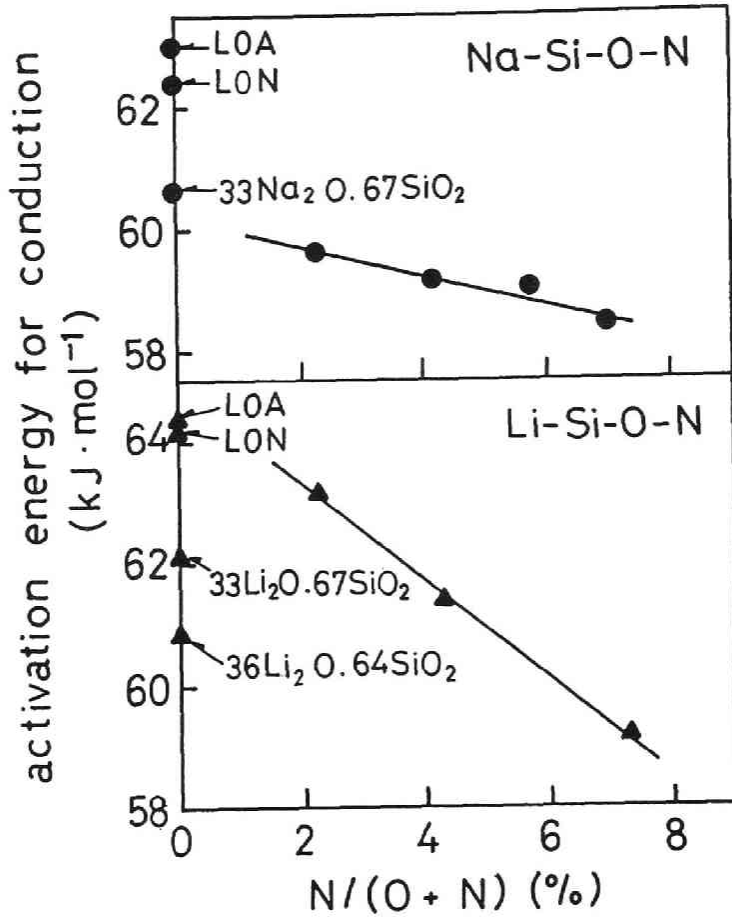
Fig. 7.   Change of the activation energies for conduction of the
Na-Si-O-N and the Li-Si-O-N glasses as a function of
the nitrogen content.

decrease in the water content, an increase in the density and the formation of Si-N bonds in the glass network.   Before discussing the effect of the presence of nitrogen in the glass structure as Si-N bonds, the indirect effects of the increase in the density and the decrease in the water content will be checked.

In the range of relatively small water content, a decrease in the water content enhances the ionic conductivity[10].   The effect of the water content was checked by comparing the electrical conductivity between two kinds of non-nitrided glasses with different water contents.   As shown in Fig. 6, LON and NON which were melted under flowing nitrogen show only slight increases in conductivity compared with LOA and NOA, respectively, which contain about ten times more water than the formers.   The increase in the conductivity on nitridation is far larger than the difference of the conductivity between LOA and LON or NOA and NON.   This indicates that the slight increase in the conductivity due to the decrease in the water content may be neglected for the discussion of the effect of nitrogen incorporation.

Increase in the density of glass on nitridation may increase the apparent alkali concentration in terms of the number of alkali ions per unit volume.   To check the effect of densification, the conductivities of the glasses of the compositions $33Na_2O \cdot 67SiO_2$, $33Li_2O \cdot 67SiO_2$ and $36Li_2O \cdot 64SiO_2$ have been measured and are plotted in Fig. 6.   It is found that nitrided glasses N3, N4, L2 or L3 can compete with the 10 to 20 % increase in alkali concentration in terms of conductivity.   The real increase in the alkali concentration per unit volume of glass due to densification of these glasses is 4 % at most. This indicates that the change of the electrical conductivity caused by nitridation of glass can be attributed to the effect of

nitrogen present in the glass structure.

(2) Effect of nitrogen present in the glass structure on electrical conductivity

The interpretation of the effects of nitrogen on the electrical conductivity is made on the basis of the equation proposed by Anderson and Stuart[8]:

$$\Delta E = (2.1-r)ZZ_0e^2/3.5\gamma(r+r_0) + 4\pi Gr_D(r-r_D)^2 \qquad (1)$$

where ΔE is the activation energy for conduction, γ is the covalency parameter which accounts for deformability of the electron cloud of the network anion, G is the shear modulus, r is the ionic radius of the transporting ion, r_0 is the radius of oxide anion (O^{2-}) and r_D is the doorway radius (0.6 Å). γ is equivalent to the dielectric constant and square of the refractive index. This equation indicates that the activation energy is the sum of the electrostatic energy, the first term, and the network strain energy, the second term. The activation energy for conduction would decrease when the covalency of the glass network increases and the shear modulus decreases.

When Si-N bonds are formed in nitrided glasses, the negatively charged electron cloud of nitrogen may be more highly susceptible to deformation than that of oxygen because nitrogen is less electronegative than oxygen. This consideration may be supproted by the molecular orbital calculations conducted by Murakami and Sakka[11] on model molecules quarried out from the framework structure of silicon oxynitride glass, which indicates that the atomic charge on silicon atoms bonded to oxygen and nitrogen are 1.38 and 1.30, respectively. In other words, nitrogen has more covalent nature than oxygen. The covalency parameter, γ, would therefore increase on nitridation of glass. The increase in γ is experimentally supported by the facts that

the refractive index increases when nitrogen atoms are incorporated in oxide glasses[12] and that the dielectric constant increases in this study as shown in Table 1. An increase in γ means a decrease in the negative electric field exerted on the alkali ions on the average, which contributes to a decrease in the activation energy for conduction.

On the other hand, the shear modulus is also supposed to increase by nitridation, which may cause an increase in network strain energy, giving an increase in the activation energy. In other words, this is a competitive effect of nitridation on the activation energy for ionic conduction. It will be plausible to assume that the decreasing effect of the electrostatic energy may be larger than the increasing effect of the network strain energy in the present Li- and Na-glasses.

Equation (1) implies that the contribution of the electrostatic energy on the activation energy is larger than that of network strain energy when the size of the transporting ion is close to r_D, 0.6 Å. Since the size of Li^+ ion (0.68 Å) is close to that of r_D, the decreasing effect of electrostatic energy may be more pronounced than increasing effect of the network strain energy. resulting in the total decrease in the activation energy for conduction on nitridation. The size of Na^+ ion (0.97 Å) is larger than that of Li^+ ion. Accordingly, the contribution of the increasing effect of network strain energy is larger in Na-glasses than in Li-glasses and the activation energy for conduction of Na-glasses decreases on nitridation to a lesser extent than in Li-glasses.

SUMMARY OF CHAPTER 3

The efects of the incorporation of nitrogen on the electrical conductivity in Li-Si-O-N and Na-Si-O-N oxynitride

glases have been systematically investigated. For both glasses, the electrical conductivity increases and the activation energy for conduction decreases with increasing nitrogen content. The experimental results have been interpreted based on the equation proposed by Anderson and Stuart that the activation energy for conduction can be expressed as the sum of the contributions of the electrostatic energy and the network strain energy. It is assumed that the incorporation of nitrogen into alkali-silicate glass network decreases the electrostatic energy and increases the network strain energy. For small ions such as Li^+ or Na^+, the contribution of the former is predominant compared with that of the latter. The experimental results are consistent with the implication of the equation of Anderson and Stuart because the conductivity increases and the activation energy for conduction decreases on nitridation to a larger extent for Li-Si-O-N oxynitride glasses than for Na-Si-O-N oxynitride glasses.

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CHAPTER 4　Chemical Durability of Alkali-Silicate Oxynitride Glasses

INTRODUCTION

Oxide glasses of high chemical durability are needed for producing reinforcing fibers for concrete, glass filters, protective coating films on metals and glasses for nuclear waste solidification.　It is well known that the addition of zirconium oxide improves the chemical durability of glass in alkaline conditions[1].　Also, glasses such as $BaO-TiO_2-SiO_2$[2], $Na_2O-CaO-FeO-MnO-SiO_2$[3], $Y_2O_3-La_2O_3-TiO_2-Al_2O_3-SiO_2$[4,5] exhibit good chemical durability to alkaline solutions.　In such glasses, a protective layer of ZrO_2 or TiO_2 is formed on the surface of the glass after a small amount of other components is leached out.

The attempts to improve the chemical durability have been made by selecting appropriate cationic compositions. Alternatively, substitution of anions, that is, substitution of a part of oxygen by nitrogen has been found to improve the chemical durability of glasses in acidic and alkaline environments[6-11]. At the same time, mechanical strength, elastic modulus and refractoriness are also improved[10] by incorporation of nitrogen.　This indicates that oxynitride glasses are promising materials as reinforcing fiber for concrete or glasses for nuclear waste solidification, for example.　The mechanism of the improvement of chemical durability by incorporation of nitrogen into glasses, however, has not been studied.

In the present chapter, the study on the chemical durability of R-Si-O-N oxynitride glasses (R=Li or Na) in acidic and alkaline solutions is described.　The effects of nitrogen on the

chemical durability of these oxynitride glasses are discussed with respect to the change of the rate of ionic transport and the change of the covalency of the glass network.

EXPERIMENTAL

(1) Preparation and analysis of glasses

Oxynitride glasses of the compositions $30R_2O \cdot (70-3x)SiO_2 \cdot xSi_3N_4$ (where R=Li or Na, x=0 to 3 and 4, respectively) were prepared.   These glasses were chosen because the mechanism of chemical corrosion of the corresponding oxide glasses has been well understood.   Two kinds of non-nitrided glasses, containing different amounts of water, were prepared to examine the effect of the water content on the chemical durability.   The detailed procedures for the preparation and analysis of glasses are described in CHAPTER 2.   The glasses used were identical to those used in the experiments in CHAPTER 3.   The analyzed compositions are shown in Table 1 of CHAPTER 3.

(2) Measurement of chemical durability

The glasses were cut into plates of about $5 \times 5 \times 2$ mm^3 in size. The surfaces of the glass plates were polished with #800 grade silicon carbide abrasive powder.   The apparent surface area of the glass plates were calculated from the lengths of the edges of the plates.   The apparatus for the measurement of chemical durability is schematically shown in Fig. 1.   The test solutions were 0.1 N-NaOH and 0.1 N-HCl aqueous solutions.   The quantity of the solution was changed so that the amount of the solution might be 100 ml for 1 cm^2 apparent surface area of the glass plate.   The glass plate was immersed in the test solution for a
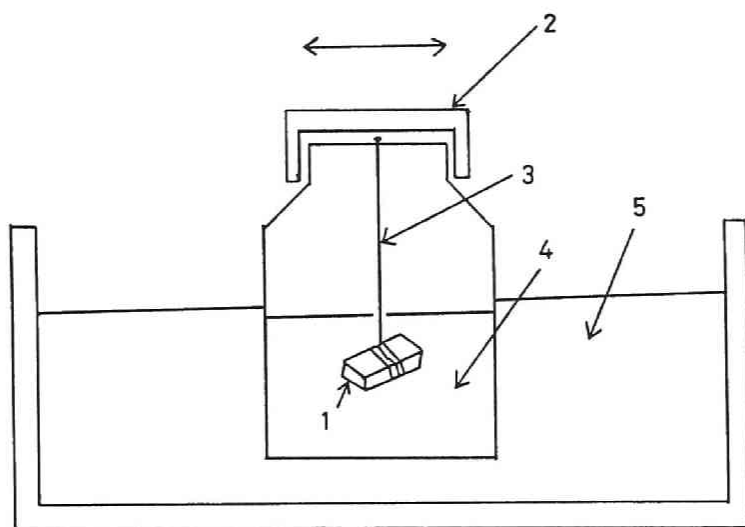
Fig. 1   A schematic arrangement of the apparatus for the
          measurement of the chemical durability of glasses.
          1: sample, 2: polyethylene container, 3: platinum
          wire, 4: test solution, 5: water bath.

desired period ranging from 1 day to 22 days depending on the chemical durability of the glass. The temperature of the test solution was fixed at 40 $^{\circ}$C with a temperature controller and the solutions were shaken at a rate of 120 strokes per minute. The chemical durability was determined as the weight loss of the glass plate per unit apparent surface area. Silicon and alkali ions which leached out into the test solution were quantitatively analyzed by means of the inductively coupled argon plasma analysis (ICAP) and the flame emission technique, respectively.

RESULTS

(1) Chemical durability to acidic solution

Fig. 2 shows the weight loss of Na-Si-O-N oxynitride glasses due to the immersion in 0.1 N-HCl test solution for 1 day. The weight loss decreases with increasing nitrogen content. That is, the chamical durability of Na-Si-O-N oxynitride glasses to acidic solution is improved progressively with increasing nitrogen content. Fig. 3 shows the concentration of ions leached out from Na-Si-O-N oxynitride glasses into the acidic test solution for 1 day. It is seen that sodium ions are predominantly leached into the test solution.

Fig. 4 shows the concentration of lithium ions leached out from Li-Si-O-N oxynitride glasses due to the immersion in the acidic test solution for 5 days. The chemical durability of Li-Si-O-N oxynitride glasses is also improved progressively with increasing nitrogen content.

In Figs. 2 to 4, circles with asterisk (*) represent the non-nitrided glasses containing larger amounts of water. It is known that the chemical durability of Na_2O-SiO_2 glasses to water decreases with increasing water content in the glasses[12]. It
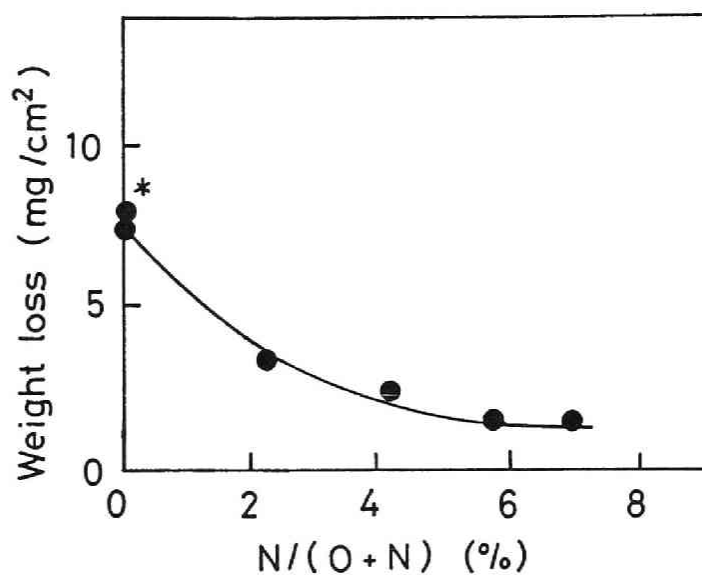
Fig. 2   Change of the weight loss of Na-Si-O-N oxynitride
          glasses due to the immersion in 0.1 N-HCl solution for
          1 day as a function of the nitrogen content.
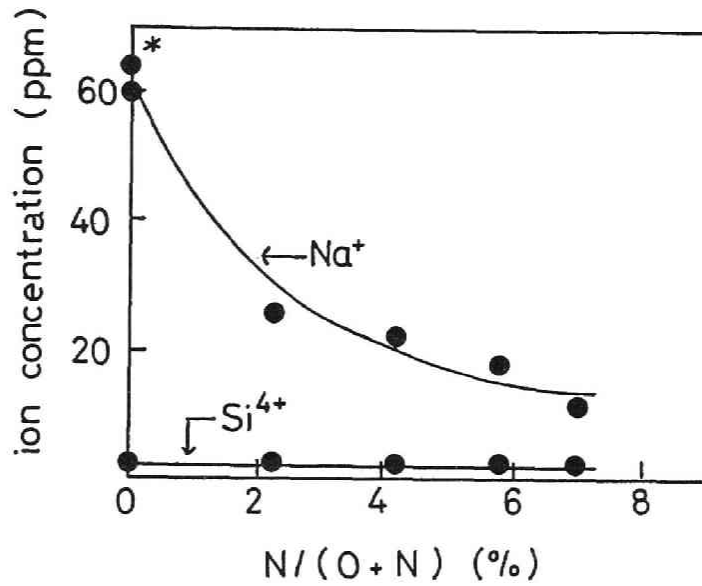
Fig. 3   Change of the concentrations of ions leached out from
           Na-Si-O-N oxynitride glasses due to the immersion in
           0.1 N-HCl solution for 1 day as a function of the
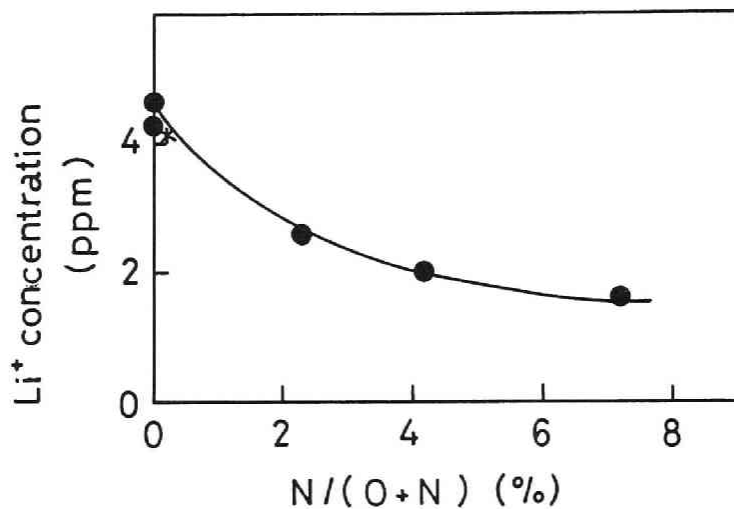   nitrogen content.

Fig. 4   Change of the concentration of lithium ion leached out
          from Li-Si-O-N oxynitride glasses due to the immersion
          in 0.1 N-HCl solution for 5 days as a function of the
          nitrogen content.

is clearly seen from these figures, however, that the effect of the nitrogen content on the chemical durability of these glasses to acidic water is far larger than that of the water content.
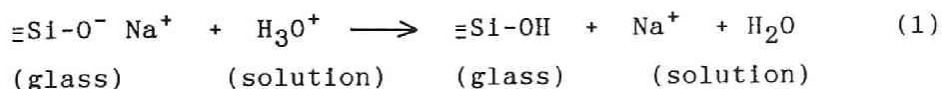
(2) Chemical durability to alkaline solution

Fig. 5 shows the weight loss of Na-Si-O-N oxynitride glasses due to the immersion in 0.1 N-NaOH test solution for 3 days. The chemical durability of these glasses to alkaline solution is improved progressively with increasing nitrogen content. Fig. 6 shows the concentration of silicon ion leached out into the test solution. In contrast to the case of acidic solution, silicon ions are leached out of the glasses to a considerable extent.

Fig. 7 shows the weight loss of Li-Si-O-N oxynitride glasses due to immersion in the alkaline test solution for 22 days. The chemical durability of Li-Si-O-N oxynitride glasses to alkaline solution is also progressively improved with increasing nitrogen content. Fig. 8 shows the concentration of silicon ion leached out into the alkaline test solution. It is seen that silicon ions are leached out of the glasses.

DISCUSSION

(1) Chemical durability to acidic solution

It is known that the chemical dissolution of Na_2O-SiO_2 glasses in water or acidic solutions proceeds by the ion exchange between alkali ions in the glasses and hydroxonium ion (H_3O^+) as expressed by equation (1)[13].

$$\equiv Si-O^- \ Na^+ \ + \ H_3O^+ \ \longrightarrow \ \equiv Si-OH \ + \ Na^+ \ + \ H_2O \qquad (1)$$
$$\text{(glass)} \qquad \text{(solution)} \qquad \text{(glass)} \qquad \text{(solution)}$$
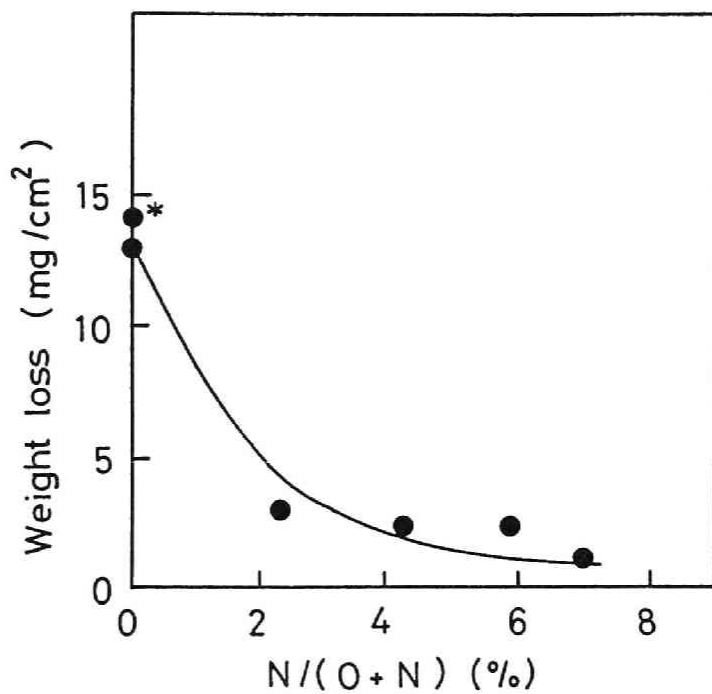
Fig. 5   Change of the weight loss of Na-Si-O-N oxynitride
          glasses due to the immersion in 0.1 N-NaOH solution for
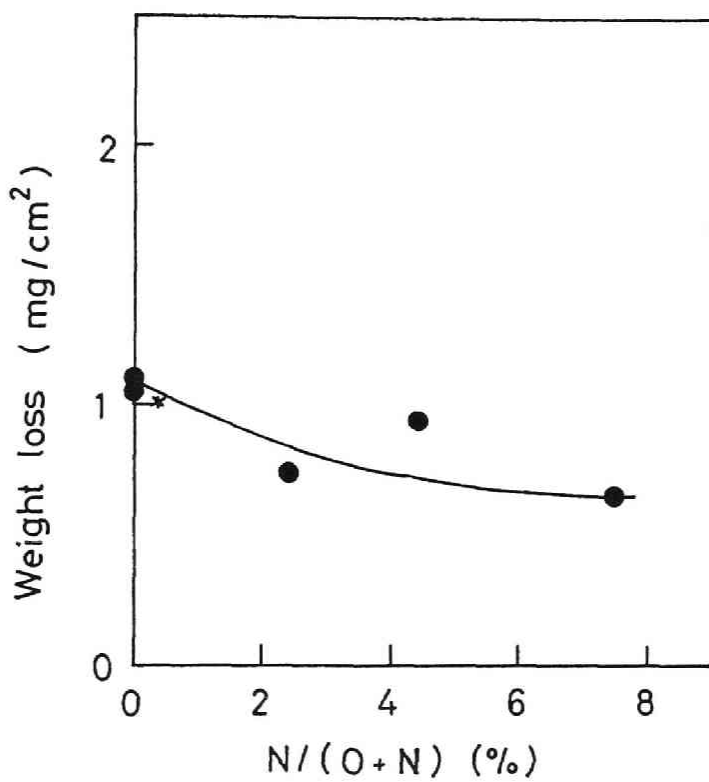   3 days as a function of the nitrogen content.

Fig. 6   Change of the weight loss of Li-Si-O-N oxynitride
         glasses due to the immersion in 0.1 N-NaOH solution for
         22 days as a function of the nitrogen content.
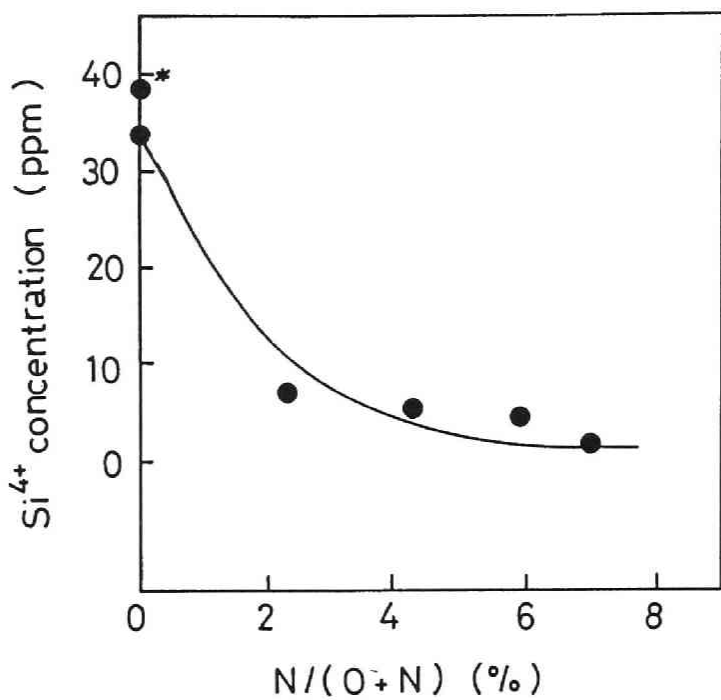
Fig. 7   Change of the concentration of silicon ion leached out
          from Na-Si-O-N oxynitride glasses due to the immersion
          in 0.1 N-NaOH solution for 3 days as a function of the
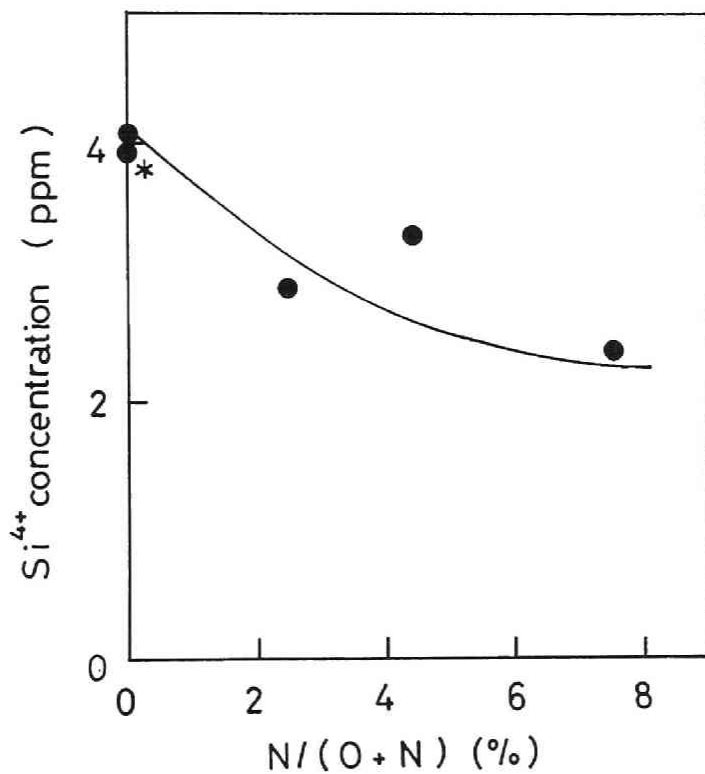   nitrogen content.

Fig. 8. Change of the concentration of silicon ion leached out
from Li-Si-O-N oxynitride glasses due to the immersion
in 0.1 N-NaOH solution for 22 days as a function of the
nitrogen content.

Sakka et al.[11] calculated the weight change of Na-Si-O-N oxynitride glasses from the amount of Na$^+$ ions leached out into 0.1 N-HCl solution based on equation (1), and found that the calculated weight change quantitatively coincide with the measurement. This indicates that the chemical dissolution of the present oxynitride glasses to acidic solution also proceeds by the ion exchange process.

The inter-diffusion coefficient which describes the kinetics of the ion exchange process, D, is expressed as equation (2)[14].

$$D = D_H D_R / (D_H N_H + D_R N_R) \tag{2}$$

where the subscripts H and R represent hydroxonium ion and alkali ion, respectively, N represents the molar fraction of the ion, and $N_H + N_R = 1$ at any point in the glass. Since the term $D_R N_R$ is far larger than $D_H N_H$, the above equation is approximated by the following equation:

$$D = D_H / N_R \tag{3}$$

This indicates that the diffusion of the hydroxonium ion largely determines the rate of corrosion of the glass.

In CHAPTER 3, the effect of nitrogen on the ionic transport has been discussed based on the equation proposed by Anderson and Stuart[15]. That is, the incorporation of nitrogen in glass causes an increase in the elastic modulus of glass and a decrease in the electrostatic attractive force exerted on the transporting ions. As the result, the diffusivity of small ions such as Li$^+$ (ionic radius: 0.68 Å) or Na$^+$ (0.97 Å) increases because the latter effect is more pronounced than the former one. However, for large ions such as hydroxonium ion (1.4 Å), the former effect would become predominant, causing a decrease in the diffusivity.

Therefore, it would be plausible to assume that the chemical durability of these oxynitride glasses to acidic solution is

improved as a result of the suppression of the diffusion of hydroxonium ion as a result of nitridation.

(2) Chemical durability to alkaline solution

The corrosion of alkali-silicate glasses in alkaline solution is described by the nucleophilic attack of hydroxyl anion (OH^-) as shown below:

$$\equiv Si-O-Si\equiv \ + \ OH^- \ \longrightarrow \ \equiv Si-O- \ + \ HO-Si\equiv \qquad (4)$$

Assuming that the positive charge on silicon atoms is reduced by the deformation and displacement of electron cloud of nitrogen toward the silicon atoms, the frequency of the attack of hydroxyl anion would be reduced or the activation energy for the attack would be enlarged. Since nitrogen is less electronegative than oxygen, the negatively charged electron cloud on nitrogen atoms may be more highly susceptible to deformation toward silicon atoms than that of oxygen atoms. The positive charge on silicon atoms directly bonded to nitrogen atoms, therefore, would be reduced. This assumption may be supported by the molecular orbital calculation conducted by Murakami and Sakka[16]. They showed that the overlap population of electron in Si-N bond is higher than that in Si-O bond and the atomic charge on silicon is less positive when it is bonded to nitrogen than to oxygen.

This indicates that the chemical durability to alkaline solution may be attributed to the increased covalency of Si-N bond compared with that of Si-O bond.

SUMMARY OF CHAPTER 4

The effect of incorporation of nitrogen on the chemical

durability of Na-Si-O-N and Li-Si-O-N oxynitride glasses has been studied. An increase in the nitrogen content improves the chemical durability of these glasses to both acidic and alkaline aqueous solutions. The improved chemical durability to acidic solution is attributed to a decreased diffusivity of hydroxonium ion in the glasses on nitridation, which is due to an increase in the elastic modulus of glass as a result of nitridation. The improved chemical durability to alkaline solution is attributed to the increased covalency of Si-N bonds, which reduces the possibility of the attack of hydroxyl anions to silicon atoms.

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CHAPTER 5 Liquid-Liquid Phase Separation in Li-Si-O-N Oxynitride Glasses

INTRODUCTION

Liquid-liquid phase separation, abbreviated to phase separation, is often observed in oxide glasses and has been studied for many years in glass science and technology. Porous and dense high silica glasses are manufactured by utilization of phase separation of $Na_2O-SiO_2-B_2O_3$ glasses into SiO_2 rich phase and $Na_2O-B_2O_3$ phase.

It is also known that, phase separation plays an important role in producing glass-ceramics by accelerating nucleation of crystals. It is generally observed that bulk nucleation occurs on crystallizing oxynitride glasses[1-3]. Hayashi and Tien[1] suggested that nitridation might enhance the tendency of glasses to phase separation, and in turn, the phase separation may enhance the bulk nucleation. However, the effect of nitrogen on the phase separation itself has net been fully understood.

In the present chapter, the phase separation in Li-Si-O-N oxynitride glasses is examined to clarify and discuss the effect of nitrogen on the miscibility of Li_2O-SiO_2 system.

EXPERIMENTAL

(1) Preparation and analysis of glasses

Two series of oxynitride glasses of the batch compositions $25Li_2O \cdot (75-3x)SiO_2 \cdot xSi_3N_4$ and $30Li_2O \cdot (70-3x)SiO_2 \cdot xSi_3N_4$ (x=0, 1, 2 and 3) were prepared. These compositions have been chosen because the miscibility region and the phase separation behavior

has been extensively studied for the base oxide system Li_2O-SiO_2[4, 5]. The glasses were prepared and analyzed for the nitrogen and lithium contents in the same manner as that described in the previous chapters. The guaranteed purity of the β-silicon nitride powder used is higher than 98 wt% in the content and the major impurities are oxygen (0.9 wt%), carbon (0.25 wt%) and free Si (less than 0.2 wt%). Contents of Al, Fe and Ca impurities are approximately 0.6 wt% in total. The amount of Al, Fe and Ca in the resultant oxynitride glasses is estimated to be less than 0.05 wt%.

Glass transition temperature (T_g) was measured by differential thermal analysis with a MAC Science Company model TG-DTA 2000 instrument at a heating rate of 10 $^\circ$C/min under a flow of argon.

(2) Determination of the miscibility temperature

Glass specimens were heat-treated to determine the miscibility temperature. The schematic arrangement of the furnace is shown in Fig. 1. Specimens of about 3x3x3 mm^3 in size attatched to the tip of a sheathed Pt-Pt(Rh) thermocouple were inserted into an electric furnace, which was heated at desired temperatures beforehand, for the heat-treatment. Every specimen was heated up to the desired temperature within 90 seconds. The heat-treatment was conducted under a flow of nitrogen to avoid the oxidation of the specimens. Each specimen was heat-treated at temperatures near its miscibility temperature for 1 to 40 minutes depending on the composition and the heat-treatment temperature. After the heat-treatment, the specimen was quenched below the glass transition temperature within 15 seconds by withdrawing the specimen to the cold zone of the furnace.
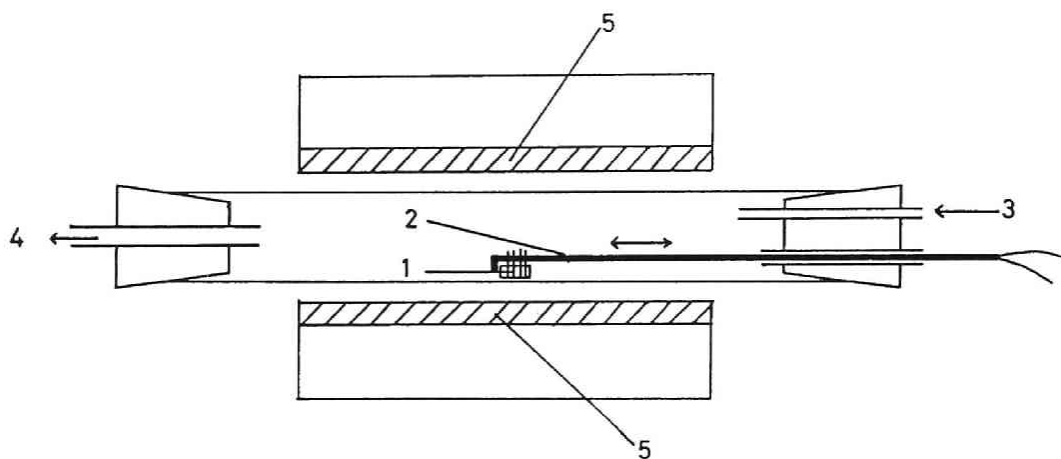
Fig. 1. A schematic arrangement of the furnace for the heat-
treatment of specimens. 1: specimen, 2: thermocouple,
3: N_2 gas inlet, 4: gas outlet, 5: heater.

The fractured surface of heat-treated specimens was etched in 5 % hydrofluoric acid for 5 minutes, rinsed carefully in distilled water and examined on the occurrence of the phase separation with a scanning electron microscope (JEOL, T330A) under the magnification from x15,000 to x50,000. A gold film was sputter-deposited onto the surface of the specimen to avoid the charging.

Randomly distributed spherical particles, 0.1 to 0.3 μm in diameter, were seen in the phase-separated specimens. The examples are shown in Fig. 2. The diameter of the particles increased with increasing heat-treatment time. As the heat-treatment temperature became higher, the distribution of the particle became sparcer and eventually the particles disappeared. The miscibility temperature (T_m) was defined as the lowest temperature at which no phase separation was observed. The error range and the reproducibility of the data were estimated to be within ± 10 $^{\circ}$C.

RESULTS

(1) Chemical analysis of glasses

Table 1 shows the analyzed compositions and the glass transition temperatures of the oxynitride glasses. Nitrogen is incorporated up to about 10 eq% (3[N]/(2[O]+3[N])) in both series. Lithium was not seriously lost during the preparation of oxynitride glasses.

(2) Miscibility temperature

The miscibility temperature of the oxynitride glasses is listed in Table 1 and depicted in Fig. 3 as a function of the Li_2O content. The solid lines indicate the immiscibility
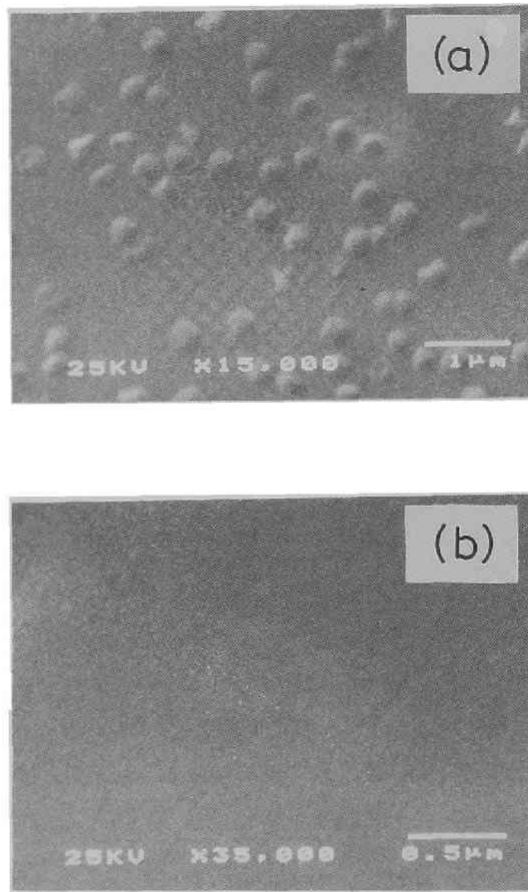
Fig. 2. Examples of the etched surface of $25Li_2O \cdot 69SiO_2 \cdot 2Si_3N_4$ glass showing (a) phase separation and (b) homogeneous glass. The glass specimens were heat-treated at (a) 34 $^{\circ}C$ below T_m and (b) 23 $^{\circ}C$ above T_m.

Table 1   Analyzed compositions, glass transition temperatures (T_g) and the miscibility temperatures (T_m) of oxynitride glasses.

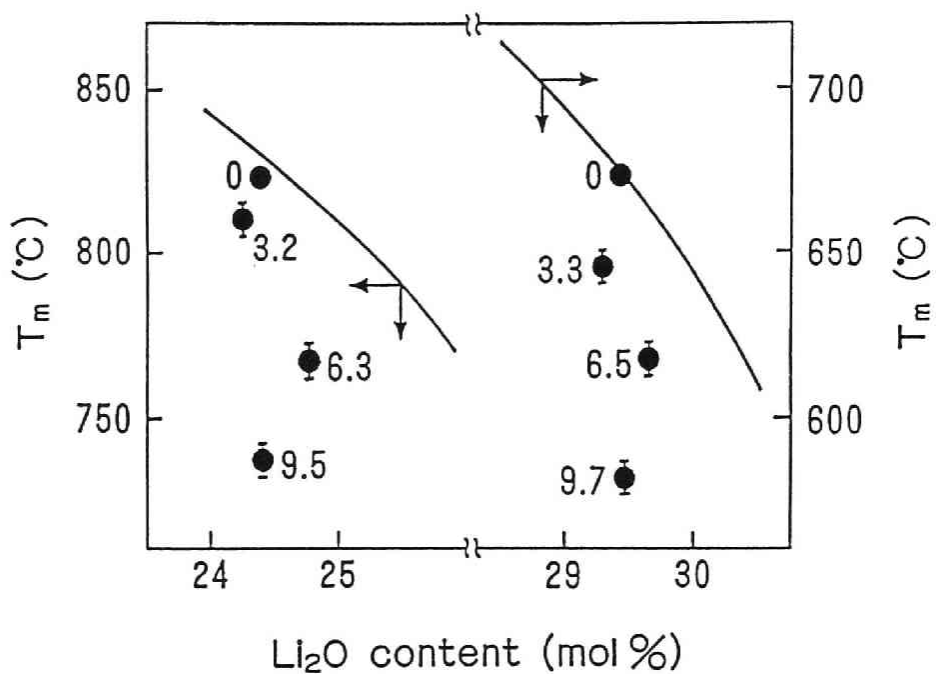| Sample No. (x value)	Li_2O (mol%)	SiO_2 (mol%)	$SiN_{4/3}$ (mol%)	N (eq%)	T_g (°C)	T_m (°C)
$25Li_2O \cdot (75-3x)SiO_2 \cdot xSi_3N_4$ series
0	24.37	75.63	0	0	465	823
1	24.24	72.96	2.80	3.21	489	810
2	24.79	69.65	5.55	6.31	513	767
3	24.39	67.29	8.31	9.47	535	738
$30Li_2O \cdot (70-3x)SiO_2 \cdot xSi_3N_4$ series
0	29.44	70.56	0	0	461	673
1	29.26	67.97	2.79	3.27	483	650
2	29.63	64.84	5.52	6.48	503	618
3	29.45	62.29	8.25	9.68	520	582

Fig. 3.   Miscibility temperature (T_m) of the oxynitride
          glasses as a function of the Li_2O content.   The
          numbers represent the nitrogen content (eq%,
          3[N]/(2[O]+3[N])).   The solid lines indicate the
          immiscibility boundary of Li_2O-SiO_2 system based on the
          data of Haller et al[5].

boundary of Li_2O-SiO_2 glasses reported by Haller et al[5]. The numbers beside the solid circles represent the nitrogen contents (eq%) of glasses. Non-nitrided glasses show miscibility temperatures consistent with the immiscibility boundary reported by Haller et al[5]. It is seen from Fig. 3 that the miscibility temperature of both series becomes lower with increasing nitrogen content. In other words, the phase separation of Li-Si-O-N oxynitride glasses is more suppressed with increasing nitrogen content.

Figs. 4 and 5 show the deviations of the miscibility temperature from the temperature of the immiscibility boundary line of the Li_2O-SiO_2 composition of the corresponding Li_2O content (ΔT_m) as a function of the nitrogen content. The deviation follows a linear dependence on the nitrogen content for both series of glasses. The incorporation of 10 eq% of nitrogen lowers the miscibility temperatures by about 90 $^\circ$C for both series of glasses.

DISCUSSION

Levin[6] pointed out that the immiscibility of silicate and borate systems can be related to the difference between the electrostatic attractive force of the network-forming cation with oxygen and that of network-modifying cation with oxygen. In most silicate and borate systems, the tendency of a melt to immiscibility is strong when the ionic field strength of the network-modifying cation, defined as Z/r, is high, where Z is the ionic charge and r is the ionic radius of the network-modifying cation. Moriya[4, 7, 8] studied the effects of additives on the miscibility of binary alkali-silicate glasses, showing that the
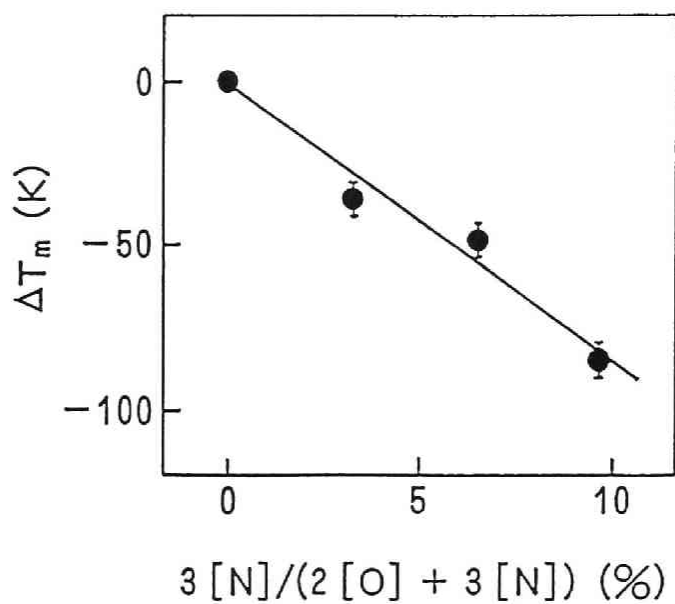
Fig. 4. Deviation of the miscibility temperature of
$25Li_2O \cdot (75-3x)SiO_2 \cdot xSi_3N_4$ glasses from the
immiscibility boundary line (ΔT_m) for the
corresponding Li_2O-SiO_2 system as a function of the
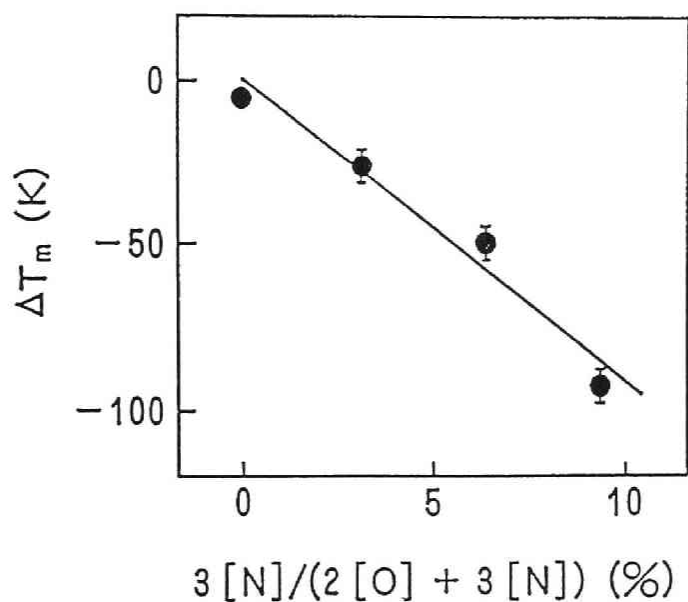nitrogen content.

Fig. 5.　Deviation of the miscibility temperature of
$30\text{Li}_2\text{O} \cdot (70-3\text{x})\text{SiO}_2 \cdot \text{xSi}_3\text{N}_4$ glasses from the
immiscibility boundary line (ΔT_m) for the
corresponding $\text{Li}_2\text{O-SiO}_2$ system as a function of the
nitrogen content.

network-modifying additives with high ionic field strength promote the phase separation while those with low ionic field strength suppress it, in accordance with the idea of Levin[6]. These may imply that the phase separation is promoted when the electrostatic interaction between the network-modifying cations and the network anion is strong.

In the present system, the substitution of a part of oxygen atoms by nitrogen atoms lowers the miscibility temperature. The effect of minor impurities of Al, Fe and Ca can be neglected because the contents are too low. The observed change of the miscibility temperature may be attributed to the change of the electrostatic interaction between lithium ion and the anions.

It has been shown in CHAPTER 3 that the activation energy for transport of lithium ion in Li-Si-O-N oxynitride glasses decreases with increasing nitrogen content, which may be attributed to the decrease in the electrostatic attractive force exerted on lithium ions on nitridation. The change of the electrostatic interaction on nitridation arises from the lower electronegativity of nitrogen than that of oxygen. It is known that the incorporation of fluorine, which is more highly electronegative than oxygen, enhances phase separation[9].

Consequently, the lowering of the miscibility temperature on nitridation may be attributed to a decrease in the electrostatic interaction between the lithium ions and the network anions. Shaw et al.[10] observed the phase separation in the Mg-Si-O-N system, indicating that the glasses separated into MgO-rich phase and SiO_2-rich phase, nitrogen atoms were present in both separated phases, and the immiscibility gap in the MgO-SiO_2 system became narrower as a result of incorporation of nitrogen. The narrowing of the immiscibility gap of Mg-Si-O-N system may be interpreted by the same discussion as in the present study.

SUMMARY OF CHAPTER 5

The miscibility temperature of Li-Si-O-N oxynitride glasses becomes lower with increasing nitrogen content, indicating that the phase separation is suppressed by the incorporation of nitrogen. The incorporation of 10 eq% of nitrogen lowers the miscibility temperature by about 90 ^{O}C. The lowering of the miscibility temperature has been attributed to the decrease in the electrostatic interaction between the lithium ions and the network anions due to the incorporation of nitrogen.

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CHAPTER 6   Crystallization of Oxynitride Glasses

It is expected that novel glass-ceramics mey be prepared by crystallizing oxynitride glasses because crystals which have useful properties may be precipitated in oxynitride glasses. It has been found that oxynitride glasses can be converted to fine-grained glass-ceramics without addition of a special nucleating reagent[1, 2].   Also, Wusirika and Chyung reported that X-phase crystals precipitated in the bulk of oxynitride glasses reinforce the matrices of high-quartz, cordierite and β-spodumene phases[1].

The crystallization of oxynitride glasses is also important for sintered silicon nitride ceramics.   Certain oxides such as Y_2O_3 and Al_2O_3 added to promote the sintering of silicon nitride may form oxynitride glass inclusions in the grain boundaries of the nitride ceramics, deteriorating their creep resistance at high temperatures[3].   In order to improve the high temperature mechanical strength of the nitride ceramics, crystallization of the glassy phases is necessary[4].

The effect of the incorporation of nitrogen on the crystallization behavior, however, is not fully understood.

In the present chapter, the effect of nitrogen on the crystallization of oxynitride glasses is described.   In Section 6. 1, crystallization of Li-Si-O-N oxynitride glasses is described.   In Section 6. 2, crystallization of Li-Al-Si-O-N oxynitride glasses and properties of the resultant glass-ceramics are described.

Section 6.1 Crystallization of Li-Si-O-N Oxynitride Glasses

INTRODUCTION

Generally, incorporation of nitrogen into oxide glasses increases the viscosity[5-7], raising the glass transition[6-11] and crystallization temperatures[2, 6, 8, 12, 13], while in some glasses the crystallization temperature does not vary so much[14, 15]. On crystallization, nitrogen precipitates as a constituent of Si_2N_2O[3, 6, 16], X-phase[1], unidentified phase[2, 14] or solid solution of compounds[4, 6], or it remains in the glassy phase[17].

In the present section, the crystallization behavior of Li-Si-O-N oxynitride glasses has been described in comparison with that of a Li_2O-SiO_2 glass. Effect of nitrogen on the crystallization temperature, nucleation mechanism and precipitated crystalline phases has been extensively discussed.

EXPERIMENTAL

(1) Preparation and analysis of oxynitride glasses

Oxynitride glasses of the composition $30Li_2O\cdot(70-3x)SiO_2\cdot xSi_3N_4$ (x=0, 1, 2 and 3), in which the ratio of lithium to silicon is kept at 6 to 7, have been prepared. Two kinds of non-nitrided glasses were prepared to examine the effects of water content on crystallization: one glass was melted in air and the other was melted in a dry nitrogen atmosphere. The glasses were analyzed for the nitrogen, lithium and water

contents in the same manner as described in the previous chapters. The analyzed compositions are shown in Table 1. The maximum nitrogen content is 3.1 wt%. Lithium is not seriously lost during the preparation of oxynitride glasses. The water content of nitrided glasses is very small. The nitrided glasses are gray in color.

Decomposition of silicon nitride resulting in the deposition of metallic silicon may occur during the preparation of nitrided glasses, to which the color of the oxynitride glasses may be attributed[18]. If the amount of the deposition is large, it would result in a change in the composition. The amount of the deposition of metallic silicon was examined by X-ray photoelectron spectroscopy (XPS). A 10 kV AlKα X-ray source was used. A spectrum of Si$_{2p}$ photoelectron of an oxynitride glass, No. 3 of Table 1, was measured. The calibration of the line shift was made by referring to the C$_{1s}$ line (284.6 eV[19]) of the hydrocarbon contaminant. Fig. 1 shows the spectrum. The position of the main peak (102.8 eV) agrees well with the result of Kaneko[20] for a $30Li_2O \cdot 70SiO_2$ glass (103.0 eV). Deposition of metallic silicon, which would cause an marked change in the composition, was not detected even in the nitrided glass of maximum nitrogen content, that is, a peak around 98 eV attributable to metallic silicon was completely absent.

(2) Differential thermal analysis

Crystallization behavior was investigated by the differentioal thermal analysis (DTA). The analysis was conducted on both the bulk specimens of approximately 3x3x1 mm^3 in size and the powder specimens with sizes of 37 to 63 μm. The heating rate was 10 $^{\circ}$C/min. Nitrogen gas of 99.9995 % purity was passed in the equipment to avoid any possible oxidation of the specimens.

Table 1   Analytical compositions of $30Li_2O \cdot (70-3x)SiO_2 \cdot xSi_3N_4$ oxynitride glasses

Sample (x value)	N_{calc} (wt%)	N_{anal} (wt%)	Li* (wt%)	Water (wt%)
OA**	0	0	8.16	9×10^{-3}
ON+	0	0	8.25	1×10^{-3}
1	1.11	1.06	8.23	$<1 \times 10^{-4}$
2	2.23	1.97	8.17	$<1 \times 10^{-4}$
3	3.37	3.13	8.24	$<1 \times 10^{-4}$

*Theoretical lithium content in a $30Li_2O \cdot 70SiO_2$ glass is 8.16 wt%.

**Melted in air at 1500 °C for 2h.

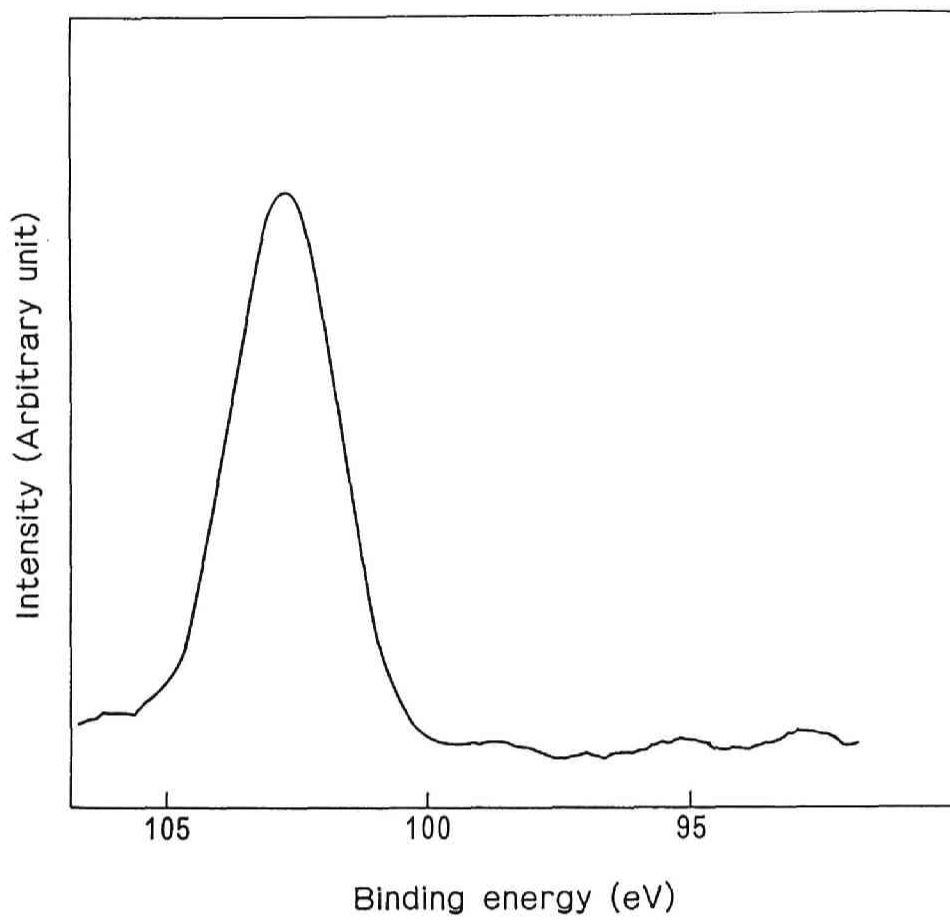+Melted in a nitrogen atmosphere at 1400 °C for 1h.

Fig. 1.　An Si$_{2p}$ photoelectron spectrum of oxynitride glass 3.

(3) Crystallization of glasses and identification of precipitated crystalline phases

Glass specimens of about 1 mm in thickness were heat treated for crystallization at 670 to 925 $^{\circ}$C for 1 or 24 hours under a flow of nitrogen gas. Glass specimens were wrapped with tantalum foils and heated at a rate of 10 $^{\circ}$C/min to the desired temperatures. After the heat-treatment, specimens were quickly withdrawn to the cold zone of the furnace.

The precipitated crystalline phases were identified by X-ray diffraction (XRD). The X-ray d-spacings of (110), (130), (040), (111) and (002) planes of lithium disilicate ($Li_2Si_2O_5$) were determined using CuKα radiation. The diffraction from a silicon (111) plane (d=0.3138 nm) was used as a reference.

(4) Microscopic observation

In order to investigate the nucleation mechanism, the fractured surfaces of the heat-treated glasses were observed with a scanning electron microscope (SEM). The specimens were heated in the DTA equipment at a rate of 10 $^{\circ}$C/min under a flow of nitrogen gas and the power of the furnace was turned off at the desired temperatures.

RESULTS

(1)Glass transition and crystallization temperatures

Fig. 2 shows the DTA profiles of the bulk and powder specimens. The glass transition temperature is indicated by the endotherm. The incipient temperature of the exothermic reaction is taken as the crystallization temperature. The glass
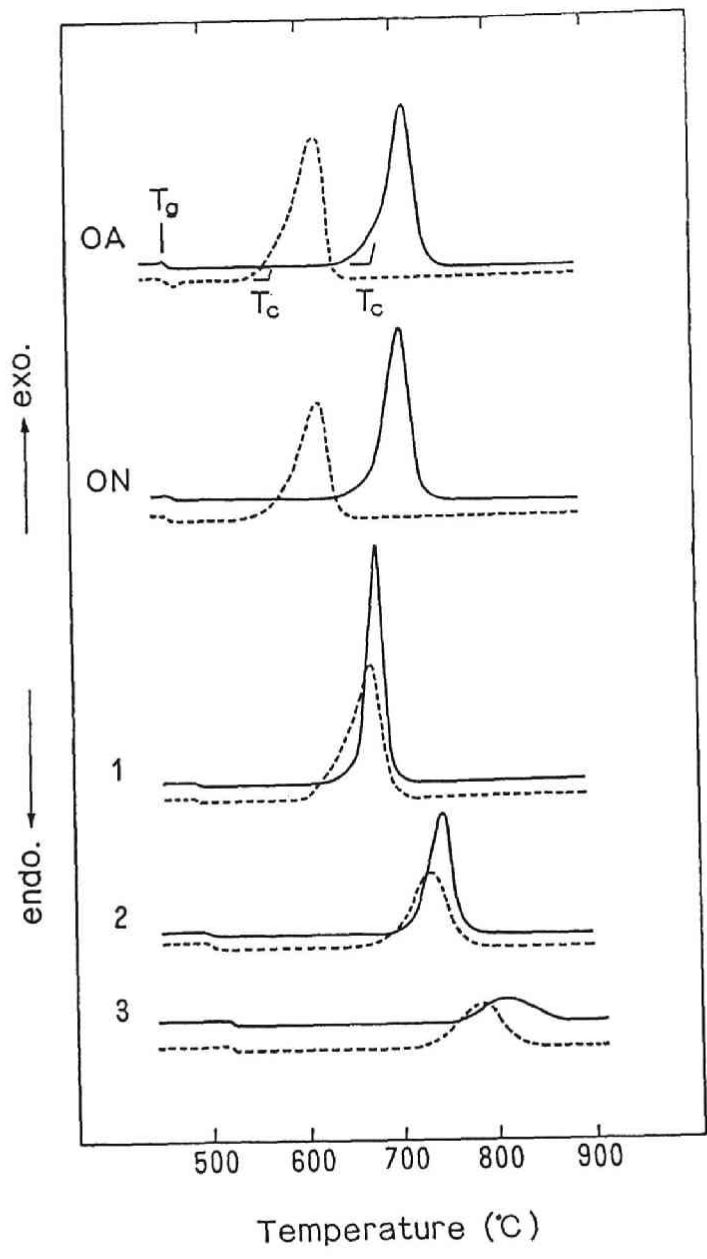
Fig. 2.   DTA curves of oxynitride glasses.   (———)Bulk and
(————)powder specimens.

transition and crystallization temperatures are shown in Table 2.

The glass transition temperature of the bulk specimen agrees with that obtained for the powder specimen within 4 °C. The glass transition temperature rises with increasing nitrogen content. The incorporation of 3.1 wt% nitrogen raises the glass transition temperature by about 60 °C.

As seen from Fig. 2, an exothermic peak due to crystallization is seen in each specimen in the temperature range from 550 to 850 °C. For the non-nitrided glasses, the crystallization temperature of the powder specimen (broken line) is lower than that of the bulk specimen (solid line) by about 100 °C. On the other hand, for the nitrided glasses, the crystallization temperatures of the powder and bulk specimens coincide with each other within 30 to 40 °C. In nitrided glasses, the crystallizaiton temperature rises, the peak width broadens and the peak hight is lowered as the nitrogen content increases.

The DTA profiles of two non-nitrided glasses, 0A and 0N, are almost identical. Although a decrease in the water content of glasses raises the glass transition temperature[21, 22] and lowers the temperature of the initiation of crystallization[21], the effect of the water content is very small compared with that of the nitrogen content.

(2) Crystalline phases

The XRD profiles of the specimens after the heat-treatments are shown in Figs. 3 to 6. The results for glass 0N are identical to those for glass 0A shown in Fig. 3. For non-nitrided glasses, 0A and 0N, $Li_2Si_2O_5$ first precipitats, followed by the precipitation of cristobalite at 820 °C.

From the nitrided glasses, however, lithium metasilicate (Li_2SiO_3) as well as $Li_2Si_2O_5$ are precipitated at relatively low

Table 2   The glass transition temperature (T_g) and the
crystallization temperature (T_c) of oxynitride glasses

Sample		$T_g(^{\circ}C)$	$T_c(^{\circ}C)$
0A	bulk	463	682
	powder	461	576
0N	bulk	467	676
	powder	463	576
1	bulk	491	656
	powder	488	623
2	bulk	501	718
	powder	500	688
3	bulk	520	761
	powder	520	722
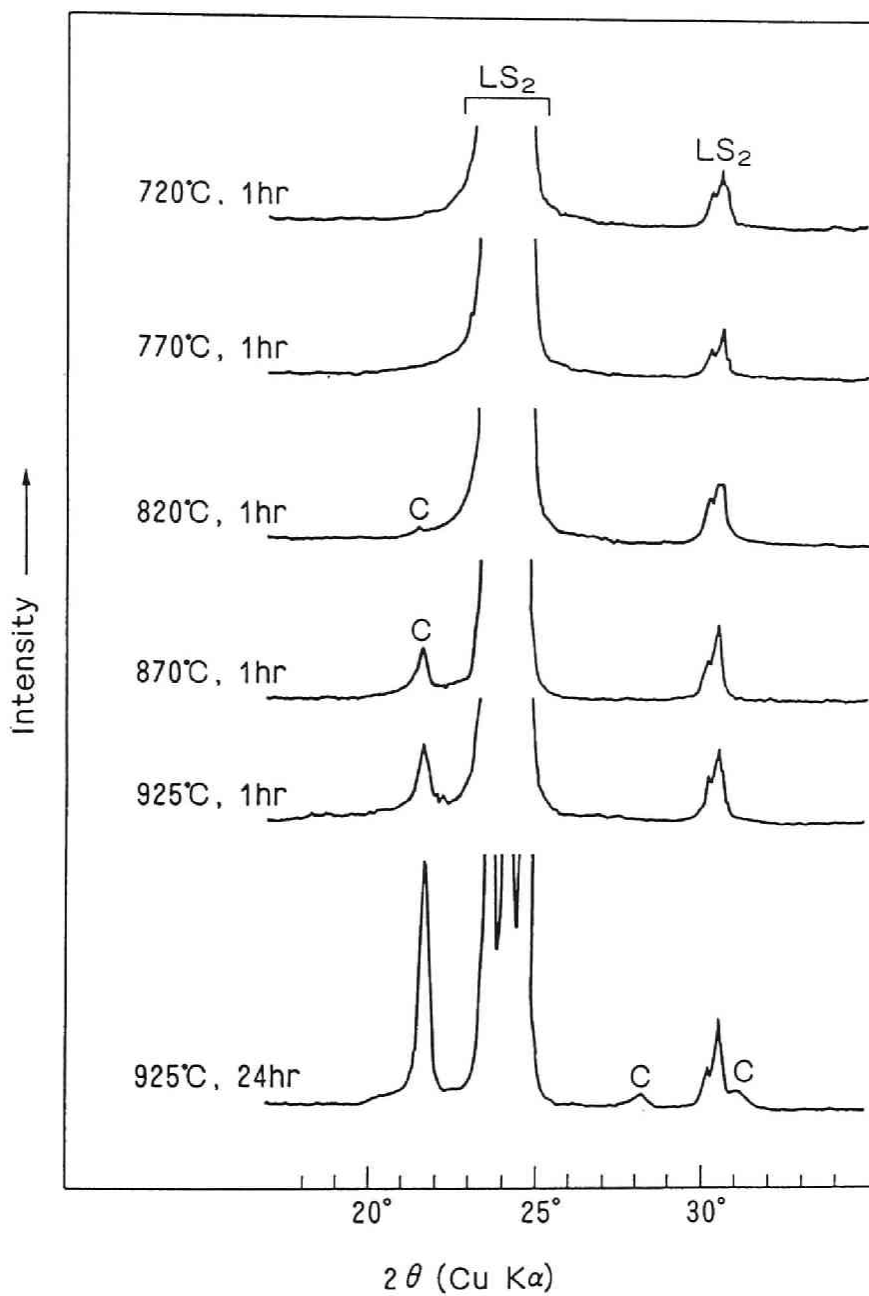
Fig. 3. XRD patterns of glass 0A heat-treated under various
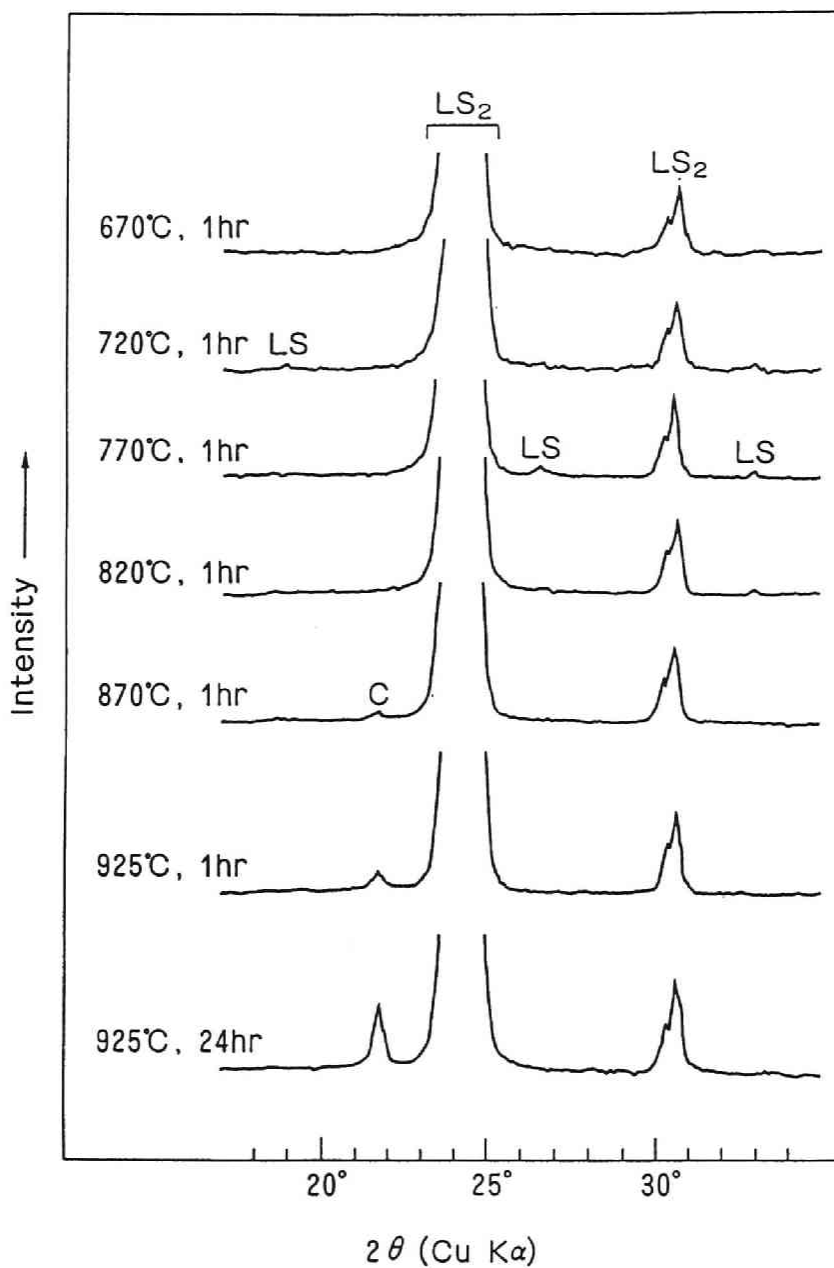conditions. LS_2 and C represent $Li_2Si_2O_5$ and
cristobalite, respectively.

Fig. 4. XRD patterns of glass 1 heat-treated under various conditions. Abbreviations are the same as those in Fig. 3 and LS represents Li_2SiO_3.
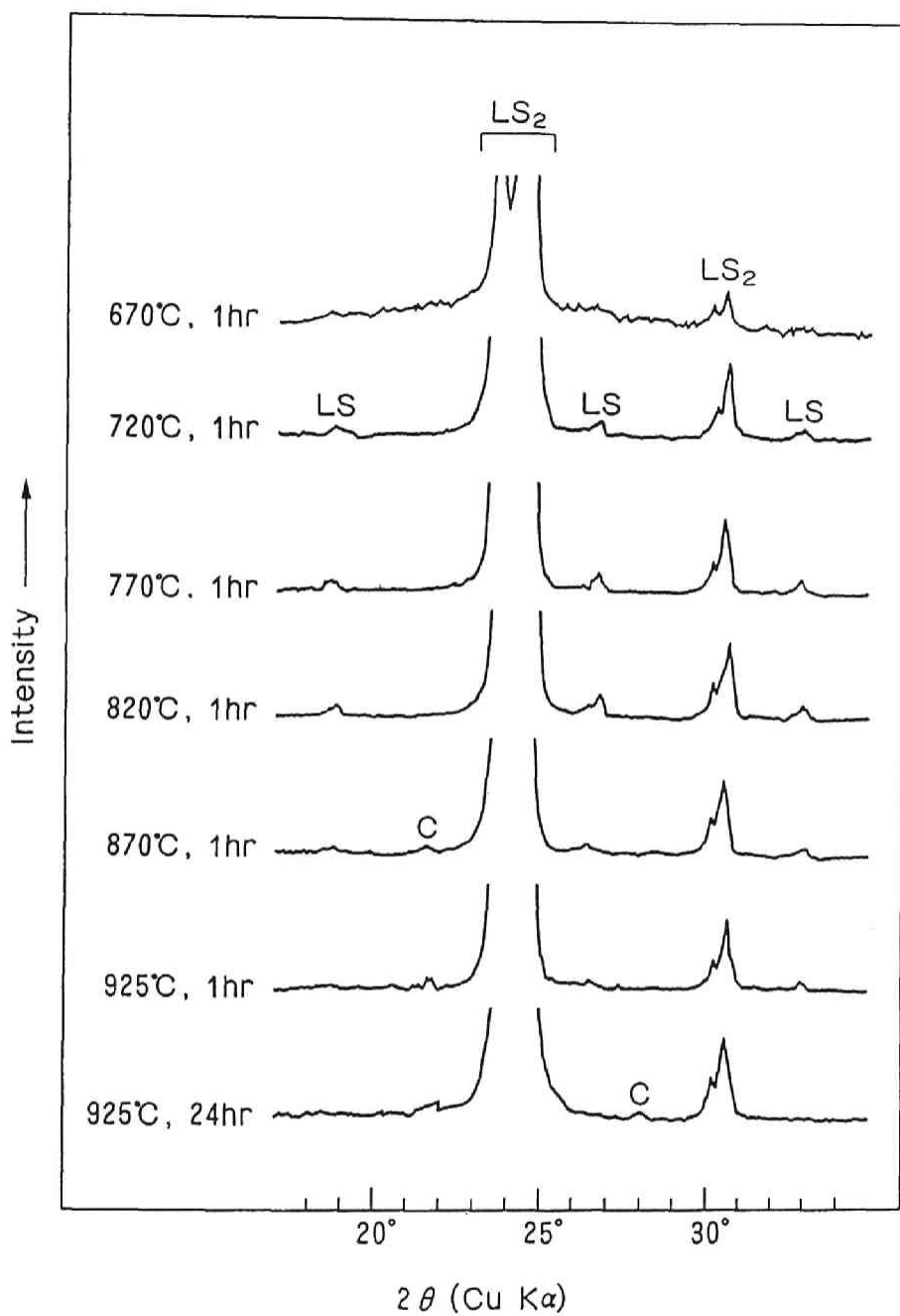
Fig. 5.   XRD patterns of glass 2 heat-treated under various
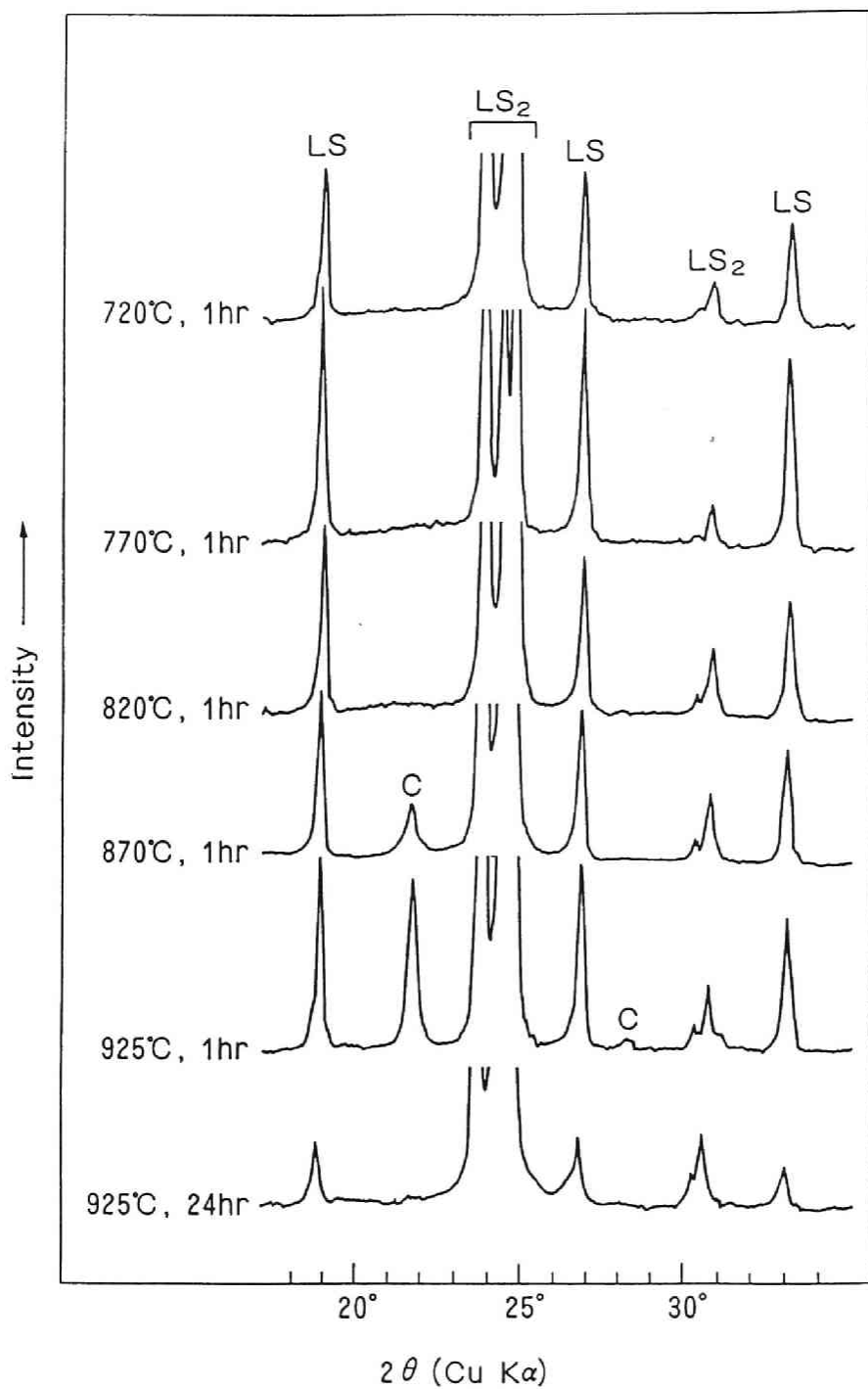conditions.   Abbreviations are the same as in Figs. 3
and 4.

Fig. 6.   XRD patterns of glass 3 heat-treated under various conditions.   Abbreviations are the same as in Figs. 3 and 4.

temperatures.   The tendency to the precipitation of Li_2SiO_3 becomes more prenounced as the nitrogen content increases. After a heat-treatment at 870 ^{o}C, cristobalite is also seen in the nitrided glasses.   As the result, $Li_2Si_2O_5$, Li_2SiO_3 and cristobalite are found to coexist.   Since Li_2SiO_3 and cristobalite react with each other to produce $Li_2Si_2O_5$, Li_2SiO_3 disappears from glasses 1 and 2 and cristobalite disappears from glass 3 after a heat-treatment at 925 ^{o}C for 24 hours.   Any crystalline phases containing nitrogen were not precipitated after the heat-treatments.

   Table 3 shows the X-ray d-spacings of $Li_2Si_2O_5$ precipitated after the heat-treatment at 925 ^{o}C for 24 hours together with the values from a reference[23].   No progressive change in the X-ray d-spacings is seen with the change of the nitrogen content. Therefore, it is assumed that nitrogen is not dissolved in precipitated $Li_2Si_2O_5$ crystal.   Table 4 shows the intensities of the scattering at 26 degree (2θ) from the specimens heat-treated at 925 ^{o}C for 24 hours, which correspond to the amount of residual glasy phase[24].   The scattering from the glassy phase increases with increasing nitrogen content.   The results shown in Tables 3 and 4 may indicate that nitrogen remains in the glassy phase even after a heat-treatment at 925 ^{o}C for 24 hours.

(3) Nucleation
   Fig. 7 shows the fractured surface of heat-treated glass specimens.   It is obvious from the figure that both surface crystallization and bulk crystallization occur in the non-nitrided glass, whereas nitrided glasses show only bulk crystallization.   Furthermore, numerous crystalline particles are precipitated in nitrided glasses.

   The difference in the nucleation between non-nitrided and

Table 3   X-ray d-spacings of $Li_2Si_2O_5$ precipitated from
oxynitride glasses after crystallization at 925 $^{\circ}$C for
24 hours

Sample	d(nm)				
	(110)	(130)	(040)	(111)	(002)
OA	0.5411	0.3738	0.3657	0.3583	0.2389
ON	0.5423	0.3733	0.3659	0.3585	0.2390
1	0.5411	0.3732	0.3645	0.3584	0.2393
2	0.5413	0.3734	0.3650	0.3585	0.2394
3	0.5417	0.3736	0.3652	0.3588	0.2395
ref[23]	0.543	0.375	0.367	0.359	0.2395

Table 4   Intensities of the scattering at 26 degree
           from oxynitride glasses heat treated at
           925 ^{O}C for 24h

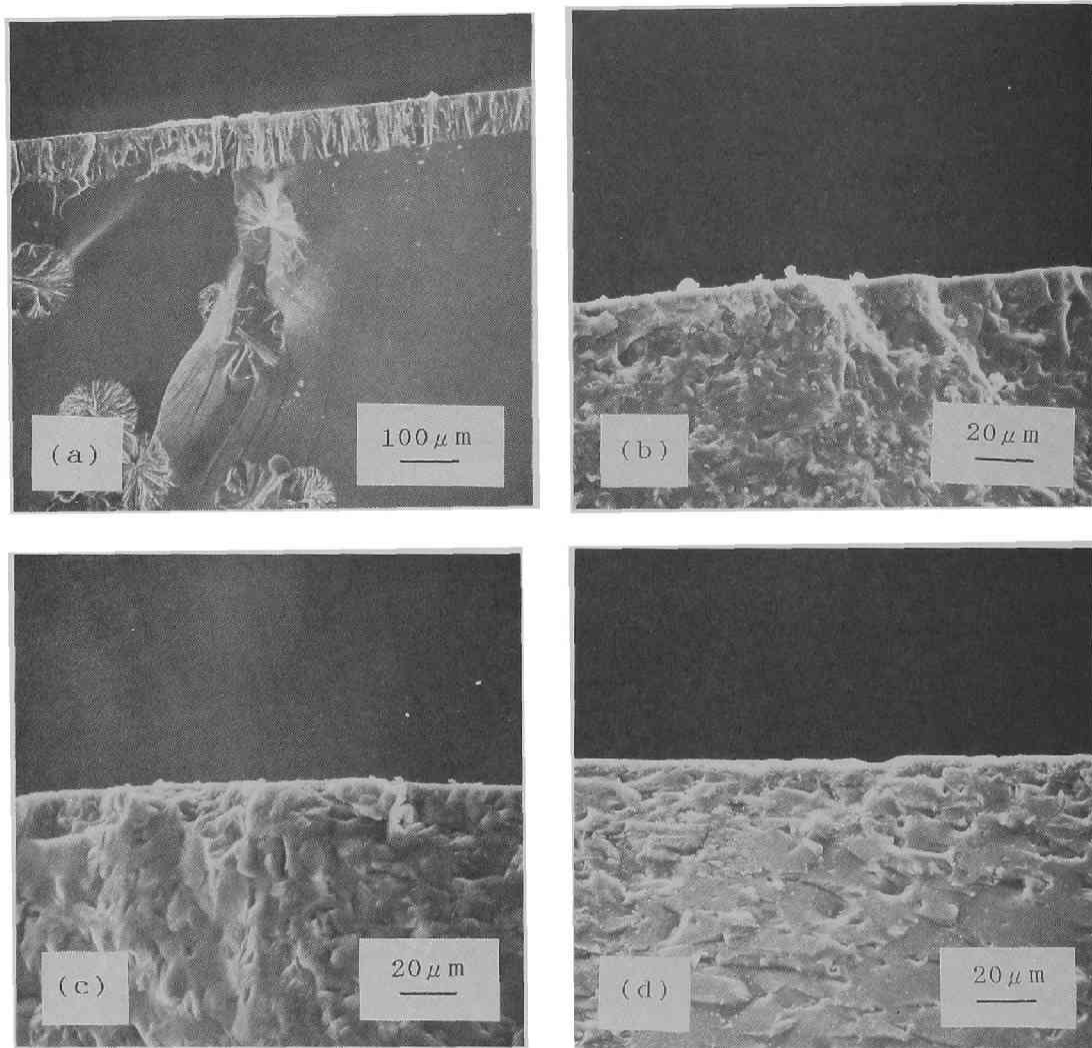| Sample	Intensity (counts/sec)
OA	44
ON	42
1	60
2	70
3	90

Fig. 7.   Electron micrograph of fractured surfaces of oxynitride
           glasses during crystallizaiton.   (a) 0A, (b) 1, (c) 2
           and (d) 3.

nitrided glasses is also observed in the DTA profiles. For
non-nitrided glasses, the crystallization temperature of the
powder specimens is lower by about 100 $^{\circ}$C than that of the bulk
specimens, as seen from Fig. 2 and Table 2, suggesting that the
crystallization occurs from the surface. In fact, it is known
that the glasses of the compositions around $Li_2O \cdot 2SiO_2$
composition crystallize both from the surface and in the
bulk[25]. For nitrided glasses, however, the differences in the
crystallization temperature between the powder and the bulk
specimens is smaller, supporting that the crystallization occurs
only in the bulk.

DISCUSSION

(1) Effect of nitrogen on the glass transition and
    crystallization temperatures

The incorporation of nitrogen raises the glass transition
and crystallization temperatures as shown in Table 2. These
changes can be attributed to the effect of nitrogen. The
lithium content is constant for all the glasses and the effect of
the water content is very small to explain these changes.

A rise in the glass transition temperature corresponds to an
increase in the viscosity at a certain temperature. In general,
the viscous flow of glass takes place via the dissociation of the
bonds constituting the glass network. Therefore, the increase
in the viscosity on nitridation may be attributed to an increase
in the average dissociation energy of the bonds between silicon
and anions; the dissociation energy of Si-N bonds per unit volume
is higher than that of Si-O bonds[7].

The crystallization temperature rises with increasing
nitrogen content. The temperature of the initiation of the

exothermic reaction of crystallization is the temperature at which the nuclei of a critical size start to grow[21]. For the growth of the crystals, the pertinent atomic species should diffuse in the glass, and the rate of the diffusion would be suppressed by an increase in the viscosity of the glass. Therefore, the rise in the crystallization temperature with increasing nitrogen content may be attributed to the formation of Si-N bonds which increase the viscosity of the glass.

The changes of the DTA profiles with increasing nitrogen content (Fig. 2), that is, the broadening of the exothermic peak and the lowering of the peak height with increasing nitrogen content, indicate that the diffusion of the atomic species necessary for the crystal growth is suppressed by the incorporation of nitrogen.

(2) Crystalline phases

Crystalline phases vary with the nitrogen content. Li_2SiO_3 is precipitated from nitrided glasses after the heat-treatments at low temperatures and the tendency becomes more pronounced with increasing nitrogen content. The crystalline phases and their relative amounts precipitated after the heat-treatment at 925 ^{O}C for 24 hours also change with the nitrogen content.

It is shown that the nitrogen atoms do not dissolve in the $Li_2Si_2O_5$ crystal but are condensed in the residual glassy phase. This implies that the silicon atoms bonded to nitrogen atoms can not participate in crystallization.

In the glasses before heat-treatment, the following structural groups would be present in the glass structure as described in CHAPTERs 1 and 2.

$$(-O-)_3Si-N^--Si(-O-)_3 \tag{1}$$

$$(-O-)_3Si-N-Si(-O-)_3$$
$$| \atop Si(-O-)_3$$

(2)

In nitrided glasses, the ratio of lithium ions to silicon atoms which can participate in crystallization would become larger than 1:1, because silicon atoms bonded to nitrogen atoms can not participate in crystallization. This would make it possible to precipitate Li_2SiO_3 which has a lithium to silicon ratio of 2.   The results shown in Figs. 3 to 6 indicate that the tendency to precipitation of Li_2SiO_3 becomes more pronounced with increasing nitrogen content.

As the heat-treatment temperature is raised, the amount of $Li_2Si_2O_5$ increases and cristobalite is precipitated.   This would be explained on the assumption that silica component would be released from structural groups (1) and (2), condensing nitrogen atoms in the residual glassy phase.   The crystalline phases precipitated after a heat-treatment at 925 ^{O}C for 24 hours may be well explained on the assumption that the composition of the residual glassy phase is close to Si_2N_2O as described below. The composition of the glasses can be written as $30Li_2O \cdot (70-4x)SiO_2 \cdot 2xSi_2N_2O$.   Then, the ratio of SiO_2 to Li_2O for glasses 1, 2 and 3 is 2.20, 2.09 and 1.96, respectively. When the ratio is larger than 2 (glasses Nos. 1 and 2), the cristalline phases would be $Li_2Si_2O_5$ and cristobalite, and when the ratio is smaller than 2 (glass No. 3), those would be $Li_2Si_2O_5$ and Li_2SiO_3.

(3) Nucleation mechanism

Nitrided glasses crystallize in the bulk and numerous crystalline particles are precipitated upon crystallization.

There are two mechanisms for the bulk nucleation: homogeneous and inhomogeneous nucleation.

First, the possibility of homogeneous nucleation will be
examined.   The texture of the heat-treated nitrided glasses
shown in Fig. 7 may indicate the rate of crystal growth is low
compared with that of nucleation.   It is known that
crystallization of glasses takes place through the nucleation and
growth.   The rate of nucleus formation in a glass, I, is
expressed[21, 24, 26] as

$$I = C \cdot \exp(-W^*/RT) \cdot \exp(-\Delta E/RT) \tag{3}$$

where W^* is the thermodynamic barrier for nulceation, ΔE is the
kinetic barrier and C is a constant.   Since $\exp(-\Delta E/RT)$ is
proportional to $1/\eta$, where η is the viscosity of the melt,
equation (3) can be rewritten as

$$I = (C''/\eta) \cdot \exp(-W^*/RT) \tag{4}$$

where C" is a constant.   Equation (4) implies that an increase
in the viscosity lowers I whereas an decrease in W^* enlarges I.

    In a lower temperature region, Li_2SiO_3 is precipitated from
the nitrided glasses, which is not precipitated from the non-
nitrided glasses.   The composition of the nulcei formed in
nitrided glasses, therefore, might be close to Li_2SiO_3.   If so,
the values of W^* for nitrided and non-nitrided glasses may be
different from each other because the composition of the nuclei
may be different.   If W^* for nitrided glasses is smaller than
that for non-nitrided glasses, the decrease in the thermodynamic
barrier for nucleation may compensate for the effect of the
increase in the viscosity.   The rate of crystal growth may be
lowered by an increase in the viscosity.   Then, the rate of
nucleation would become higher compared with that of crystal
growth, which would eventually increase the number of nuclei.

    On the other hand, the possibility of inhomogeneous
nucleation can not be ruled out.   The present nitrided glasses

are gray in color.   It has been considered that the color of oxynitride glasses may be caused by the precipitation of a small amount of metallic silicon arising from the decomposition of silicon nitride[18] even though the amount is so little that the metallic silicon can not be detected by XPS or XRD.   Therefore, there may be a possibility that the metallic silicon may act as substrates of inhomogeneous nucleation.

If homogeneous nucleation really occurs in nitrided glasses, the number of the nuclei increases and the texture of the crystallized glasses becomes finer with increasing nitrogen content.   However, such effects of nitrogen content can not be observed in Fig. 7.   Therefore, the inhomogeneous nucleation may be more likely to occur than the homogeneous nucleation in the present nitrided glasses.

CONCLUSION

The glass transition and crystallization temperature rise with increasing nitrogen content, which may be attributed to the formation of Si-N bonds in the glass structure causing an increase in the viscosity.   Precipitation of Li_2SiO_3, which is not precipitated from non-nitrided glasses, is promoted with increasing nitrogen content.   The change of the crystalline phases has been explained by considering that the silicon atoms bonded to nitrogen atoms can not participate in crystallization. Bulk crystallization is dominant in nitrided glasses and numerous crystalline particles are precipitated in the bulk of nitrided glasses upon crystallization.   A possibility has been proposed that a small amount of fine metallic silicon may be responsible for the inhomogeneous nucleation although the possibility of homogeneous nucleation can not be eliminated.

Section 6. 2 Crystallization of Li-Al-Si-O-N Oxynitride Glasses and Properties of the Resultant Glass-Ceramics

INTRODUCTION

Incorporation of nitrogen atoms in oxide glasses increases the chemical durability, refractoriness, microhardness and elastic modulus, and decreases the thermal expansion coefficient[21].   It is also expected that novel glass-ceramics may be prepared by crystallizing oxynitride glasses.   There are many studies on the crystallization of oxynitride glasses[1, 2, 4, 14, 16, 17, 27].   In the previous section, the effect of nitrogen on the crystallizaiton of Li-Si-O-N oxynitride glasses has been described.   However, there are only a few studies on the properties of the glass-ceramics derived from oxynitride glasses[27].

There are many practically important glass-ceramics. Glass-ceramics based on the $Li_2-Al_2O_3-SiO_2$ system are practically important because of the extremely low thermal expansion coefficient.   They are applied to precision optics materials[28] or matrices of fiber-reinforced glass-ceramics[29, 30].

In the present section, the crystallization of Li-Al-Si-O-N oxynitride glasses and the properties of the resultant glass-ceramics have been described in view of the practical importance of $Li_2O-Al_2O_3-SiO_2$ glass-ceramics.   The effect of nitrogen on the crystallization of Li-Al-Si-O-N oxynitride glasses has been compared with that of Li-Si-O-N oxynitride glasses described in Section 6. 1.

EXPERIMENTAL

(1) Preparation and analysis of glasses

The nominal compositions of the oxynitride glasses studied are shown in Table 1. The ratio of Li:Al:Si was 1:1:2, which is based on β-spodumene composition, and the nitrogen content was varied by a progressive substitution of AlN for $AlO_{3/2}$. The glasses were prepared according to the procedure described in the previous chapters. For comparison, two kinds of non-nitrided glasses, with or without nucleating reagents, were prepared, which will be referred to as ON and OA, respectively. The nucleating reagents added were 2 wt% of TiO_2 and ZrO_2. The glasses were analyzed for the nitrogen and lithium contents by the Kjeldahl mehtod and the flame emission technique, respectively.

(2) Differential thermal analysis

The glasses, cut into blocks of about 3x3x3 mm^3, were analyzed by differential thermal analysis (DTA) with a MAC Science Co. model TG-DTA 2000. DTA measurements were conducted up to 1300 ^{O}C at a heating rate of 10 ^{O}C/min under a flow of argon.

(3) Crystallization

The glasses were cut into rods of about 3x3x10 mm^3 in size. The rods were heat-treated for crystallization at 800, 1000 and 1200 ^{O}C for 4 hours under a flow of nitrogen. The heating rate was 10 ^{O}C/min. For glass ON, a heat-treatment for nucleation at 760 ^{O}C for 4 hours was conducted prior to crystallization to obtain crack-free specimens. However, the heat-treatment for nucleation was not necessary to crystallize nitrided glasses.

Table 1 Nominal compositions of Li-Al-Si-O-N oxynitride glasses (molar ratio).

Sample	$LiO_{1/2}$	$AlO_{3/2}$	SiO_2	AlN	others
OA	1	1	2	0	0
ON	1	1	2	0	excess 2wt% TiO_2
					excess 2wt% ZrO_2
A	1	0.8	2	0.2	0
B	1	0.7	2	0.3	0
C	1	0.6	2	0.4	0

The ground glass powders were also heat-treated for crystallization in air, by which nitrogen atoms in the glasses are replaced by oxygen atoms, to compare the kinds of crystalline phases with those precipitated in nitrogen atmosphere.

(4) Characterization of glass-ceramics

The precipitated crystalline phases were identified by powder X-ray diffraction analysis (XRD) with a Rigaku Co. Geigerflex equipment using CuKα radiation. The tube voltage and current were 35kV and 30mA, respectively. The scanning speed was 2 degree/min in 2θ. For the precise determination of the lattice parameters of the precipitated high-quartz solid solution (ss), a scanning speed of 0.2 degree/min was employed. The lattice parameters, a_0 and c_0, were calculated from the CuKα_1 diffraction of the (200), (112), (212) and (203) planes. High purity silicon powder was used as internal standard.

The Knoop hardness was measured under a load of 1.96 N for 20 seconds with an Akashi Co. MVK-G1 hardness tester. The density was determined by the Archimedes method using carbontetrachloride (CCl_4) as substituting liquid. The thermal expansion coefficient was measured with a MAC Science Co. model TD-5010 differential push-rod dilatometer using silica glass as reference. A heating rate of 10 $^{\circ}C$/min was used. The average linear thermal expansion coefficient from 50 to 500 $^{\circ}C$ was estimated.

RESULTS

(1) Analysis of glasses

Table 2 shows the nitrogen and lithium contents of glasses. 93 to 99 % of nitrogen calculated from nominal batch compositions are retained in oxynitride glasses. There is no significant

Table 2   Nitrogen and lithium contents of Li-Al-Si-O-N oxynitride glasses.

Sample	N_{calc} (wt%)	N_{anal} (wt%)	Li_{calc} (wt%)	Li_{anal} (wt%)	Tg (°C)	Tc (°C)
OA	0	0	3.73	3.88	699	795
ON	0	0	3.59	3.70	688	827
A	1.52	1.47	3.77	3.83	734	998
B	2.20	2.18	3.79	3.88	748	1023
C	3.08	2.85	3.81	3.89	760	1060

change in the lithium content between calculated and analyzed values. The nitrided glasses were translucent, gray in color, and had no crystalline phase.

(2) Differential thermal analysis

Fig. 1 shows the DTA profiles of the glasses. A large exothermic peak due to crystallization is observed at temperatures from 800 to 1100 $^{\circ}$C. The exothermic peak is associated with the precipitation of high-quartz ss. A small exothermic peak found in ON around 1080°C is associated with the precipitation of m- and t-ZrO_2. The small peaks found in glasses B and C around 1170 $^{\circ}$C, indicated by a downward arrow mark in the figure, may be associated with the precipitation of Si_2N_2O. The glass transition temperature, T_g, and the onset of crystallzation, T_c, become higher with increasing nitrogen content. T_g and T_c are listed in Table 2.

(3) Crystalline phases

Table 3 shows the crystalline phases precipitated from the glasses under a flow of nitrogen and in air. From the non-nitrided glasses, metastable high-quartz ss[31] is precipitated after the crystalliation at 800 $^{\circ}$C in both atmospheres, and the diffraction pattern is shown in Fig. 2(a). High-quartz ss, $Li_2O \cdot Al_2O_3 \cdot nSiO_2O$, has a wide solid-solution range of $2 \leqq n \leqq 8$. Assuming from the compositions of the present glasses, the precipitated high-quartz ss may have a composition of n=4, which corresponds to stoichiometric β-spodumene[31, 32]. The high-quartz ss transforms to β-spodumene around 1000 $^{\circ}$C, as shown in Fig. 2(b). A small amount of t- and m-ZrO_2, the nucleating reagent, is observed in glass ON crystallized at 1000 $^{\circ}$C and 1200 $^{\circ}$C. Crystalline TiO_2 was not detected.
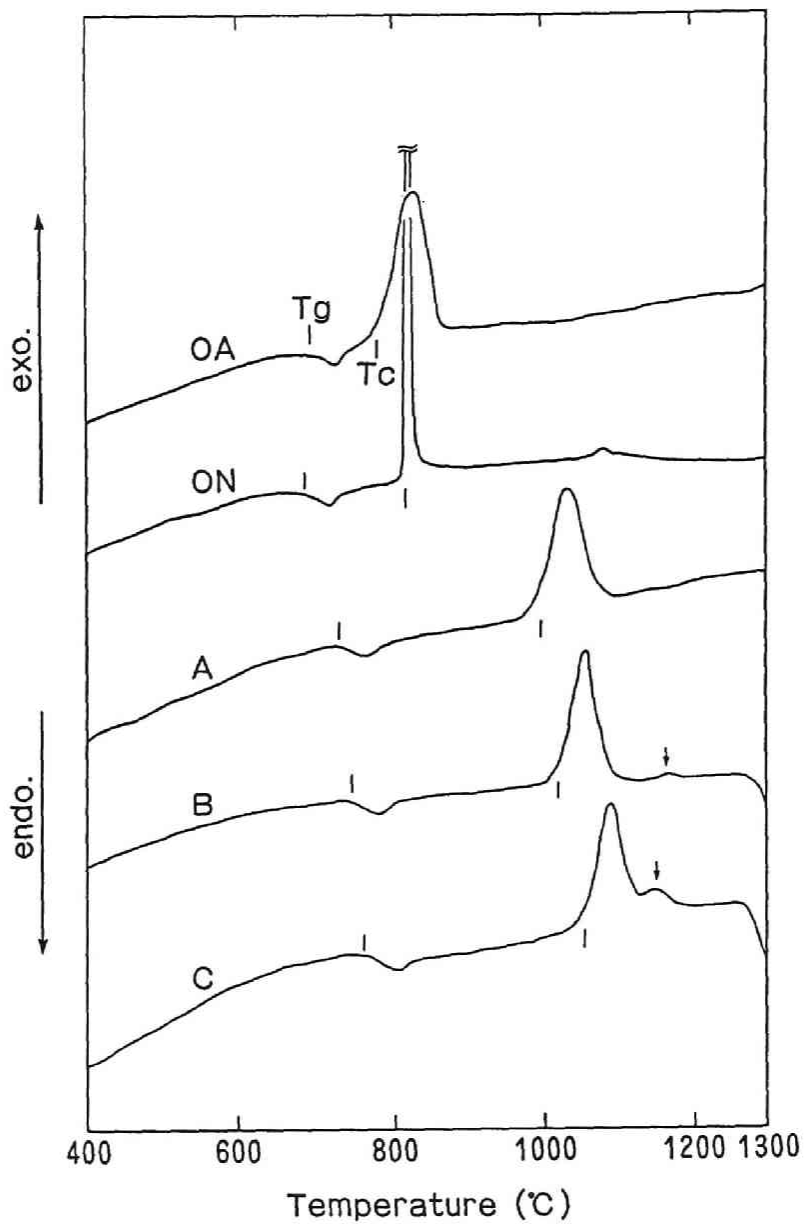
Fig. 1.   DTA curves of Li-Al-Si-O-N oxynitride glasses

Table 3   Crystalline phases precipitated from the glasses after the heat-treatments in nitrogen and in air

Sample	Nitrogen				Air		
	800 °C	1000 °C	1200 °C		800 °C	1000 °C	1200 °C
OA	hq	sp	sp		hq	sp	sp
ON	hq	sp, ZrO_2	sp, ZrO_2		hq	sp, ZrO_2	sp, ZrO_2
A	g	hq	hq, sp		hq	sp	sp
B	g	hq >> g	hq		hq	sp	sp
C	g	hq, g	hg >> Si_2N_2O		hq	sp	sp

g: glass, hq: high-quartz solid solution, sp: β-spondumene.
Heat treatment time is 4h.
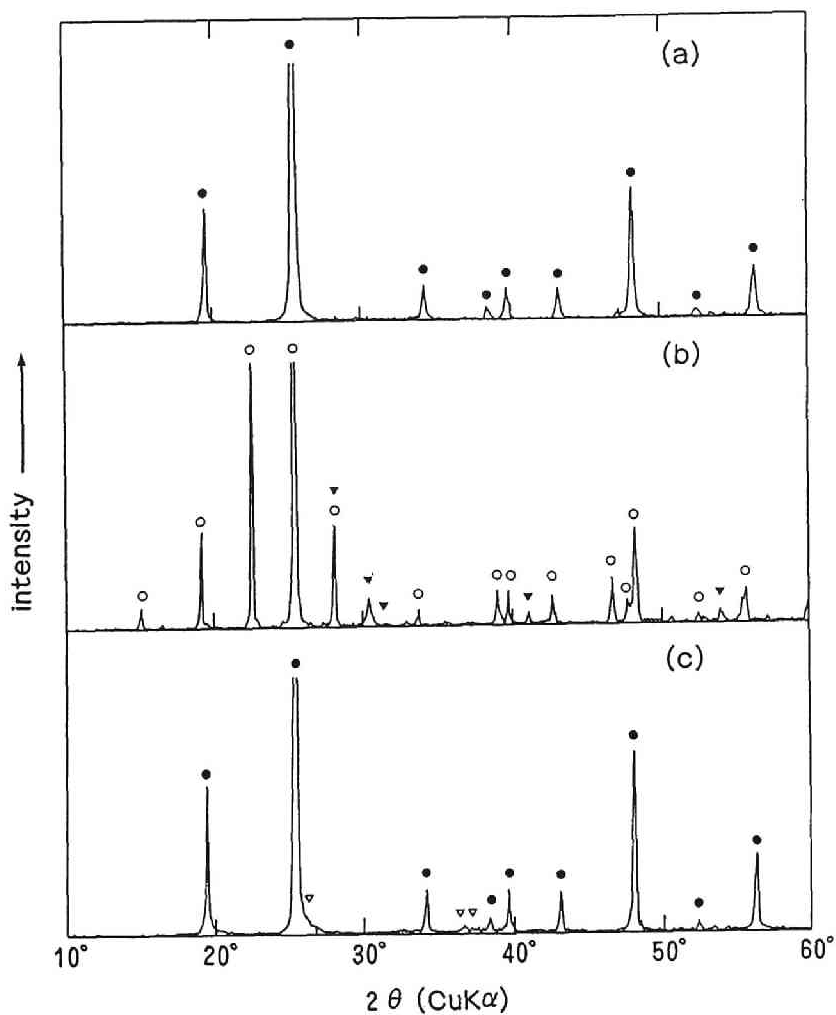
Fig. 2. X-ray diffraction patterns of glass-ceramics crystallized in nitrogen atmosphere: (a)ON crystallized at 800 $^{\circ}$C, (b)ON crystallized at 1000 $^{\circ}$C and (c)C crystallized at 1200 $^{\circ}$C; ($\bullet$)high-quartz ss, (O)β-spodumene, ($\blacktriangledown$)t- and m-ZrO_2 and ($\triangledown$)Si_2N_2O

In crystallization of the nitrided glasses under a flow of nitrogen, the temperatures of the precipitation of high-quartz ss and transformation from the high-quartz ss to β-spodumene become higher with increasing nitrogen content. β-spodumene is precipitated in glass A on crystallizing at 1200 ^{O}C for 4 hours, while it is not found in glasses B and C crystallized at 1200 ^{O}C. A small amount of Si_2N_2O is observed in glass C crystallized at 1200 ^{O}C, as shown in Fig. 2(c). X-ray scattering from the residual glassy phase, if any, is too small to be seen in all the glasses crystallized at 1200 ^{O}C.

When the nitrided glass powders are heat-treated in air, the crystalline phases are identical to those precipitated from the non-nitrided glasses; that is, high-quartz ss appears after crystallizing at 800 ^{O}C, and it transforms to β-spodumene around 1000 ^{O}C, as shown in Table 3.

Fig. 3 shows the change of the lattice parameters of high-quartz ss precipitated under a flow of nitrogen as a function of the nitrogen content. The lattice parameters a_0 and c_0 of crystallized non-nitrided glass OA are 5.217 and 5.459 A, respectively. Ray and Muchow[32] reported that those of crystallized $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ glass (high-quartz ss) are 5.215 and 5.452 A, respectively. being consistent with the present result. As the nitrogen content increases, the c_0 contracts and the a_0 elongates.

(4) Density, Knoop hardness and thermal expansion coefficient

Fig. 4 shows the change of the density with a change of the crystallization temperature. The densities of high-quartz ss and β-spodumene[33] are indicated in the figure as broken lines. The density of the high-quartz ss was calculated from the a_0 and c_0 of crystallized OA (Fig. 3). On crystallization, the density of ON increases up to 800 ^{O}C and then decreases with increasing
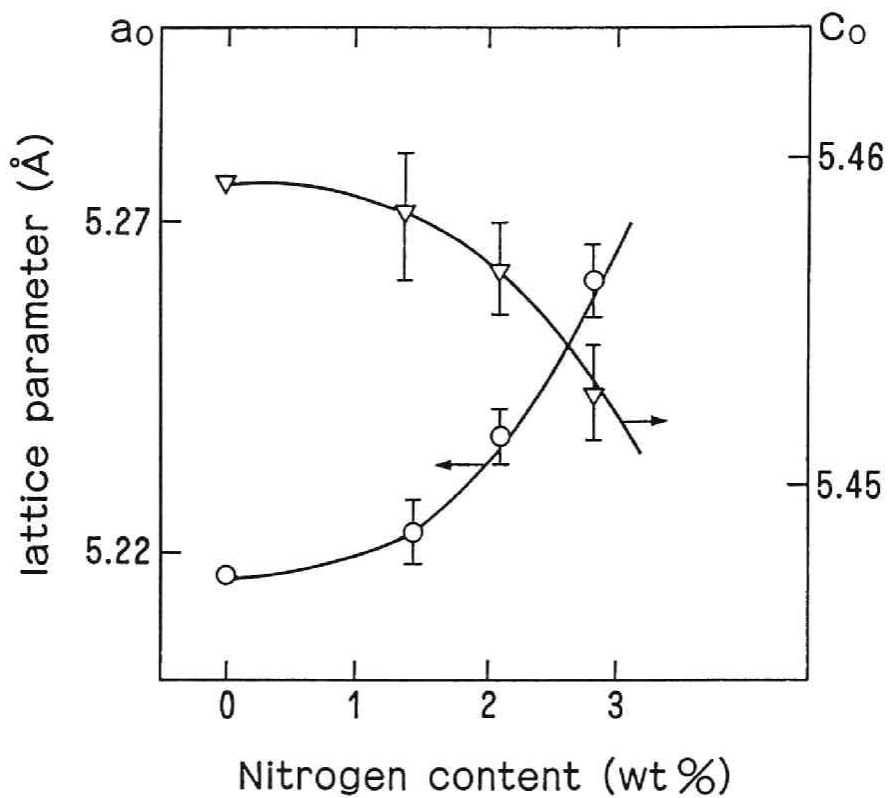
Fig. 3. Change of the lattice parameters of the precipitated
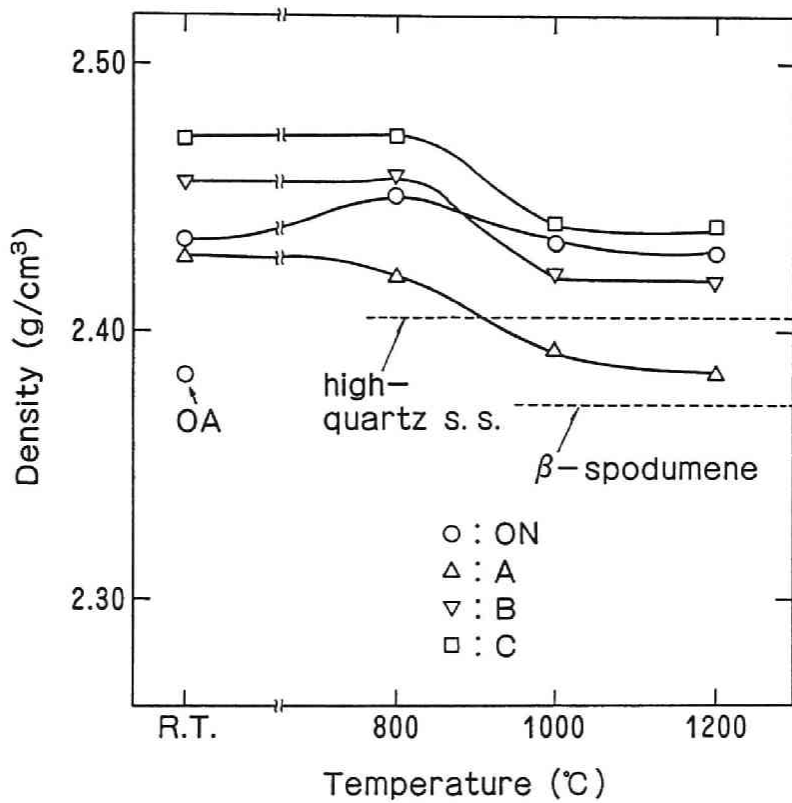high-quartz ss as a function of the nitrogen content

Fig. 4.   Change of the density as a function of the
          crystallization temperature

crystallization temperature.   The density of crystallized ON is higher than that shown on these lines, because ON contains TiO_2 and ZrO_2.   The density of nitrided glasses decrease monotonously with increasing crystallization temperature.   There are no pores in the microstructure of resultant glass-ceramics.   The density increases in the order A<B<C after the crystallization at any given temperature.   It should be noted that the density of specimen A crystallized at 1000 $^{\circ}$C, consisting of high-quartz ss, is lower than that of non-nitrided high-quartz ss.

Fig. 5 shows the change of the Knoop hardness with a change of the crystallization temperature.   The Knoop hardness increases on crystallization.   At any given temperature, Knoop hardness of glasses and glass-ceramics increases with increasing nitrogen content.

Fig. 6 shows the change of the thermal expansion coefficient with a change of the crystallization temperature.   The thermal expansion coefficient of ON crystallized at 800 $^{\circ}$C is -11×10^{-7}/K. It increases up to 7×10^{-7}/K after crystallizing at 1000 and 1200 $^{\circ}$C.   The thermal expansion coefficient of nitrided glasses decreases on crystallization, and it does not increase with an increase in the crystallization temperature.   Nitrided glass-ceramics exhibit negative thermal expansion even after they are crystallized at 1200 $^{\circ}$C.

4. Discussion

(1) Effect of nitrogen on crystallization

It was shown in Section 6. 1 that the incorporation of nitrogen into a Li_2O-SiO_2 glass changes the precipitated crystalline phases.   In Li-Si-O-N glasses, $Li_2Si_2O_5$ and
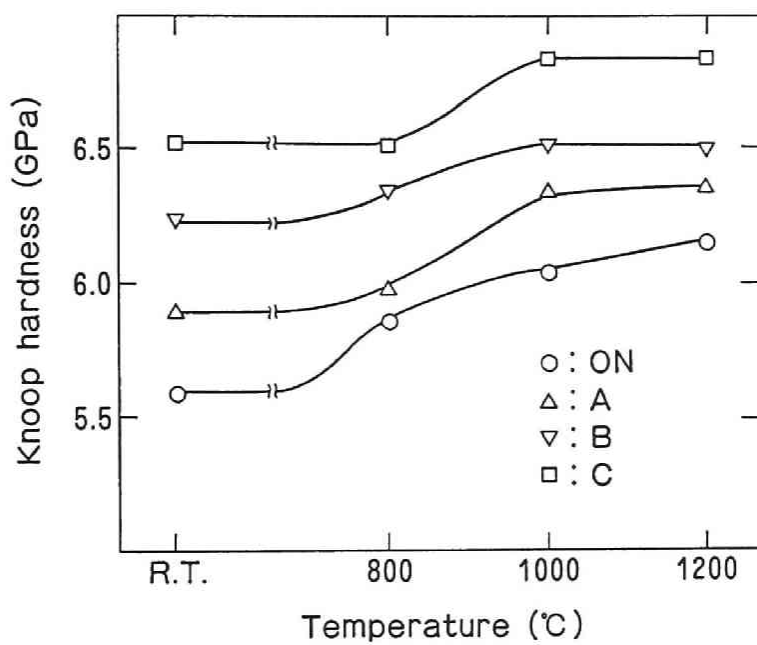
Fig. 5. Change of the Knoop hardness as a function of the
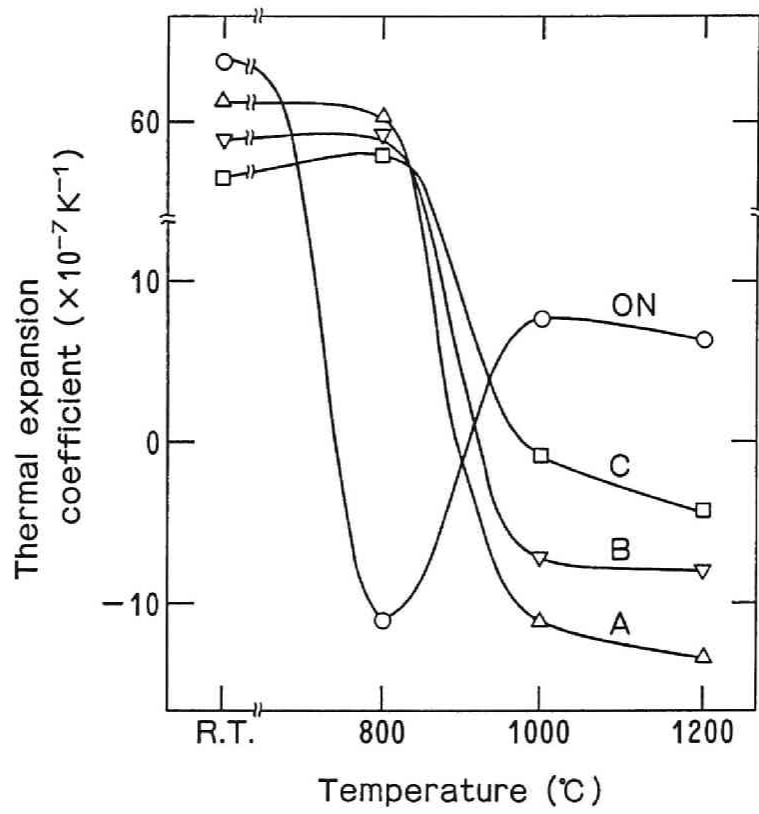crystallization temperature

Fig. 6.   Change of the thermal expansion coefficient as a
          function of the crystallization temperature

cristobalite were precipitated from non-nitrided glass whereas Li_2SiO_3 was precipitated from nitrided glasses. The change of the crystalline phases arising from the ioncorporation of nitrogen was explained by considering that the silicon atoms bonded to nitrogen atoms can not participate in crystallization, and that the nitrogen atoms are not incorporated in the structure of the precipitated $Li_2Si_2O_5$ crystal but are condensed in the residual glassy phase. On the other hand, Fischer et al.[27] showed that the nitrogen atoms can be incorporated into β-eucryptite crystal with high-quartz structure.

In the present Li-Al-Si-O-N system, it is assumed that a part of the nitrogen atoms are incorporated in the crystal structure of the high-quartz ss based on the following experimental observations. Firstly, as shown in Fig. 3, the lattice parameters of precipitated high-quartz ss change with the nitrogen content. The elongation of a axis and the contracton of c axis with increasing nitrogen content is consistent with the case of nitrogen-containing β-eucryptite glass-ceramics as reported by Fischer et al[27]. Secondly, the temperature of the transformation of the high-quartz ss to β-spodumene becomes higher with increasing nitrogen content as shown in Table 3. This result should be attributed to the effect of nitrogen atoms incorporated in the crystal structure, because the temperature of the transformation does not become higher when the nitrided glass powders are crystallized in air, by which nitrogen atoms are replaced by oxygen atoms. When nitrogen atoms are incorporated in high-quartz ss structure, more thermal energy may be required to rearrange atoms into β-spodumene structure than when no nitrogen atoms are incorporated. The dissociation energy per unit volume of $SiN_{4/3}$ (92.0 kJ/cm^3) is higher than that of SiO_2 (64.5 kJ/cm^3)[7].

A part of the nitrogen atoms in highly nitrided glass-

ceramics, B and C, may exist as Si_2N_2O or, as residual glassy
phase. Si_2N_2O is detected by XRD in specimen C crystallized at
1200 °C, as seen from Fig. 2(c).   The exothermic DTA peak around
1170 °C which appears in B and C may correspond to the
precipitation of Si_2N_2O, although Si_2N_2O is not clearly detected
in glass-ceramics B by XRD.

(2) Effect of nitrogen on properties of glass-ceramics

As described in CHAPTER 1, the nitrogen atoms bonded to
three network forming (NWF) cations make the glass structure
tightened and are responsible for an increase in the density.
Accordingly, the increase in the density of the present glasses
before crystallization with increasing nitrogen content is
attributed to the presence of nitrogen atoms bonded to three NWF
cations.   The strengthening of the bonds arising from the
formation of Si-N and Al-N bonds may also be responsible for the
increase in the Knoop hardness and the decrease in the thermal
expansion of the glasses before crystallization.

The change of the properties of the glass-ceramics with
increasing nitrogen content, however, may be discussed by
considering (a) the effect of nitrogen incorporated in the
crystal structure of the precipitated high-quartz ss and (b) the
effect of the minor phase of Si_2N_2O and residual glassy phase.
The Knoop hardness may be affected by both effects.   The
density, however, is more affected by the latter than the former.
If all the nitrogen atoms are incorporated in the crystal
structure, the density of the glass-ceramics consisting of the
same crystalline phases should decrease with increasing nitrogen
content, because the unit cell size increases while the average
atomic weight of constituting elements remains almost unchanged.
In fact, the measured density of glass-ceramics A crystallized at

1000 $^{\circ}$C is lower than that of non-nitrided high-quartz ss. The
density of glass-ceramics B and C crystallized at 1000 $^{\circ}$C and
1200 $^{\circ}$C, however, is higher than that of non-nitrided high-quartz
ss. The increase in the density of glass-ceramics with
increasing nitrogen content must be attributed to the
contribution of the minor phase. The density of Si_2N_2O is 2.84
g/cm^3[34] and even a small amount of Si_2N_2O would substantially
increase the density of the glass-ceramics.

Thermal expansion coefficient of glass-ceramics is mainly
affected by the suppression of the transformation from high-
quartz ss to β-spodumene. As the result, the negative thermal
expansion is retained after the crystallization of nitrided
glasses at 1000 $^{\circ}$C or higher. The thermal expansion coefficient
of the nitrided glass-ceramics crystallized at 1000 $^{\circ}$C and 1200
$^{\circ}$C increases with increasing nitrogen content. Fischer et
al.[27] found on the basis of high-temperature XRD that the
thermal expansion coefficient of nitrogen-containing β-
eucryptite glass-ceramics is larger than that of non-nitrided
one. If it is also the case for the present high-quartz ss
containing nitrogen, the thermal expansion coefficient of high-
quartz ss would increase with increasing nitrogen content. In
addition, the presence of the minor phase such as Si_2N_2O would
also increase the thermal expansion coefficient of the glass-
ceramics.

CONCLUSION

The temperature of the onset of crystallization of
Li-Al-Si-O-N oxynitride glasses becomes higher with increasing
nitrogen content. High-quartz solid solution (ss) first
precipitates from the glasses. The lattice parameters of the

precipitated high-quartz ss change depending on the nitrogen content and the temperature of the transformation of the high-quartz ss to β-spodumene also becomes higher with increasing nitrogen content.   It has been assumed from these results that a part of nitrogen atoms are incorporated in the crystal structure of the precipitated high-quartz ss.   The rest of the nitrogen atoms are condensed in a small amount of Si_2N_2O and residual glassy phase.   In consistent to the delayed transformation of high-quartz ss to β-spodumene, the glass-ceramics derived by the crystallization of the nitrided glasses at 1200 $^\circ C$ show a negative thermal expansion whereas that derived from a non-nitrided glass shows a positive thermal expansion.   The Knoop hardness and density of the glass-ceramics increase with an increase in the nitrogen content.

SUMMARY OF CHAPTER 6

In oxynitride glasses, the glass transition and crystallization temperatures rise with increasing nitrogen content, which may arise from the formation of Si-N bonds in the glass structure, causing an increase in the viscosity.   On crystallization, the crystalline phases precipitated from Li-Si-O-N oxynitride glasses changed on nitridation, that is, the tendency toward presipitation of Li_2SiO_3 becomes pronounced with increasing nitrogen content.   The change of the crystalline phases has been explained by considering that the nitrogen atoms in Li-Si-O-N oxynitride glasses are not incorporated into the precipitated $Li_2Si_2O_5$ but are condensed in the residual glassy phase.   On the other hand, the nitrogen atoms in Li-Al-Si-O-N oxynitride glasses are incorporated in the crystal structure of

precipitated high-quartz solid solution (ss).   The temperature
of the phase transformation of the high-quartz ss containing
nitrogen becomes higher compared with that of non-nitrided high-
quartz ss.   These results imply that nitrogen atoms may be
incorporated into crystal structures depending on the crystalline
species.

Li-Si-O-N oxynitride glasses crystallize only in the bulk
although non-nitrided glasses crystallize both from the surface
and in the bulk.   A plausible explanation is given that a small
amount of metallic silicon formed by the thermal decomposition of
Si_3N_4 may act as the substrates for inhomogeneous nucleation.

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CHAPTER 7   Interaction of Oxynitride Glass With Metals

INTRODUCTION

Composite materials consisting of glasses and other metals are often used in electronic devices and utensils. Glazes or solder glasses are the examples of the glasses used in composites. For glasses as component of composite materials, high mechanical strength and high chemical durability are required. Therefore, oxynitride glass appears quite suitable as a component of a composite. In composite materials, a component should adhere firmly to the other component, that is, chemical bonds must be formed at the interface. However, there have been only a few works on the interaction of oxynitride glasses with other materials[1]. Since oxynitride glasses contain nitrogen atoms besides oxygen atoms, the behavior of oxynitride glasses in bonding with other materials may be different from that of oxide glasses.

In the present chapter, the interaction of a Na-Si-O-N oxynitride glass with Ni, Fe and Cr metals has been examined. The effect of nitrogen on the interfacial reaction between the oxynitride glass and the metals has been discussed on the basis of the thermodynamics of the reactions of silicon nitride with pertinent chemical species.

EXPERIMENTAL

(1) Preparation of glasses and metals

A non-nitrided glass of the composition $30Na_2O \cdot 70SiO_2$ and a

nitrided glass of the composition $30Na_2O \cdot 61SiO_2 \cdot 3Si_3N_4$ were
prepared.   The glasses were analyzed for the nitrogen and water
contents by the Kjeldahl method and infrared spectroscopy,
respectively.   The procedures of the preparation and the
analysis were the same as those described in the previous
chapters.   The analyzed nitrogen and water contents are shown in
Table 1.   The nitrogen content of the nitrided glass was 2.25
wt%.   The glasses were cut into plates about $10 \times 10 \times 3$ mm^3 in
size, and the surfaces were optically polished with diamond paste
for the use in the heat-treatment for interfacial reaction.

The metals used were Ni, Fe and Cr plates of 99.7, 99.9 and
99.9 % purity, respectively (Nilaco Co.).   These metals were
chosen because they were major components of stainless steels.
The metal plates were cut into about $10 \times 10 \times 1$ mm^3 in size, and the
surfaces were optically polished with diamond paste.

The heat-treatment for interfacial reaction, described
below, was made with the metals with or without pre-oxidation
treatment.   For pre-oxidation, metals were heat-treated at 1000
$^{\circ}$C for 1 hour in static air.   An oxidized layer about 0.2 mm in
thickness was formed.   The thickness of the oxidized layers was
estimated by observation of the cross-section with a scanning
electron microscope (SEM).   The pre-oxidized metals will be
referred to as Ni(NiO), Fe(Fe$_3$O$_4$) and Cr(Cr$_2$O$_3$), respectively.

(2) Heat-treatment for interfacial reaction

Heat-treatment for interfacial reaction was conducted for 12
pairs (2 glasses and 6 metals).   The schematic arrangement of
the apparatus is shown in Fig. 1.   A metal and a glass were
attached with each other on the polished surfaces.   The pairs of
the metals and glasses were wrapped with molybdenum foils,
inserted into graphite vessels, and heated up to a given

Table 1   Analyzed nitrogen and water contents of
          glasses

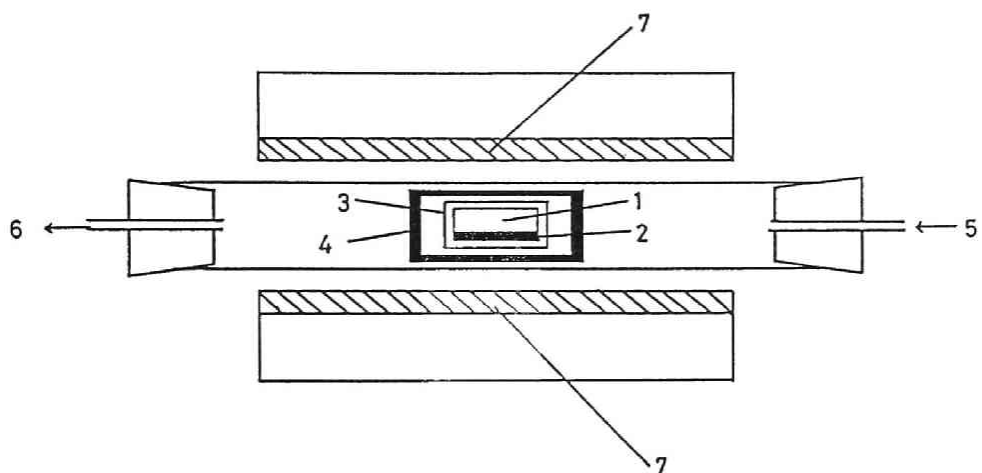| Sample	Nitrigen (wt%)	Water (wt%)
nitrided glass	2.25	$<1 \times 10^{-4}$
non-nitrided glass	0.0	5×10^{-3}

Fig. 1   A schematic arrangement of the apparatus for
the heat-treatment for interfacial reaction.   1:glass,
2:metal, 3:Mo foil, 4:graphite vessel, 5:Ar gas inlet,
6:Ar gas outlet, 7:heaters

temperature at a rate of 10 °C/min.   Dry argon was passed
through the furnace to avoid oxidation of the samples.   The
furnace was evacuated prior to the introduction of argon.   The
heat-treatment was made at 1000 °C for 1 hour for non-oxidized
metals and at 900 °C for 30 minutes for pre-oxidized metals.

(3) Characterization

The interaction between the glasses and the metals was
characterized by visual examination of the adherence of the pairs
and SEM observation, and the determination of the distribution of
metal elements near the interface with an electron probe
microanalyzer (EPMA).   The extent of adherence was evaluated
according to the following four rankings; (A) adherence is good
and the pair can not be detached by hand, (B) adherence is good
but there are pores in the joint interface, (C) adherence is poor
and the pair can be detatched easily by hand, (D) no adherence
between metal and glass.

(4) Identification of interfacial reaction products

The direct identification of the possible reaction products
formed at the joint interface by X-ray diffraction (XRD) is
difficult because the amounts of the reaction products are very
small.   Therefore, the indirect method was employed.   The
pellet of a powder mixture of metal and glass was heat-treated,
ground to powder, and examined by XRD using CuKα radiation.

RESULTS

(1) Interaction of non-nitrided glass with metals

Adherence of the nitrided and non-nitrided glasses to metals
is shown in Table 2.   It is seen that the non-nitrided glass

Table 2.   Evaluation of adherence

	Ni	Fe	Cr	Ni(NiO)	Fe(Fe_3O_4)	Cr(Cr_2O_3)
nitrided glass	D	C	A	D	D	B
non-nitrided glass	A	A	A	A	A	A

A: good,   B: good but pores are found in the interface,

C: weak adherence (detached easily),

D: no adherence

adheres to all the metals, regardless of the presence of pre-oxidized layers on the surfaces.

Fig. 2 shows the SEM pictures and the distribution of elements near the interface. It is seen that in all the pairs the element of the base metal diffuses into non-nitrided glass. The diffusion is more extensive when the surface of the metal is pre-oxidized. It was found by visual observation that the interfaces of the non-nitrided glass with Ni, Fe and Cr are colored in brown, blue and gray, respectively, corresponding to the color of the oxide of the base metal.

(2) Interaction of nitrided glass with metals

Table 2 shows that a good adherence is attained only in the pair of nitrided glass with Cr metal without pre-oxidation treatment. The nitrided glass shows almost no adherence to Ni, $Ni(NiO)$ and $Fe(Fe_3O_4)$. The adherence to Fe was so weak that the pair could be detached easily. The adherence to $Cr(Cr_2O_3)$ was fairly well, but many pores were observed in the interface.

Fig. 3 shows the SEM pictures and the distribution of elements for the pairs of nitrided glass with Cr, Fe and $Cr(Cr_2O_3)$. In the interfaces of the pairs of nitrided glass with Cr and $Cr(Cr_2O_3)$, particles of reaction products are observed (Fig. 3. (a) and (b)). The particles are identified to be Cr_3Si and β-Cr_2N as examined by XRD. In the case of nitrided glass with Fe, diffusion of Si into Fe is observed, which is not observed in the combination of non-nitrided glass with Fe. Any other crystalline phase than Fe, however, is not identified by XRD.

DISCUSSION
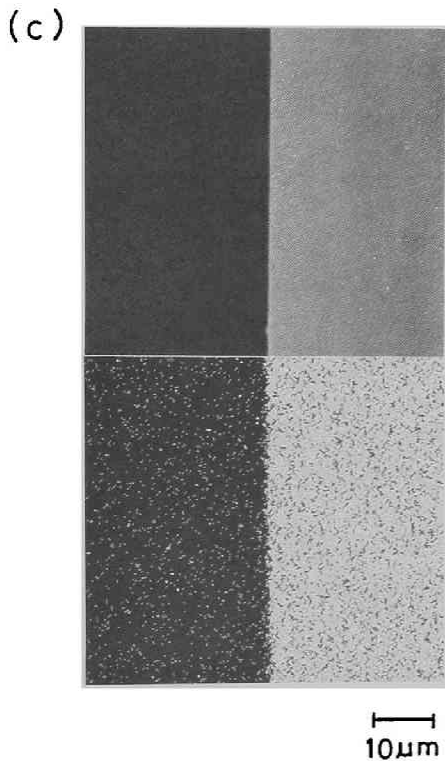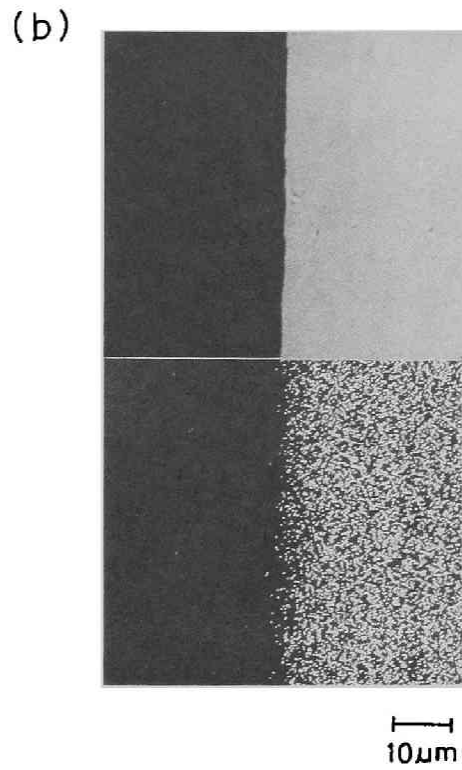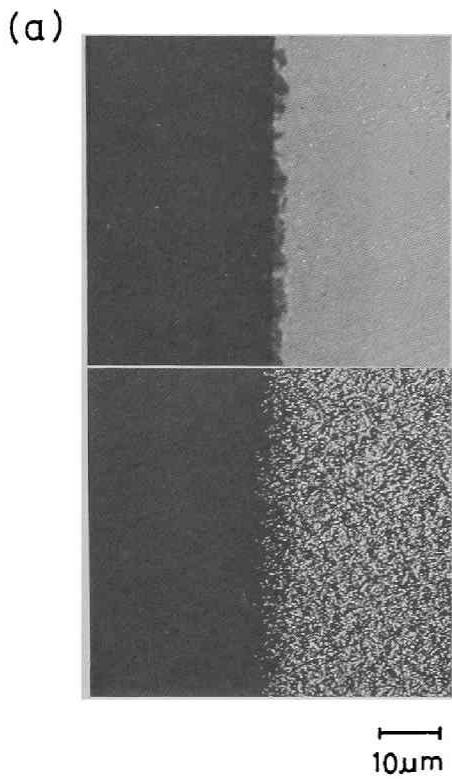
(a)

(b)

10μm

10μm

(c)

10μm

Fig. 2
SEM pictures and the distribution of
metal elements near the joint
interface of the pairs of
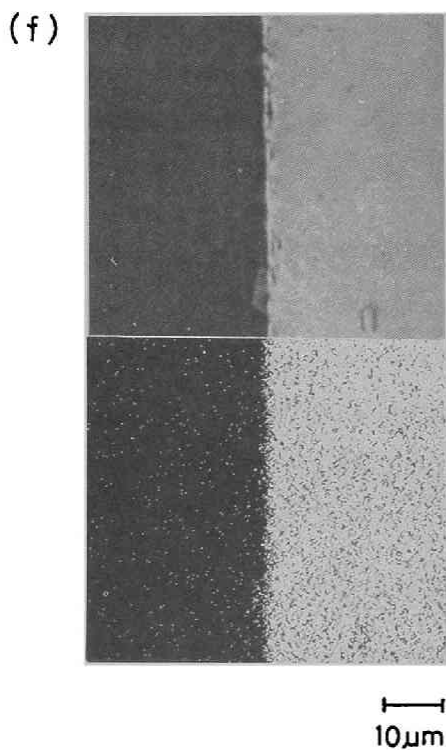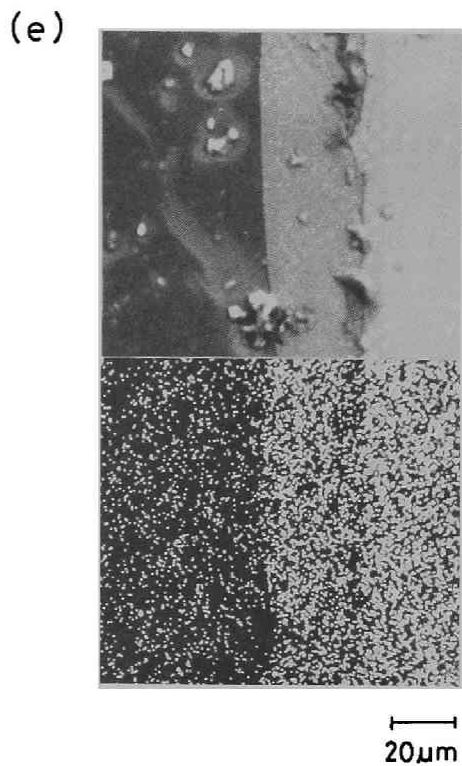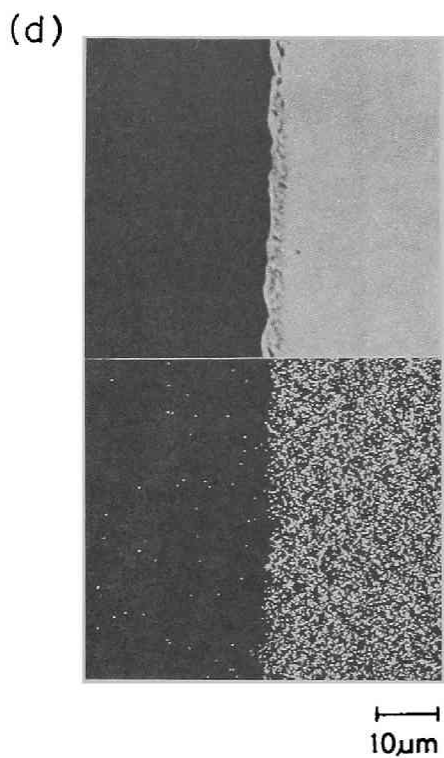non-nitrided glass with metals.
(a)Ni, (b)Fe and (c)Cr.

(d)

10μm

(e)

20μm

(f)

10μm

Fig. 2

SEM pictures and the distribution of
metal elements near the joint
interface of the pairs of
non-nitrided glass with metals.
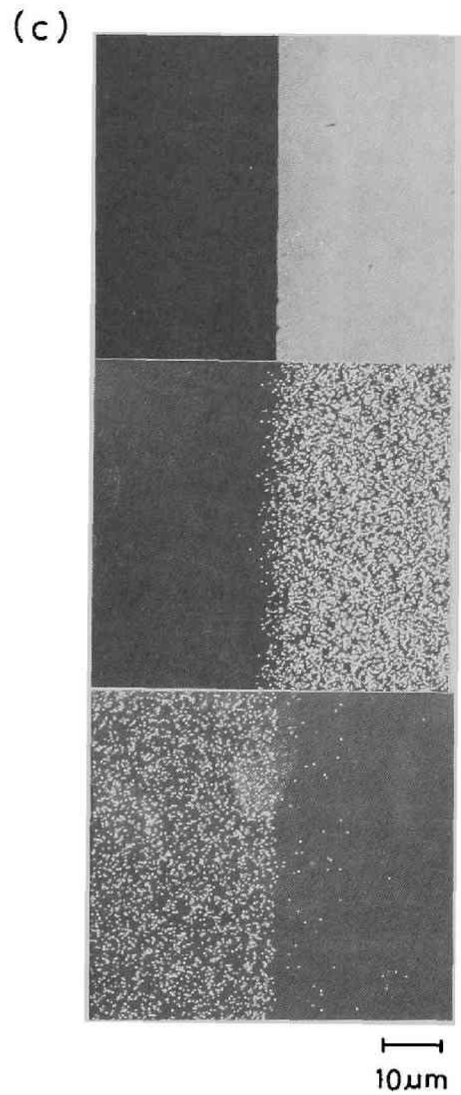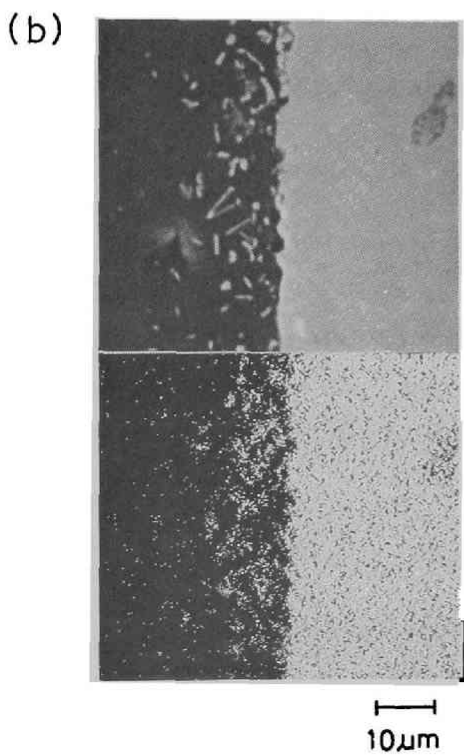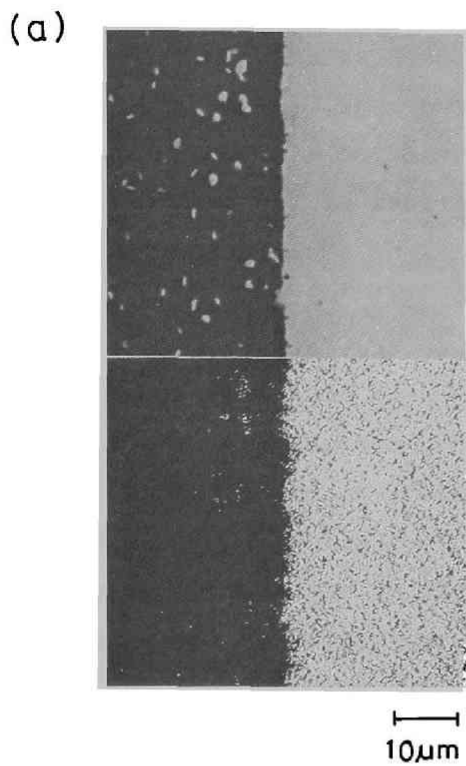(d)Ni(NiO), (e)Fe(Fe_3O_4) and
(f)Cr(Cr_2O_3).

(a)

(b)

(c)

10μm

10μm

Fig. 3
SEM pictures and the distribution of
metal elements near the joint
interface of the pairs of nitrided
glass with metals.   (a)Cr, (b)Cr(Cr_2O_3)
and (c)Fe.   Distribution of Si is
shown in the bottom of (c).

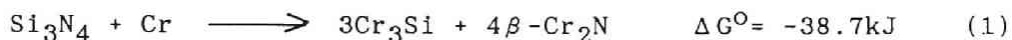## (1) Interaction of non-nitrided glass with metals

Mechanism of the adherence of oxide glasses to metals has been proposed by Pask[2]. He suggested that M-O-Si bonds (M = metals) formed as a result of the interaction are responsible for the adherence. This means that the oxides of the base metals play an important role in the occurrence of adherence of oxide glasses to metals.

The present experiments showed that the interface between the non-nitrided glass and metal is colored by the oxide of the metal. The EPMA analysis confirmed the diffusion of the ions of the base metal into the non-nitrided glass as shown in Fig. 2. These indicate that the surface of the non-oxidized metals has been oxidized during the heat-treatment for interfacial reaction. The oxidation of the metals may have been caused by the oxygen adsorbed on the metals and the water contained in the non-nitrided glass. A schematic representation of the interaction causing the adherence of the non-nitrided glass to metals is shown in Fig. 4.

It is assumed that the surface of the pre-oxidized metals would supply the ions of the base metals and make possible the adhesion under a milder condition.

(2) Interaction of nitrided glass with non-oxidized metals

The present experiments showed that only Cr adheres well to nitrided glass, and β-Cr_2N and Cr_3Si particles are formed in the interface. The Gibbs free energy change (ΔG^O) for the reaction of Si_3N_4 and Cr leading to the formation of Cr_3Si and β-Cr_2N (equation (1)) is negative at 1000 ^{O}C.
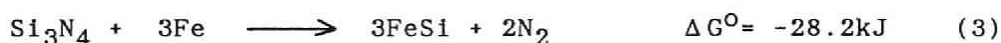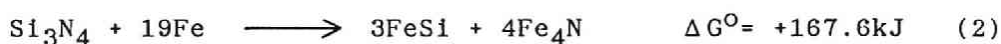
$$Si_3N_4 + Cr \longrightarrow 3Cr_3Si + 4\beta\text{-}Cr_2N \qquad \Delta G^O = -38.7kJ \qquad (1)$$

In the calculation, thermodynamic parameters (enthalpy for

Fig. 4   A schematic representation of the mechanism of adherence
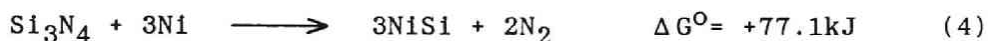between non-nitrided glass and metal.   M represents
metal.

formation H and entropy S) of each substance have been taken from reference[3].   The negative Gibbs free energy in the reaction expressed in equation (1) indicates that the formation of Si-Cr and N-Cr bonds in the interface may be responsible for the occurrence of adherence.   A schematic representation of the interaction causing adherence is shown in Fig. 5.

In the combination of Fe with nitrided glass, a weak adhesion has resulted and silicon diffuses into Fe.   The Gibbs free energy changes of pertinent reactions are shown below.

$$Si_3N_4 + 19Fe \longrightarrow 3FeSi + 4Fe_4N \qquad \Delta G^O = +167.6kJ \qquad (2)$$

$$Si_3N_4 + 3Fe \longrightarrow 3FeSi + 2N_2 \qquad \Delta G^O = -28.2kJ \qquad (3)$$

Since ΔG^O of reaction (2) is highly positive and that of reaction (3) is negative, it would be plausible to assume that reaction (3) may proceed.   Hence, the formation of Fe-Si bonds in the interface may be responsible for the occurrence of the adherence.   The formation of Fe-Si bonds, however, is not so extensive because the concentration of nitrogen necessary for equation (3) is not high in the nitrided glass.   This may account for the fact that the adherence is not so strong and crystalline FeSi is not detected by XRD.

In the case of Ni, no adherence resulted and no reaction product was observed.   Since the Gibbs free energy change of reaction (4) is positive at 1000 ^{O}C, there may be no interaction between nitrided glass and Ni.

$$Si_3N_4 + 3Ni \longrightarrow 3NiSi + 2N_2 \qquad \Delta G^O = +77.1kJ \qquad (4)$$

The adsorbed water may not contribute to the occurrence of adherence, because the adsorbed water, if any, may be consumed for the oxidation of Si-N bonds.
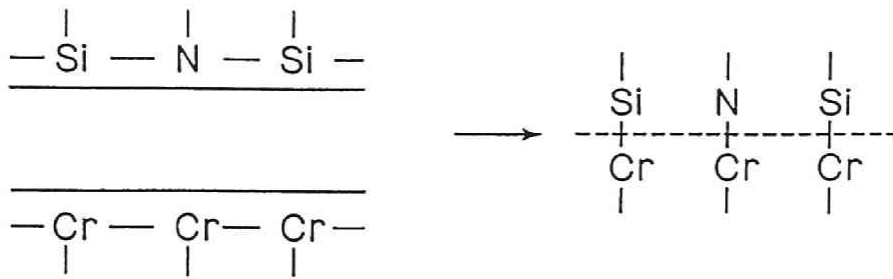
Fig. 5   A schematic representation of the mechanism of adherence

between nitrided glass and Cr.

(3) Interaction of nitrided glass with pre-oxidized metals

It was found that the presence of the pre-oxidized layers on the base metals inhibits the occurrence of adherence. This could be explained from the stability of the metal oxides in oxynitride glass melts. If the free energy change of formation of a metal oxide (ΔG_f^O) is less negative than that of oxidation of Si_3N_4 (ΔG_O^O) at temperatures of heat-treatments, the oxide would not be stable in oxynitride glass melts[4, 5] and oxidation of Si-N bonds accompanied by liberation of nitrogen gas would occur according to equation (5).

$$MO_x + xSi\text{-}N \longrightarrow xSi\text{-}O + M + x/2N_2 \qquad (5)$$

ΔG_f^O values shown in Table 3 indicate that NiO, Fe_3O_4 and Cr_2O_3 oxidize Si-N bonds at 900 °C. As long as reaction (5) proceeds, the formation of the bonds responsible for the occurrence of adherence is not possible since the liberated nitrogen gas may detach the nitrided glass from pre-oxidized metals.

It was shown that $Cr(Cr_2O_3)$ adhered to nitrided glass and Cr_3Si and β-Cr_2N were precipitated in the interface. This may be explained by considering that reaction (5) was completed and reaction (1) proceeded during the heat-treatment. The small pores found in the interface may be attributed to liberation of a trace of nitrogen gas.

SUMMARY OF CHAPTER 7

The interaction of a Na-Si-O-N oxynitride glass with Ni, Fe and Cr has been studied. The oxynitride glass adheres well only to Cr. It is assumed from the precipitation of Cr_3Si and β-Cr_2N particles near the joint interface that the formation of Cr-Si and Cr-N bonds in the interface is responsible for the

Table 3　The free energy change of the formation of metal oxides (ΔG_f^O) and that of the oxidation of silicon nitride (ΔG_O^O) at 1173 K.

Reaction	ΔG_f^O, ΔG_O^O (kJ/mol)
Ni + 1/2O$_2$ $\longrightarrow$ NiO	-130
Fe + 2/3O$_2$ $\longrightarrow$ 1/3Fe$_3$O$_4$	-239
Cr + 3/4O$_2$ $\longrightarrow$ 1/2Cr$_2$O$_3$	-404
1/3Si$_3$N$_4$ + O$_2$ $\longrightarrow$ SiO$_2$ + 2/3N$_2$	-575

occurrence of adherence. The oxynitride glass adheres weakly to Fe, which is attributed to the formaiton of Fe-Si bonds to a small extent. The oxynitride glass does not adhere to Ni because the bonds or species responsible for the adherence are absent.

The pre-oxidized layer on the surface of the base metals inhibits the occurrence of adherence of nitrided glass to metals. The oxides of the base metals may oxidize the Si-N bondings in nitrided glass and liberate nitrogen gas at temperatures for the interfacial reaction, detaching the oxynitride glass from metals.

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GENERAL SUMMARY

Studies have been made on the structure and properties of oxynitride glasses. The local structure around nitrogen atoms in oxynitride glasses is investigated in relation to the composition. The electrical and chemical properties, liquid-liquid phase separation and crystallizaiton of oxynitride glasses have been investigated and the effect of nitrogen on the properties has been discussed.

In Chapter 1, the results of the molecular dynamics calculations on the structure and properties of Na-Si-O-N oxynitride glasses have been presented. It has been shown that the nitrogen atoms bonded to one, two and three silicon atoms coexist in the glass structure. The mean of the number of silicon atoms bonded to a nitrogen atom decreases with increasing sodium content. It has been assumed that the nitrogen atoms bonded to two or less silicon atoms may be formed when nitrogen atoms substitute for non-bridging oxygen atoms. The dependences of the density, bulk modulus and bulk thermal expansion coefficient on the nitrogen content are consistent with those observed in the real glasses. The increase in the density may arise from the formation of the nitrogen atoms bonded to three silicon atoms in the glass structure.

In Chapter 2, the structure of Na-Si-O-N oxynitride glasses deduced from ^{29}Si MAS NMR has been presented. It has been estimated that about a half of the total nitrogen atoms are bonded to three silicon atoms and the rest are bonded to two silicon atoms. It is consistent with the result described in Chapter 1 that not all the nitrogen atoms are bonded to three silicon atoms.

In Chapter 3, the effect of nitrogen on the electrical conductivity in Na-Si-O-N and Li-Si-O-N oxynitride glasses has

been described.　The conductivity increases and the activation energy for conduction decreases with increasing nitrogen content. It has been assumed that the electrostatic attractive force exerted on the transporting ions may decrease on nitridation because the electronegativity of nitrogen is lower than that of oxygen, by which the conductivity may increase and the activation energy for conduction may decrease.

In Chapter 4, the chemical durability of Na-Si-O-N and Li-Si-O-N oxynitride glasses to acidic and alkaline aqueous solutions has been described.　The incorporation of nitrogen improves the chemical durability of the glasses to both solutions.　The improvement of the chemical durability to acidic solution on nitridation has been attributed to a decreased diffusivity of H_3O^+ ions, because the elastic modulus of the glasses may increase on nitridation.　The improved chemical durability to alkaline solution on nitridation has been attributed to more covalent nature of Si-N bonds than that of Si-O bonds.　In other words, the positive charge on the silicon atoms of Si-N bonds is reduced, by which the probability of the nucleophilic attack of OH^- may be reduced.

In Chapter 5, the liquid-liquid phase separation of Li-Si-O-N oxynitride glasses has been described.　The incorporation of nitrogen lowers the miscibility temperature and suppresses the phase separation.　A linear correlation between the miscibility temperature and the nitrogen content is found, 10 eq% nitrogen lowers the miscibility temperature by about 90 $^\circ$C. The lowering of the miscibility temperature is attributed to a decrease in the electrostatic attractive force between lithium ions and the network anions on nitridation as discussed in Chapter 3.

In Chapter 6, crystallization of Li-Si-O-N and Li-Al-Si-O-N

oxynitride glasses has been described.   The effect of nitrogen
on the glass transition and crystallization temperatures,
precipitated crystalline phases and nucleation mechanism is
discussed.   Glass transition and crystallization temperatures
rise with increasing nitrogen content.   Bulk crystallization is
dominant in nitrided glasses.   In Li-Si-O-N oxynitride glasses,
Li_2SiO_3 phase, which is not precipitated in a $30Li_2O \cdot 70SiO_2$
glass, is precipitated.   Nitrogen atoms in nitrided glasses are
not incorporated in the structure of the precipitated $Li_2Si_2O_5$
crystal but are condensed in the residual glassy phase.   For
Li-Al-Si-O-N oxynitride glasses, nitrogen atoms are incorporated
in the crystal structure of the precipitated high-quartz solid
solution (ss) phase.   As the result, the temperature of the
phase transformation of the high-quartz ss to β-spodumene
becomes higher on nitridation.   The density and the hardness of
the resultant glass-ceramics increase with increasing nitrogen
content.

In Chapter 7, the interaction of a Na-Si-O-N oxynitride glass
with nickel, iron and chromiun metals has been described.   The
reactivity of the oxynitride glass with the metals has been
discussed from a viewpoint of the thermodynamics of the reactions
between silicon nitride and the metals.   The oxynitride glass
adheres well only to chromium, which is explained by a negative
Gibbs free energy change for the reaction between silicon nitride
and chromium producing chromium nitride and chromium silicide.
It is assumed that the adherence of the oxynitride glass to
chromium may arise from the formation of Si-Cr and N-Cr bonds in
the interface.   The oxynitride glass does not adhere firmly to
the oxides of nickel, iron or chromium, since Si-N bonds in the
glass may be oxidized to liberate nitrogen gas, detaching the
glass from the metal oxides.

In summarizing, the incorporation of nitrogen in oxide

glasses affects the structure and properties of the glasses. The formation of the nitrogen atoms bonded to three network forming cations increases the density. Not all the nitrogen atoms are bonded to three network forming cations. The lower electronegativity of nitrogen than that of oxygen causes an increase in the diffusivity of alkali ions and suppresses the liquid-liquid phase separation. The covalent nature of the Si-N bonds improves the chemical durability of oxynitride glasses. The crystallization behavior and the properties of the resultant glass-ceramics are affected by the incorporation of nitrogen to a considerable extent. The chemical reactivity of oxynitride glasses with metals is mainly affected by the presence of Si-N bonds. The changes of these properties of glasses on nitridation are shown to be interpreted by the nature of Si-N bonds formed in the glass structure.

LIST OF PUBLICATIONS

Chapter 1

H. Unuma, K. Kawamura, N. Sawaguchi, H. Maekawa and T. Yokokawa, "A Molecular Dynamics Study on the Structure and Properties of Na-Si-O-N Oxynitride Glasses and Melts", in "Science and Technology of New Glasses", ed. by S. Sakka and N. Soga, Ceramic Society of Japan, Tokyo, 1991, pp. 341-346.

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Chapter 2

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