

# Crystallization of Li-Si-O-N oxynitride glasses

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Effects of nitrogen incorporation on the crystallization of a  $30\text{Li}_2\text{O} \cdot 70\text{SiO}_2$  glass have been studied in terms of the glass transition and crystallization temperatures, nucleation mechanism and precipitated crystalline phases. Glass transition and crystallization temperatures rise with increasing nitrogen content. Bulk crystallization is dominant in these oxynitride glasses. Precipitated crystallization phases and their relative amounts vary with nitrogen content. The experimental results are discussed assuming the formation of an  $[(-\text{O}-)_3\text{Si}-)_3\text{N}]$  unit and its evolution to an  $[\text{SiON}_3]$  unit in the residual glassy phase during the crystal growth.

## 1. Introduction

Glassy oxynitride phases formed in the grain boundaries of the sintered nitride ceramics deteriorate their creep resistance [1]. Crystallization of these glassy oxynitride phases can improve the high-temperature mechanical strength of nitride ceramics [2].

Another importance of crystallization of oxynitride glasses is the possibility of the preparation of novel glass-ceramics. A series of glass-ceramics has been prepared [3-6]. Oxynitride glasses can be converted to fine-grained glass-ceramics without addition of a special nucleating reagent [4, 5].

Although many studies have been carried out on the high-temperature behaviour of oxynitride glasses [1-14], the effects of nitrogen incorporation are not yet fully understood. Incorporation of nitrogen into oxide glasses increases the viscosity [15-17] and raises the glass transition [9, 16-20] and crystallization temperatures [5, 9, 10, 13, 16]. There are some systems in which the crystallization temperature does not vary so much [11, 21]. Nitrogen precipitates as a constituent of  $\text{Si}_2\text{N}_2\text{O}$  [1, 14, 16], unidentified phases [3, 5, 11] or solid solution compounds [2, 16], or it remains in the glassy phase [4].

In this work, the crystallization of Li-Si-O-N oxynitride glasses has been studied in terms of crystallization temperature, nucleation mechanism and precipitated crystalline phases in order to understand better the effects of nitrogen on the crystallization of oxynitride glasses. The crystallization behaviour of the  $\text{Li}_2\text{O-SiO}_2$  glasses has been extensively studied.

## 2. Experimental procedure

### 2.1. Preparation of glasses

Oxynitride glasses of the compositions  $30\text{Li}_2\text{O} \cdot (70-3x)\text{SiO}_2 \cdot x\text{Si}_3\text{N}_4$  ( $x = 0, 1, 2$  and  $3$ ), in which the ratio of lithium to silicon is kept at  $6/7$ , have been prepared [22]. The mixtures consisting of pertinent amounts of base oxide glass and  $\beta\text{-Si}_3\text{N}_4$  were melted at  $1400$  to  $1450^\circ\text{C}$  for  $1$  to  $3$  h in boron nitride crucibles

under a flow of nitrogen. The melts were quenched in the flow of nitrogen by withdrawing the crucibles quickly to the cold zone of the furnace. Oxynitride glasses thus prepared were translucent, grey in colour and visually homogeneous.

Two kinds of non-nitrided glasses were prepared to determine the effects of water content on crystallization: one glass was melted in air and the other was melted in a dry nitrogen atmosphere. All the glasses had no crystalline phases as examined by X-ray diffractometry (XRD).

### 2.2. Analysis of the glasses

The glasses were chemically analysed for the nitrogen and lithium contents by the Kjeldahl method and the flame emission technique, respectively. The water content was determined by the infrared absorption of the bands around  $3560$  and  $2850\text{ cm}^{-1}$ . The values of  $63$  and  $1301\text{ ml}^{-1}\text{ cm}^{-1}$  were used as molar extinction coefficients, respectively [23]. Another absorption band attributable to water around  $2350\text{ cm}^{-1}$  was not detected. The analytical compositions are listed in Table I. The maximum nitrogen content is  $3.1\text{ wt}\%$ . Lithium is not lost during the preparation of oxynitride glasses. The water content of oxynitride glasses is very small.

Decomposition of silicon nitride resulting in the deposition of metallic silicon may occur during the preparation of oxynitride glasses [24], to which the colour of the oxynitride glasses may be attributed [24]. If the amount of deposition is extensive, it would result in a change in the composition. Hence, the extent of the deposition of metallic silicon was examined by X-ray photoelectron spectroscopy (XPS). A  $10\text{ kV AlK}\alpha$  X-ray source was used. A spectrum of  $\text{Si}_{2p}$  photoelectron of an oxynitride glass, no. 3, was obtained. The calibration of the line shift was made by referring to the  $\text{C}1s$  line ( $284.6\text{ eV}$  [25]) of the hydrocarbon contaminant. Fig. 1 shows the spectrum. The position of the main peak ( $102.8\text{ eV}$ ) agrees well with

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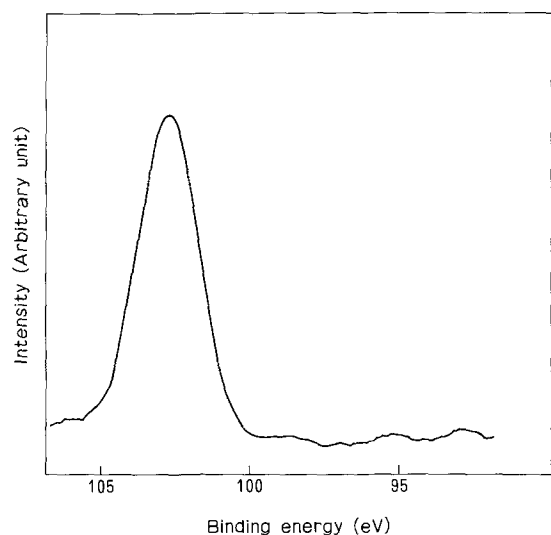


Figure 1 An  $\text{Si}_{2p}$  photoelectron spectrum of oxynitride glass 3.

the result of Kaneko [26] for a  $30\text{Li}_2 \cdot 70\text{SiO}_2$  glass (103.0 eV). Deposition of metallic silicon (98 eV), which would cause an extensive change in the composition, is not obviously detected even in the oxynitride glass of maximum nitrogen content.

### 2.3. Differential thermal analysis

Crystallization behaviour was investigated by differential thermal analysis (DTA). The analyses were carried out on the bulk specimens of approximately  $3 \text{ mm} \times 3 \text{ mm} \times 1 \text{ mm}$  in size and the powder specimens with sizes of 37 to  $63 \mu\text{m}$  at a heating rate of  $10 \text{ K min}^{-1}$  under a flow of nitrogen of 99.9995% purity. Nitrogen gas was passed in the equipment overnight before every analysis.

### 2.4. Crystallization of glasses and X-ray diffractometry

Glass specimens about 1 mm thick were heat treated for crystallization at 670 to  $925^\circ\text{C}$  for 1 or 24 h in a horizontal tube furnace under a flow of nitrogen. The highest limit temperature for the heat-treatment was  $925^\circ\text{C}$  because softening of the specimens becomes extensive when heat-treated at higher temperatures. Glass specimens were wrapped with tantalum foils and heated at a rate of  $10 \text{ K min}^{-1}$  to the desired temperatures. After heat treatment, the specimens were quickly withdrawn to the cold zone of the furnace.

The precipitated crystalline phases were identified

TABLE I Analytical compositions of  $30\text{Li}_2\text{O} \cdot (70-3x)\text{SiO}_2 \cdot x\text{Si}_3\text{N}_4$  oxynitride glasses

Sample (x value)	$N_{\text{calc}}$ (wt %)	$N_{\text{anal}}$ (wt %)	Li* (wt %)	Water (wt %)
0A <sup>†</sup>	0	0	8.16	$9 \times 10^{-3}$
0N <sup>‡</sup>	0	0	8.25	$1 \times 10^{-3}$
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  $30\text{Li}_2\text{O} \cdot 70\text{SiO}_2$  glass is 8.16 wt %.

<sup>†</sup>Melted in air at  $1500^\circ\text{C}$  for 2 h.

<sup>‡</sup>Melted in a nitrogen atmosphere at  $1400^\circ\text{C}$  for 1 h.

by XRD. The crystallized specimens were ground to pass through a sieve of  $44 \mu\text{m}$  openings.  $\text{CuK}\alpha$  radiation with a wavelength of 0.15405 nm was used. The tube voltage and current were 30 kV and 20 mA, respectively. The scanning speed was  $2 \text{ deg min}^{-1}$  in  $2\theta$  and the time constant was 1 sec. For the precise determination of X-ray  $d$ - spacings of (1 1 0), (1 3 0), (0 4 0), (1 1 1) and (0 0 2) planes of lithium disilicate ( $\text{Li}_2\text{Si}_2\text{O}_5$ ), a scanning speed of  $0.125 \text{ deg min}^{-1}$  was employed. The diffraction of a silicon (1 1 1) plane ( $d = 0.3138 \text{ nm}$ ) was used as a reference.

### 2.5. Microscopic observation

In order to investigate the nucleation mechanism, the fractured surfaces of the glasses were observed by scanning electron microscopy (SEM) during crystallization. The specimens were heated in the DTA equipment at  $10 \text{ K min}^{-1}$  under a flow of nitrogen and the furnace power was turned off at the desired temperatures.

## 3. Results

### 3.1. Glass transition and crystallization temperatures

Fig. 2 shows the DTA profiles of the bulk and powder specimens. The glass transition and crystallization temperatures are shown in Table II. The incipient temperature of the exothermic reaction of crystallization is taken as the crystallization temperature.

The glass transition temperatures of the bulk and the powder specimens agree with each other within 4 K. The glass transition temperature rises with increasing nitrogen content. For instance, the incorporation of 3.1 wt % nitrogen raises the glass transition temperature by about 60 K.

An exothermic peak due to crystallization is seen in each specimen in the temperature range  $550$  to  $850^\circ\text{C}$ . As far as the powder specimens are concerned, the crystallization temperature rises, the peak width broadens and the peak height is lowered as the nitrogen content increases.

With the bulk specimens, the crystallization temperature of glass 1 is lower than those of non-nitrided glasses, but it shifts to higher temperatures with further increase in the nitrogen content.

The DTA profiles of two non-nitrided glasses are almost identical. Although a decrease in the water content of glasses increases the glass transition

TABLE II The glass transition temperatures ( $T_g$ ) and the crystallization temperatures ( $T_c$ ) of oxynitride glasses

Sample		$T_g$ ( $^\circ\text{C}$ )	$T_c$ ( $^\circ\text{C}$ )
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

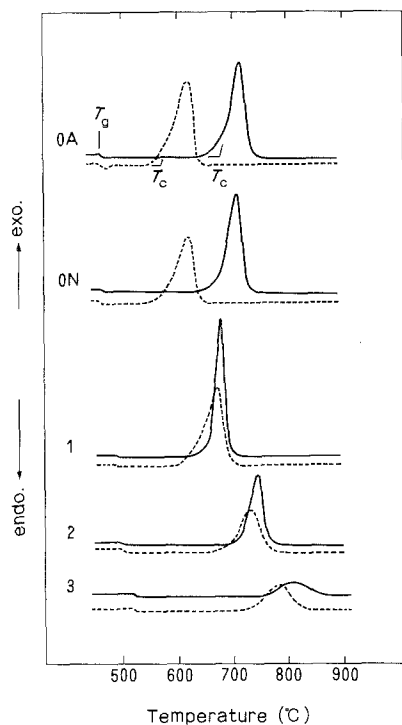


Figure 2 DTA curves of oxynitride glasses. (—) Bulk and (---) powder specimens.

temperature [27, 29] and decreases the temperatures of the initiation of crystallization [27], the effects of the water content are small compared to the effects of the incorporation of nitrogen in the present study.

### 3.2. Nucleation mechanism

In non-nitrided glasses, the crystallization temperatures of the powder specimens are lower by about 100 K than those of the bulk specimens, as seen from Fig. 2 and Table II, suggesting the occurrence of surface crystallization. In fact, it is known that the glasses of the compositions around the  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  composition crystallize both from the surface and the bulk [30]. In oxynitride glasses, however, the differences in the crystallization temperatures between the powder and the bulk specimens are smaller. This suggests that the effect of the presence of the surface on the crystallization of oxynitride glasses is small.

The difference in the nucleation mechanism between non-nitrided glasses and oxynitride glasses is verified by microscopic observation. Fig. 3 shows the fractured surfaces of the glass specimens during crystallization. It is obvious from the figure that both surface crystallization and bulk crystallization occur in non-nitrided glasses, whereas oxynitride glasses crystallize only from the bulk. Furthermore, numerous crystalline particles are produced in oxynitride glasses.

Because oxynitride glasses crystallize from the bulk, the exothermic peaks of the powder and the bulk specimens should be identical. The slight differences in the crystallization temperatures between the powder and the bulk specimens may be attributed to the oxidation of the surface of the powder specimens.

### 3.3. Crystalline phases

The crystalline phases precipitated under various heat treatments are shown in Figs. 4 to 7. The results of

TABLE III X-ray  $d$ -spacings of  $\text{Li}_2\text{Si}_2\text{O}_5$  precipitated from oxynitride glasses under heat treatment at  $925^\circ\text{C}$  for 24 h

Sample	$d$ (nm)				
	(110)	(130)	(040)	(111)	(002)
0A	0.5411	0.3738	0.3657	0.3583	0.2389
0N	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
[32]	0.543	0.375	0.367	0.359	0.2395

glass 0N are identical to glass 0A in Fig. 4 and no effect of water is seen. From the non-nitrided glasses 0A and 0N,  $\text{Li}_2\text{Si}_2\text{O}_5$  precipitates at first and cristobalite begins to precipitate at  $820^\circ\text{C}$ . According to Glasser [31],  $\text{Li}_2\text{Si}_2\text{O}_5$  precipitating from  $\text{Li}_2\text{O}-\text{SiO}_2$  glasses containing 80.08 to 84.0 wt%  $\text{SiO}_2$  is a solid solution with silica, and  $\text{SiO}_2$  is exsolved at higher temperature. This is also the case for the present non-nitrided glasses.

From oxynitrided glasses, however, lithium metasilicate ( $\text{Li}_2\text{SiO}_3$ ) precipitates as well as  $\text{Li}_2\text{Si}_2\text{O}_5$  at relatively low temperatures. The tendency for the precipitation of  $\text{Li}_2\text{SiO}_3$  becomes more pronounced as the nitrogen content increases. After heat-treatment at  $870^\circ\text{C}$ , cristobalite is also seen in oxynitride glasses, and then  $\text{Li}_2\text{Si}_2\text{O}_5$ ,  $\text{Li}_2\text{SiO}_3$  and cristobalite coexist in glasses 2 and 3. Because  $\text{Li}_2\text{SiO}_3$  and cristobalite react with each other to produce  $\text{Li}_2\text{Si}_2\text{O}_5$ ,  $\text{Li}_2\text{SiO}_3$  disappears from glasses 1 and 2 and cristobalite disappears from glass 3 after the heat treatment at  $925^\circ\text{C}$  for 24 h. No crystalline phase containing nitrogen was observed after the heat treatment at  $925^\circ\text{C}$  for 24 h.

It was ascertained that nitrogen is not dissolved in the  $\text{Li}_2\text{Si}_2\text{O}_5$  precipitated under heat treatment at  $925^\circ\text{C}$  for 24 h by the precise determination of the X-ray  $d$ -spacings of the  $\text{Li}_2\text{Si}_2\text{O}_5$ . Table III shows the X-ray  $d$ -spacings together with the values from a reference [32]. No progressive change in the X-ray  $d$ -spacings is seen with the change in the nitrogen content. The scatterings at  $26^\circ$ , which can be regarded as the scattering from the glassy phase [33], increase with increase in the nitrogen content as seen from Table IV. Therefore, nitrogen remains in the glassy phases.

## 4. Discussion

### 4.1. Effects of nitrogen on the glass transition and crystallization temperatures

In oxynitride glasses, the incorporation of nitrogen raises the glass transition and crystallization temperatures as shown in Fig. 2. These changes should be attributed to the effects of the incorporation of

TABLE IV Intensities of the scattering at  $26^\circ$  from oxynitride glasses heat treated at  $925^\circ\text{C}$  for 24 h

Sample	Intensity (counts/sec)
0A	44
0N	42
1	60
2	70
3	90

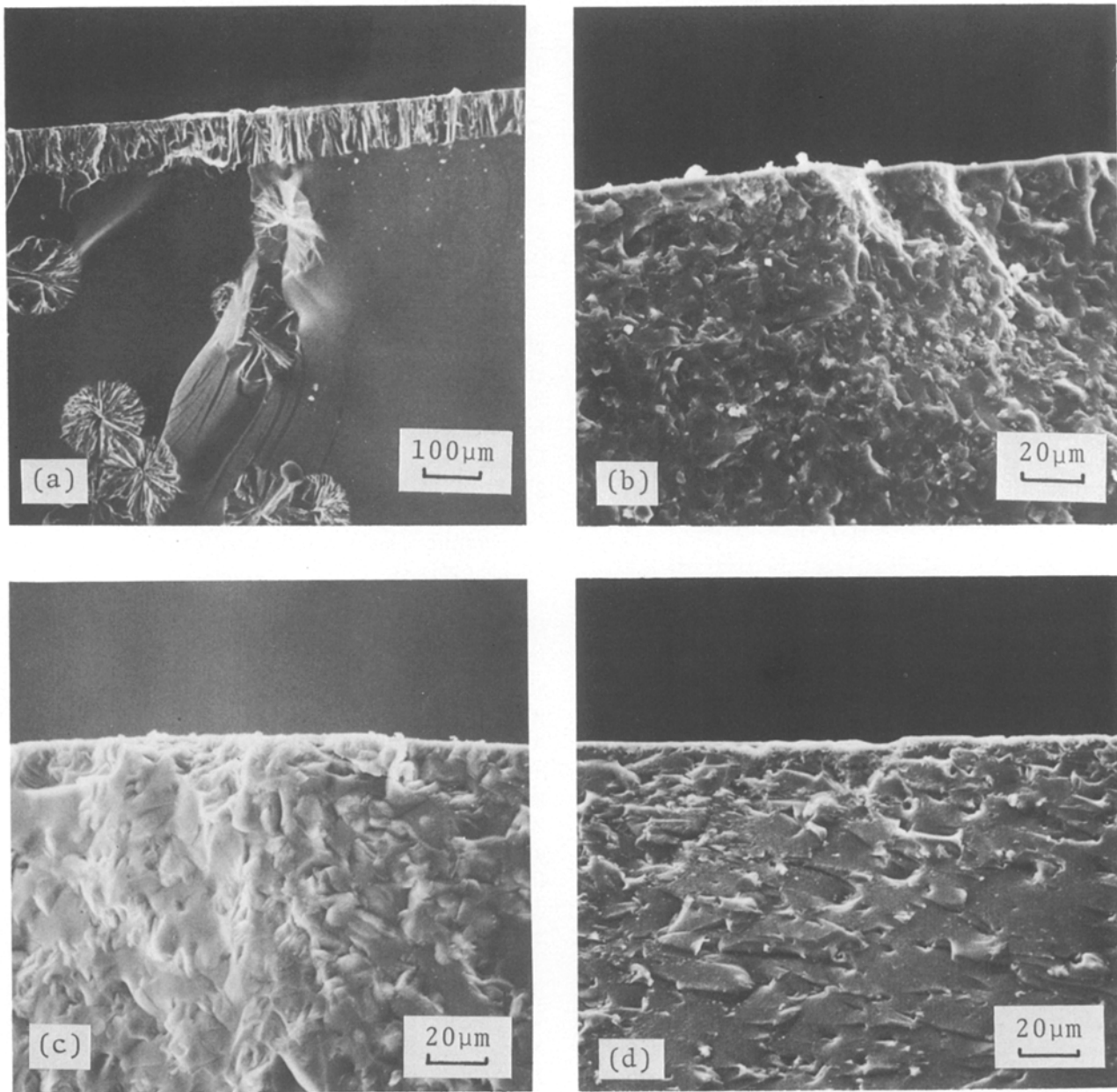


Figure 3 Electron micrographs of fractured surfaces of oxynitride glasses during crystallization. (a) 0A, (b) 1, (c) 2 and (d) 3.

nitrogen because the lithium content is constant over the samples and because the effects of the water content are insufficient to explain these changes.

It is known that crystallization of glasses takes place by the nucleation and growth process. The temperature of the initiation of the exothermic reaction is the temperature at which the nuclei of a critical size start to grow, and the time until the initiation of the exothermic reaction should be an induction period which is required for nucleation [27]. The rate of nucleus formation in a glass,  $I$ , is expressed [27, 33, 34] as

$$I = C \exp(-W^*/RT) \exp(-\Delta E/RT) \quad (1)$$

where  $W^*$  is the thermodynamic barrier in nucleation,  $\Delta E$  is the kinetic barrier and  $C$  is a constant.  $\exp(-\Delta E/RT)$  is proportional to  $1/\eta$  [32], where  $\eta$  is the viscosity of the melt. Hence Equation 1 can be rewritten as

$$I = C''/\eta \exp(-W^*/RT) \quad (2)$$

where  $C''$  is a constant. Assuming that  $W^*$  does not

vary with the nitrogen content, an increase in viscosity suppresses nucleation. The rise in the glass transition temperature with increasing nitrogen content corresponds to the increase in the viscosity at certain temperature. Therefore, the incorporation of nitrogen increases the viscosity and lowers the rate of nucleation which eventually raises the crystallization temperature.

It has been reported by many workers that nitrogen present in oxynitride glasses is coordinated by three silicon atoms to form cross-linking [15–20]. In the present study, also, the increases in the glass transition temperature and viscosity may be explained from the presence of nitrogen coordinated by three silicon atoms.

The shape of the exothermic peak also changes with increasing nitrogen content, that is, the peak width broadens, peak height lowers and the exothermic area decreases as seen from Fig. 2. Hayashi and Tien [5] and Guanqing *et al.* [10] reported similar changes. These changes may be attributed to the change in the rate of crystal growth.

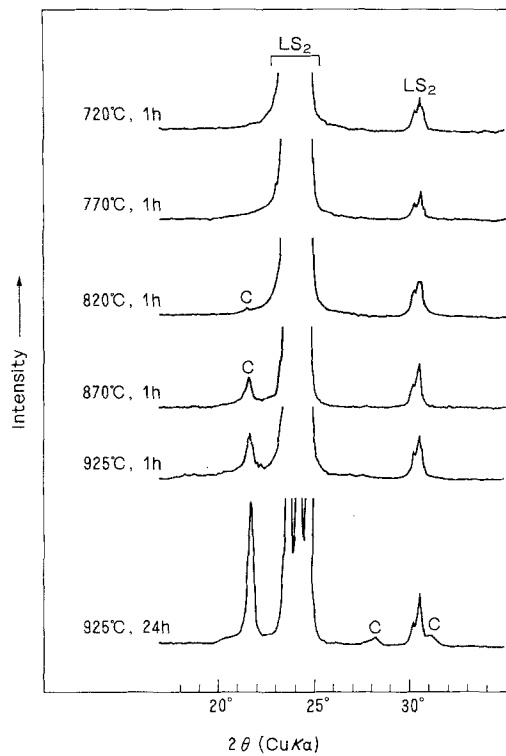


Figure 4 XRD patterns of glass 0A heat treated under various conditions.  $LS_2$  and C represent  $Li_2Si_2O_5$  and cristobalite, respectively.

#### 4.2. Nucleation mechanism

Oxynitride glasses crystallize from the bulk and large numbers of crystalline particles are produced upon crystallization.

Although it has been reported that oxynitride glasses can be converted to fine-texture glass-ceramics [3–5], the precise mechanism of the nucleation is still uncertain. Hayashi and Tien [5] suggested that the incorporation of nitrogen may promote phase separation

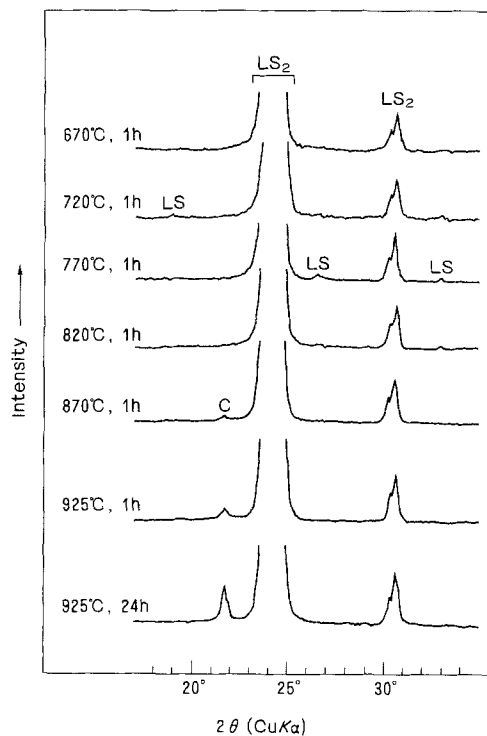


Figure 5 XRD patterns of glass 1 heat treated under various conditions. Abbreviations are the same as those in Fig. 4 and LS represents  $Li_2SiO_3$ .

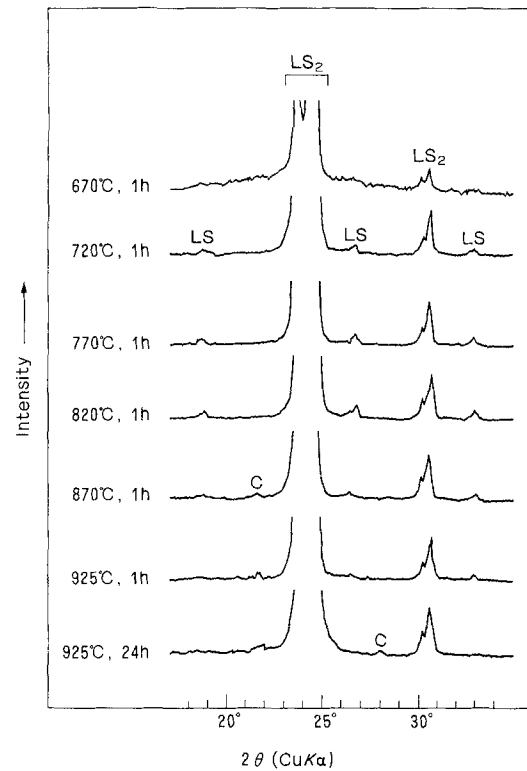


Figure 6 XRD patterns of glass 2 heat treated under various conditions. Abbreviations are the same as in Figs 4 and 5.

which might cause the evolution of large numbers of nuclei.

In general, oxynitride glasses are grey in colour as in the present case, which may be due to the presence of a small amount of fine metallic silicon arising from decomposition of silicon nitride [24] even though the extent is so little that it cannot be detected by XPS or

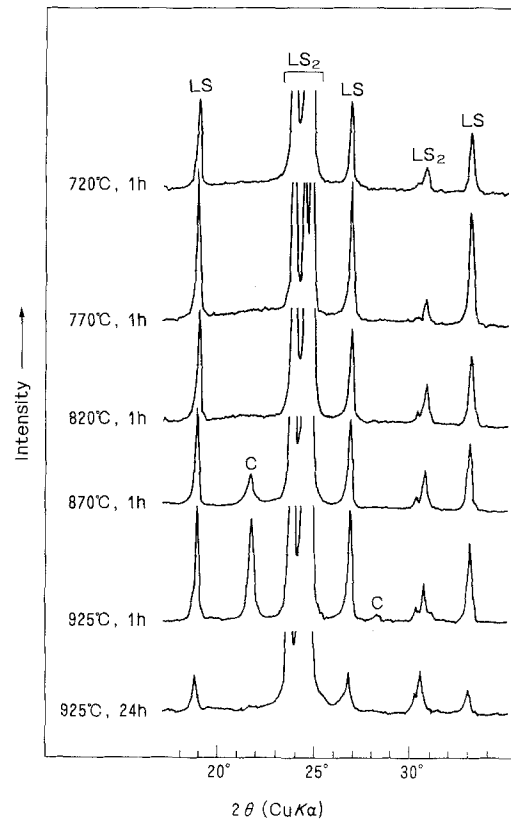


Figure 7 XRD patterns of glass 3 heat treated under various conditions. Abbreviations are the same as in Figs 4 and 5.

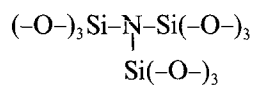
XRD. There is a possibility that the metallic silicon may react as substrates of inhomogeneous nucleation.

### 4.3. Crystalline phases

Crystalline phases vary with the nitrogen content.  $\text{Li}_2\text{SiO}_3$  precipitates from oxynitride glasses after the heat treatment at low temperatures and that tendency becomes pronounced as the nitrogen content increases. The crystalline phases and their relative amounts observed after heat treatment at  $925^\circ\text{C}$  for 24 h also change with nitrogen content.

Nitrogen is regarded to be coordinated by three silicon atoms as reported by other workers [17, 35]. Because nitrogen atoms do not dissolve in the lithium disilicate crystal, it may be assumed that any silicon atoms which are bonded to nitrogen atoms would not participate in crystallization. This would be responsible for the apparent change in the composition, affecting the kind of crystals precipitated.

Then, the formula of the oxynitride glasses, which indicates the effective ratio of the amount of  $\text{Li}_2\text{O}$  and  $\text{SiO}_2$  that can participate in crystallization, will be  $30\text{Li}_2\text{O}(70-12x)\text{SiO}_2 \cdot 4x\text{Si}_3\text{NO}_{4.5}$ , where  $\text{Si}_3\text{NO}_{4.5}$  represents the  $[\text{((-O-)}_3\text{Si-)}_3\text{N}]$  unit containing three silicon atoms that cannot participate in crystallization:



The values of  $x$  in the oxynitride glasses calculated from the analysis of nitrogen are 0.97, 1.83 and 2.82 for glasses 1, 2 and 3, respectively. The ratios of  $\text{SiO}_2$  to  $\text{Li}_2\text{O}$  would be 1.95, 1.69 and 1.21, which are less than 2, indicating the possibility of the precipitation of  $\text{Li}_2\text{SiO}_3$  from oxynitride glasses.

As the temperature is raised, crystals grow and crystalline phases vary as shown in Figs 4 to 7, causing the release of  $\text{SiO}_2$  from the  $[\text{((-O-)}_3\text{Si-)}_3\text{N}]$  unit accompanied by the dissociation of Si-N bonds. As a result, nitrogen will be condensed in the residual glassy phase.

The formula of oxynitride glasses can also be written as  $30\text{Li}_2\text{O} \cdot (70-4x)\text{SiO}_2 \cdot 2x\text{Si}_2\text{N}_2\text{O}$ , and the ratios of  $\text{SiO}_2$  to  $\text{Li}_2\text{O}$  would be 2.20, 2.09 and 1.96 for glasses 1, 2 and 3, respectively. This assumption explains the experimental results that the crystalline phases observed after the heat treatment at  $925^\circ\text{C}$  for 24 h are  $\text{Li}_2\text{Si}_2\text{O}_5$  and cristobalite in glasses 1 and 2 and  $\text{Li}_2\text{Si}_2\text{O}_5$  and  $\text{Li}_2\text{SiO}_3$  in glass 3. Furthermore, it is assumed that the compositions of the residual glassy phases containing nitrogen may be close to  $\text{Si}_2\text{N}_2\text{O}$ . The glassy phases would crystallize into  $\text{Si}_2\text{N}_2\text{O}$  if a heat treatment at higher temperatures was possible.

Because  $\text{Si}_2\text{N}_2\text{O}$  consists of an  $[\text{SiN}_3\text{O}]$  unit [1, 20], nitrogen can be condensed in the glassy phases at least up to  $[\text{SiN}_3\text{O}]$ , in which one silicon is bonded to three nitrogen atoms.

When the  $\text{SiO}_2$  necessary for crystal growth is released from the  $[\text{((-O-)}_3\text{Si-)}_3\text{N}]$  unit, Si-N bondings are dissociated. Because the dissociation energy of the Si-N bonds per unit volume is larger than that of Si-O bonds [17], the energy necessary for overall crystal growth will increase with increasing nitrogen content. Additionally, the residual glassy phase may retard the

diffusion of the atomic species necessary for crystal growth. This would explain the changes of the shape of the exothermic peak of crystallization with increasing nitrogen content.

## 5. Conclusions

1. The crystallization of Li-Si-O-N oxynitride glasses has been studied. Glass transition and crystallization temperatures rise as the nitrogen content increases, which is assumed to be due to the presence of nitrogen coordinated by three silicon atoms and increased viscosity.

2. Bulk crystallization is dominant in oxynitride glasses and large numbers of crystalline particles are produced in the bulk of oxynitride glasses upon crystallization. The possibility is suggested that a small amount of fine metallic silicon may be responsible for inhomogeneous nucleation.

3. Precipitating crystalline phases vary with the nitrogen content. Precipitation of  $\text{Li}_2\text{SiO}_3$ , which is not observed from non-nitrided glasses, is promoted by the incorporation of nitrogen. Nitrogen is condensed in the residual glassy phase as crystallization proceeds. Experimental results have been explained from the formation of an  $[\text{((-O-)}_3\text{Si-)}_3\text{N}]$  unit and its evolution during crystal growth.

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## References

1. K. H. JACK, *J. Mater. Sci.* **11** (1976) 1135.
2. K. TAKATORI, S. KOBAYASHI, S. WADA and O. KAMIGAITO, in *Proceedings of the World Congress on High Tech Ceramics*, (6th CIMTEC), Milan, June 1986, edited by P. Vincenzini (Elsevier, Amsterdam, 1987) p. 925.
3. R. R. WUSIRIKA and C. K. CHYUNG, *J. Non-Cryst. Solids* **38, 38** (1980) 209.
4. W. K. TREDWAY and S. H. RISBUD, *ibid.* **56** (1983) 135.
5. T. HAYASHI and T. Y. TIEN, *Yogyo-Kyokai-Shi* **94** (1986) 44.
6. G. R. FISCHER, R. R. WUSIRIKA and J. E. GEIGER, *J. Mater. Sci.* **20** (1985) 4117.
7. G. THOMAS, C. AHN and J. WEISS, *J. Amer. Ceram. Soc.* **65** (1982) C-185.
8. T. M. SHAW, G. THOMAS and R. E. LOEHMAN, *ibid.* **67** (1984) 643.
9. Y. LUPING, F. QUANXIN, H. GUANQING and L. JIAZHI, *J. Non-Cryst. Solids* **56** (1983) 167.
10. H. GUANQING, Y. LUPING, F. QUANXIN and L. JIAZHI, *ibid.* **80** (1986) 209.
11. P. E. JANKOWSKI and S. H. RISBUD, *J. Amer. Ceram. Soc.* **63** (1980) 350.
12. W. K. TREDWAY and S. H. RISBUD, *J. Mater. Sci. Lett.* **4** (1985) 31.
13. P. E. JANKOWSKI and S. H. RISBUD, *J. Mater. Sci.* **18** (1983) 2087.
14. G. LENGWARD and M. H. LEWIS, *Mater. Sci. Engng.* **71** (1985) 101.
15. T. H. ELMER and M. E. NORDBERG, *J. Amer. Ceram. Soc.* **50** (1967) 275.
16. S. HAMPSHIRE, R. A. L. DREW and K. H. JACK, *Phys. Chem. Glasses* **16** (1985) 182.
17. C. SCHRIMPH and G. H. FRISCHAT, *J. Non-Cryst.*

- Solids* **56** (1983) 153.
18. R. E. LOEHMAN, *J. Amer. Ceram. Soc.* **62** (1979) 491.
  19. *Idem*, *J. Non-Cryst. Solids* **56** (1983) 123.
  20. S. SAKKA, K. KAMIYA and T. YOKO, *ibid.* **56** (1983) 147.
  21. S. SAKKA, *Ann. Rev. Mater. Sci.* **16** (1986) 29.
  22. H. UNUMA, K. KOMORI and S. SAKKA, *J. Non-Cryst. Solids* **95 & 96** (1987) 913.
  23. V. H. SCHOLZE, *Glastech. Ber.* **32** (1959) 81.
  24. D. R. MESSIER and E. J. DEGUIRE, *J. Amer. Ceram. Soc.* **67** (1984) 602.
  25. R. K. BROW and C. G. PANTANO, *ibid.* **70** (1987) 79.
  26. Y. KANEKO, *Yogyo-Kyokai-Shi* **86** (1978) 330.
  27. S. SAKKA, K. KAMIYA and Z.-J. HUANG, *Res. Rep. Fac. Engng. Mie Univ.* **7** (1981) 137.
  28. S. SAKKA, K. MATUSITA, T. WATANABE and K. KAMIYA, *Yogyo-Kyokai-Shi* **89** (1981) 577.
  29. M. TOMOZAWA, M. TAKATA, J. ACOCELLA, E. B. WATSON and T. TAKAMORI, *ibid.* **91** (1983) 378.
  30. K. MATUSITA and S. SAKKA, *J. Non-Cryst. Solids* **38, 39** (1980) 741.
  31. F. P. GLASSER, *Phys. Chem. Glasses* **8** (1967) 224.
  32. JCPDS, Powder Diffraction File 17-447.
  33. Z.-J. HUANG, T. YOKO, K. KAMIYA and S. SAKKA, *Yogyo-Kyokai-Shi* **91** (1983) 215.
  34. D. TURNBULL and M. H. COHEN, in "Modern Aspects of the Vitreous State", Vol. 1, edited by J. D. Mackenzie (Butterworths, London, 1960) p. 38.
  35. R. K. BROW and C. G. PANTANO, *J. Amer. Ceram. Soc.* **67** (1984) C-72.

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