

## Oxynitride glasses—An overview

T DAS

Departments of Materials Science and Chemistry, Bankura Unnayani Institute of Engineering, Bankura 722 146, India

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**Abstract.** The theory and practice of oxynitride glass synthesis and property evaluation came into effect since late 70's. Its importance lies in the fact of its formation at the grain-boundary of synthesized silicon–nitride ceramics with additives. Earlier, heating an oxide glass with  $\text{NH}_3$  and/or  $\text{N}_2$  was the route to obtain oxynitride glass. Later on greater amount of nitrogen retention was made possible using  $\text{AlN}$  or  $\text{Si}_3\text{N}_4$  as batch material. Silicate, borate and phosphate systems were studied in isolation or in conjugation. Melting temperature of such glasses varied from 1500–1800°C. Different technological developments regarding furnace atmosphere, temperature, compositions etc have been discussed towards a successful synthesis with a thermodynamic approach. Nitrogen content in glass as high as 36.8 eq% has been reported by the application of an overpressure of 30 atm  $\text{N}_2$ . Different physical and chemical properties have been discussed in relation to nitrogen content in glass. Structural aspects have been considered with respect to XPS and IR spectroscopic studies. Finally some points have been highlighted towards some potential applications.

**Keywords.** Oxynitride glass; silicon–nitride; network former and modifier; leach resistance; nuclear waste.

### 1. Introduction

The history of oxynitride glasses is not an old one. It was only in the late 70's that some systematic studies on oxynitride glass were reported (Jack 1977; Loehman 1979), and this encouraged many investigators to explore this new field leading to accelerated research in the next decade of 80's. The idea of the existence of oxynitride (O–N) glass came in an indirect way—indirect in the sense that its preparation was not sought for from the constituents. On the other hand it was discovered that dense silicon–nitride based ceramic materials which were sintered with some metal oxide additives contained a grain-boundary glassy phase, which was identified as the oxynitride glass.

Research was initiated by a need to characterize the glassy phase that formed at the grain-boundaries of silicon nitride. The formation of this O–N glassy intergranular phase can be explained as follows: in the preparation of dense silicon nitride based ceramics some metal oxide additives like  $\text{Y}_2\text{O}_3$ ,  $\text{MgO}$  and/or  $\text{Al}_2\text{O}_3$  are given in order to promote their liquid phase sintering. These additives form an eutectic liquid during densification and on cooling produces the above glass at the grain-boundaries of the ceramic material. This discovery led to the making of the O–N glasses in bulk independently by melting the constituent materials in reducing atmosphere. Jack (1977) was the first to report the incorporation of nitrogen in large concentrations in the systems M–Si–Al–O–N where  $M = \text{Y}$  and  $\text{Mg}$ , and Loehman (1979) the first to study the physical properties viz. hardness, transition temperature etc as a function of nitrogen concentration in the Y–Si–

Al–O–N system. This finding that incorporation of N improves a number of properties of glasses and the potential for producing a good glass–ceramic derivative accelerated research on nitrogen glasses themselves, apart from their role in ceramic processing.

### 2. Previous studies

Before this, very few published reports were available on O–N glasses. Mulfinger (1966) studied the solubility of nitrogen in soda-lime glass under several atmospheres. He observed that in presence of water vapour, small amounts of nitrogen were incorporated as N–H groups viz.  $=\text{NH}$  or  $-\text{NH}_2$ ; on the other hand under reducing atmosphere nitride groups were found. Elmer and Nordberg (1967) introduced 3 wt% N into a porous borosilicate glass by heating in  $\text{NH}_3$  or  $\text{N}_2$  and also noted that this addition increased the softening point, viscosity and resistance to devitrification with respect to the oxide glass. Davies and Meherahli (1971) confirmed the chemical solubility of up to 3 at% N in aluminosilicate slag melts and suggested the exchange of nitrogen for bridging oxygen in the glass structure.

The nitrides seem to lower the eutectic temperatures in metal–oxide–silica systems,  $\text{M}_x\text{O}_y\text{--SiO}_2$  where  $M = \text{Mg}$ ,  $\text{Ca}$ ,  $\text{Y}$ ,  $\text{Al}$  etc and are lowered by the addition of nitrogen. This is shown in table 1. Nitrogen also increases the viscosity of the liquid. Thus although the binary systems shown in table 1 generally form crystalline products when quenched under ordinary furnace conditions, the corresponding M–Si–O–N systems produce limited homogeneous

glass regions when quenched under identical conditions. Nitrogen lowers the melting temperatures of a given oxide mixture as evidenced by the observation that the formation of glass at about 1600°C in the Ca–Si–Al–O–N and Mg–Si–Al–O–N systems extends down to low silica composition that would not be liquid below 1800°C in absence of nitrogen. The glass forming region in the system  $Y_2O_3$ – $Al_2O_3$ – $SiO_2$  extends with nitrogen but the glasses crystallize when the composition exceeds a certain limit of  $Si_3N_4$  concentration.

### 3. Classification and types of glass forming system

Oxynitride glasses can be classified under three broad categories: (i) silicon-based oxynitride glass, (ii) silicon-free oxynitride glass and (iii) combination of these two which can again be fragmented into subsystems.

#### 3.1 Silicon-based oxynitride glass ( $M$ – $Si$ – $O$ – $N$ )

Here the original tetrahedral structure [ $SiO_4$ ] is retained with Si as the central metal atom (former) and the surrounding O-atoms getting partially replaced by N-atoms. Here M may be any of Na, Ca, Al, Mg, La, Y etc or combination of possible two. In accordance with the versatility of silicate chemistry itself, this system of glasses also become largely abundant.

#### 3.2 Silicon-free oxynitride glass ( $M$ – $X$ – $O$ – $N$ )

Here the network forming site is occupied by  $X = Al, B, P$ , either singly or in combination, M remaining the same as in previous case in addition to Li, K and Ba. Reported systems are Na–Ba–P–O–N, Na–Mg–P–O–N, Na–Ca–P–O–N (Rajaram and Day 1987), Marchand's (1983) glass as represented by  $MPO_{3-3x}N_{2x}$ , Li–P–O–N (Larson and Day 1986), Na–B–O–N (Frischat *et al* 1984), Ca–Al–Mg–O–N (Bagaasen and Risbud 1983), Ba–Na–B–Al–O–N (Brinker *et al* 1983) etc.

#### 3.3 $M$ – $Si$ – $X$ – $O$ – $N$

Here the glass former is made up of a combination of either any or two out of Al, P, or B atoms along with Si in

common. Depending on this choice it can be further classified into the following systems.

3.3a  $M$ – $Si$ – $B$ – $O$ – $N$ : This system is perhaps the most widely explored by several workers both from its preparation and properties points of view. Due to the presence of two simultaneous good glass forming cations viz. Si and Al, this particular system becomes very versatile. With M being any one of the metals Li, Mg, Sc, Be, Cs, Ca, Ba, Y or a combination of suitable two, large number of glasses have been prepared by several authors.

3.3b  $M$ – $Si$ – $B$ – $O$ – $N$ : There are very few reported glasses under this system which are Na–Si–B–O–N (Jankowski and Risbud 1980), Ca–Al–Si–B–O–N (Jankowski and Risbud 1983), Na–Si–B–O–N (Coon *et al* 1983) and Na–Si–B–O–N (Sahar and Noordin 1995). So far there is no report on glass in the system M–Si–P–O–N.

Oxynitride glasses in the phosphate network was first reported by Marchand (1982). During the period 1985–1991 extensive work on this phosphorous oxynitride glasses were done by the group led by D E Day. This included preparation and comprehensive structural studies of such glasses. The strong motivation towards this P–O–N glass system was generated due to the improvement in chemical durability (dissolution rate decreased by several orders) compared to their oxide counterpart and the high thermal expansion coefficient of phosphate glasses.

A series of glasses based on  $TeO_2$ – $ZnO$ – $ZnCl_2$  system was prepared and their physical, thermal and optical properties were investigated. This system provides a wide and stable glass formation range in which a  $T_c$ – $T_g$  gap beyond 1400°C can be achieved (Frischat *et al* 1984; Sahar and Noordin 1995). Despite attempts involving many combinations of different cations, only one of four O atoms has been successfully replaced by N in the phosphate and silicate systems. Attempts towards chemical substitution of  $Ca_3N_2$  and  $Li_2N$  have been made. Nitride glasses were obtained by melt-quenching at high pressure, high temperature piston cylinder device. High pressure oppose thermal decomposition to gaseous  $N_2$  which previously limited the N-content in O–N glasses (Grande *et al* 1995).

The properties and structural role of N in P–O–N glasses were reported. Properties summarized for several compositions include the dissolution rate in water, thermal expansion coefficient, viscosity and refractive index. Glass formation in the  $Li_3N_4$ – $Ca_3N$ – $P_3N$  was reported (Grande *et al* 1995).

## 4. Synthesis of oxynitride glass

Oxynitride glasses can be prepared by two methods. The first and widely used method is the direct melting of the constituent oxides and nitrides under  $N_2$ /Ar atmosphere at high temperature (1500–1800°C). The second method

**Table 1.** Eutectic temperature (°C) of glasses in the pure oxide and the corresponding oxynitride counterpart (Jack 1977).

M	$M_xO_y$ – $SiO_2$ (°C)	M–Si–O–N (°C)
Mg	1540	1390
Ca	1485	1440
Y	1640	1500
Al	1595	1470

involves the preparation of the base oxide glass or melt first followed by nitridation ammonolysis at some high temperature. These two methods will be discussed here in detail while another alternative but a fine process, the sol-gel route, which is being developed in recent years will be just mentioned.

**Direct melting:** In this method typical oxide powders such as MgO, Y<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Li<sub>2</sub>O, BeO etc are mixed with AlN and/or Si<sub>3</sub>N<sub>4</sub> (source of nitrogen) in appropriate ratio corresponding to some predetermined composition, dry or wet (generally with acetone which subsequently gets evaporated out). The dried powder is next pressed into pellets and taken in BN, Mo or BN-coated graphite crucible and melted under pure nitrogen or argon atmosphere at temperatures 1500–1800°C for a certain period of time followed by quenching the melt by turning off the furnace. The time and temperature of melting depends on particular composition and the nitrogen content of the system. For typical example, Y–Si–Al–O–N glasses were prepared successfully by several workers at a temperature of 1650–1700°C for 30 min–4 h.

#### 4.1 Alternate ways to glass melting

In an alternate procedure instead of melting all the oxides and nitrides in a single step, the base oxide glass is first prepared from the ingredient oxides under air and in second step this prereacted glass powder is mixed with appropriate amounts of Si<sub>3</sub>N<sub>4</sub> and/or AlN and melted under N<sub>2</sub>/Ar in a crucible. This two-step process eliminates the possibility of the decomposition of Si<sub>3</sub>N<sub>4</sub> (leading to N<sub>2</sub> loss and bubbling) due to the reaction of some gaseous product during melting in a single step (Rajaram and Day 1986). For example, in preparing a Na–Si–B–O–N glass, addition of Si<sub>3</sub>N<sub>4</sub> to the powder of the sodium borosilicate glass (made by a separate melting operation) was found to give more satisfactory product (result).

#### 4.2 Nitridation/ammonolysis of the base glass or melt

In this method the base oxide glass is treated with nitrogen and/or ammonia gas at some high temperature for a long period of time. Since the process involves a solid-gas phase reaction naturally the level of nitrogen that can be incorporated will not be very high. On the other hand if base oxide glass at its melting stage is bubbled through gaseous nitrogen and/or ammonia (liquid-gas phase reaction) some betterment can be achieved though the concentration of nitrogen again will be low compared to that by the previous direct melting process (§ 4.1). It was claimed by Rajaram and Day (1986) and again by Day (1989) that greater amount of nitrogen solubility (12 wt%/18 at.%) was achieved when an alkalimetaphosphate frit glass was melted in anhydrous ammonia at higher temperature compared to a direct melting process (maximum 2 wt%) involving metal nitrides (Rajaram and Day 1986) and

NaPO<sub>3</sub> base glass at 900°C where the maximum amount of metal nitrides batched was only 8 wt% (for Ca<sub>3</sub>N<sub>2</sub> and Mg<sub>3</sub>N<sub>2</sub>) and higher nitride concentration was not tried. However the advantage of the latter method over the former is that in comparing some property of a glass with reference to nitrogen content isolated effect of it can be made where metal ions from nitrides will not interfere at all. Schroeder *et al* (1988) reported the formation of a clear glass with up to 7.1 wt% N through a process where SiO<sub>2</sub> powders with varying particle size were first heated to 1000°C in NH<sub>3</sub> and N<sub>2</sub> atmosphere followed by remelting the nitrided powders in Pt under high temperature and high pressure. Another disadvantage of this method over the direct melting technique is the requirement of longer period of time for nitridation.

#### 4.3 Sol-gel route

Sol-gel route in conventional glass making techniques by melt processing of constituents does not always produce glasses with desired microstructures due to high temperatures required for melting which in turn causes oxidation of N and thus result in non-homogeneous structure. The preparation of glasses via solution routes is currently of great interest since this can lead to the fabrication of monoliths with desired constituents and homogeneity at molecular level. The aim is to have Si–N bond in the solution which may be carried on in the pyrolysis. Tetraethyl-orthosilicate (TEOS) is used as the source material which is hydrolyzed followed by pyrolysis. This process involves a three-step process: (i) preparation of a base oxide monolithic porous gel, (ii) ammonolysis of the gel below  $T_g$  and  $T_c$  and (iii) finally conversion of the ammoniated gel into glass just above  $T_g$ . The advantage of this method over other methods is its low processing temperature. Thus the difficulty in the establishment of thermodynamic equilibria involving decomposition of Si<sub>3</sub>N<sub>4</sub>/AlN (to be discussed later on) at a high temperature can be avoided.

### 5. Oxynitride glass stability—a thermodynamic approach

The oxynitride glass synthesis suffers from drawbacks such as extensive frothing loss of N and metallic inclusions unless some predetermined conditions are maintained which are again thermodynamically controlled. In the following section the cause of these problems will be discussed from a thermodynamic viewpoint based on choice of ingredients, furnace atmosphere and crucible material.

#### 5.1 Choice of ingredients

The stability of an oxynitride glass melt depends upon the feasibility of the redox reactions between the metal

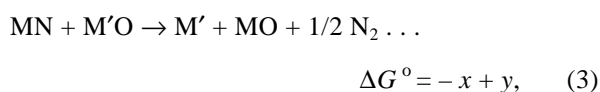
nitrides (MN) used as nitrogen source and the modifier oxides (M'O). During the preparation of O-N glasses the possible reactions between the metal nitrides and metal oxides may be depicted in a general way in terms of two half-reactions.



and



where  $\Delta G$ 's are the standard free energy changes at a particular temperature, which can be combined to give the net reaction (according to Hess's law of thermochemistry)

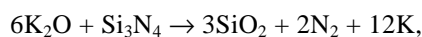


leading to decomposition of nitride and subsequent evolution of gaseous  $\text{N}_2$ . Now thermodynamics predicts that reaction (3) will be spontaneous only if the overall change in free energies of the reaction is (-)ve. For this, (-)ve value of  $x$  has to have greater magnitude than that of  $y$  (i.e.  $| -x | > | -y |$ ). This implies that the metal nitride will be stable (i.e. will not be oxidized) at melting temperature ( $T$ ) when its standard free energy of oxidation ( $\Delta G^{\circ}$ ) at  $T$  is less (-)ve than the standard free energy of formation ( $\Delta G_{\text{f}}^{\circ}$ ) of the modifier oxide at the same temperature. Now JANAF thermochemical tables provide the requisite Gibb's free energy changes of reactions (1) and (2) at different temperatures for different species. From this one can get the order of free energy changes of oxidation at a particular temperature in a qualitative way as follows:

K, Na, Sm, Mo, P, Mn, C (for CO), B, AlN, Si, Ti (for TiO), Si, Ti, ( $\text{Si}_3\text{N}_4$ ), Li, Ce, Mg, Al, Ba, Zn, La, Ca, Be, Sc, Y (-)ve value of  $\Delta G^{\circ}$  increases  $\rightarrow$

The oxides of the metals below a particular nitride will be compatible with respect to the nitride whereas oxides above the nitride will oxidize the latter itself being reduced leading to evolution of  $\text{N}_2$ . The reduced species get lost from the melt either as a liquid or gas or deposit as a solid. This theoretical consideration is supported by a lot of experimental findings. For example,  $\text{Li}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{BaO}$ ,  $\text{Y}_2\text{O}_3$  can form good glass with  $\text{Si}_3\text{N}_4$  or AlN while  $\text{B}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$  cannot in the conventional melting procedure. Large weight loss was reported in the preparation of K-Si-Al-O-N with  $\text{K}_2\text{O}$  as batch material (Wusirika 1984; Messier and Deguire 1984).

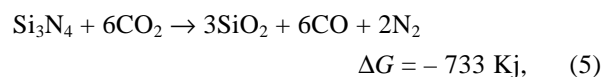
Here the actual reaction that is taking place is



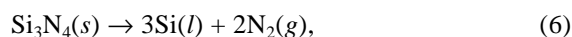
wherefrom both  $\text{N}_2$  and K get evaporated out of the melt.

Thus metal oxide below a nitride will be a favourable choice for batch material.

Sometimes CO from carbonates oxidizes  $\text{Si}_3\text{N}_4$  according to the reaction



leading to large amount of  $\text{N}_2$  loss. Thus for carbonate containing batch a two-step melting process is preferred: first preparing the base silicate glass from the metal carbonate and silica (thus removing the  $\text{CO}_2$ ) and in the next step melting it with  $\text{Si}_3\text{N}_4$ . In this way greater amount of N retention was made possible (Wusirika 1984).  $\text{Si}_3\text{N}_4$  in batch can decompose as



leading to frothing in O-N glass melt. This can be suppressed by the addition of Si in the glass batch (Baik and Raj 1985). The decomposition vapour pressure of  $\text{N}_2$  rises above atmospheric in case of  $\text{Si}_3\text{N}_4$  even at as low as  $1400^{\circ}\text{C}$  when  $a = 0.01$  while with AlN it remains below atmospheric even at as high as  $1800^{\circ}\text{C}$  at  $a = 0.01$ . Thus use of AlN is preferred over  $\text{Si}_3\text{N}_4$  as nitrogen source.

## 5.2 Choice of crucible material

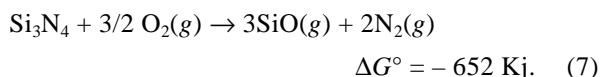
The selection of proper container for oxynitride glass melting is a matter not to be ignored. In a number of attempts it has been found that the crucible gets heavily attacked by the O-N melt at the processing temperature. Our own experience with some boron nitride crucibles resulted almost into a powdered product of the container after glass melting in the Y-Si-Al-O-N system. Alumina crucibles were also found to be reactive towards above glass melt. The criterion for the selection of a crucible material will again depend on the relative position of the metal with respect to the nitride in the free-energy change order. For example, in considering the suitability of a metal as a container, here the metal has to be more stable compared to its metal oxide counterpart in the oxynitride melt, a case just reversed as in choice of ingredient material. Here the choice of elements lying above the nitride in the free energy change order will be favoured, viz. Mo which has been widely used by many workers. The failure with BN-crucible in the AlN melt may be due to contamination of these with  $\text{B}_2\text{O}_3$  which was reduced by AlN during melting operation. However, pure BN is a good material for oxynitride melt, BN-coated graphite crucibles also give successful melts (Das *et al* 1991). The use of BN-coating has two-fold effects: (i) helps to maintain a local reducing atmosphere as well as (ii) facilitate the removal of the glass after melting from the crucible.

Successful use of alumina and silica glass crucibles in the system M–P–O–N where M = Li, Na, K and M = K, respectively were reported by Marchand (1983) without any evidence of contamination from crucibles. The melting point of the crucible must be higher than the processing temperature of the glass.

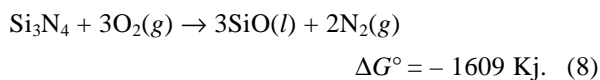
### 5.3 Effect of furnace atmosphere

As it has already been pointed out that during melting of oxynitride glasses a reducing (non-oxidizing) atmosphere is to be maintained inside the furnace since O–N glasses are prone to oxidation at high temperature. This is generally achieved through a flow of high purity (oxygen free) N<sub>2</sub> gas. The use of N<sub>2</sub> gas (preferably at high pressure > 1 atm) has two advantages—it can inhibit the decomposition of SiN (Si<sub>3</sub>N<sub>4</sub> → 3 Si(l) + 2 N<sub>2</sub>) as well as assist in increasing the N content in glass by getting dissolved into the melt. There are reports of using Ar gas atmosphere also.

The presence of oxygen in the furnace atmosphere can lead to two types of reactions with Si<sub>3</sub>N<sub>4</sub> depending on the amount of its presence. For example, at low concentration of oxygen



While at higher O<sub>2</sub> concentration



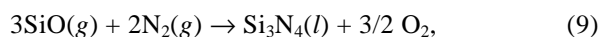
Thus thermodynamically both reactions (7) and (8) are feasible having large (–)ve value of ΔG° (both at 1900°K). Here we can see that in both ways N is getting lost from the system; additionally in case of reaction (7) SiO(g) gets evaporated out, leading to large amount of mass loss.

Equilibrium constant of reaction (7) can be expressed in terms of activity and partial pressure

$$K = \frac{p_{\text{SiO}} \times p_{\text{N}_2}^2}{a_{\text{Si}_3\text{N}_4} \times (p_{\text{O}_2})^{3/2}} = \frac{p_{\text{SiO}}^3 \times p_{\text{N}_2}^2}{(p_{\text{O}_2})^{3/2}}$$

(Since  $a_{\text{solid}} = 1$ ).

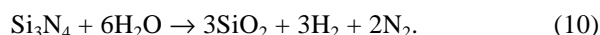
If one increases the partial pressure of N<sub>2</sub> in the system, to maintain equilibrium constant (K), the same (since equilibrium constant cannot be changed as long as the temperature remains the same), partial pressure of O<sub>2</sub> has to be increased. It implies that the backward reaction



will be favoured; in other words the equilibrium will be shifted towards the reactant side (The same conclusion can be drawn by considering Le Chatelier principle also). Thus, nitrogen loss can be hindered by maintaining an over pressure of N<sub>2</sub> over the oxynitride melt even if oxygen is present in the system.

Makishima *et al* (1993) prepared a La–Si–O–N glass with nitrogen content of 36.8 eq% (highest so far reported) by the application of an overpressure of 30 atm N<sub>2</sub>.

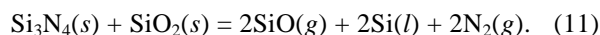
Theoretically, this type of decomposition can also be suppressed by the application of high partial pressure of SiO but this is experimentally difficult to achieve. Water if present in the furnace atmosphere can also result into loss of N<sub>2</sub> through the following reaction.



Hence furnace atmosphere should be perfectly dried.

## 6. Colour and optical transparency of oxynitride glasses

Oxynitride glasses in the silicate system are usually coloured grey to black and translucent in thin section, the intensity of which increased with increase in nitrogen content. The origin of colour could not be anticipated properly. Optical microscopy and XRD analysis could not detect any presence of crystallinity. Precipitation of silicon was suggested to be responsible (Loehman 1985) for this colour shown by high resolution electron microscopy. According to Messier and Deguire (1984) this precipitation does not arise from dissociation of Si<sub>3</sub>N<sub>4</sub>, but from the decomposition reaction at temperatures > 1650°C of the form:



Thermodynamic analyses show that the above reaction cannot be suppressed much by increasing the pressure of nitrogen during melting. This explains the experimental observations of Messier and Deguire (1984) that the silicon content in the glasses in the system Y–Si–Al–O–N cannot be much reduced by applying high nitrogen pressure. However due to Coon *et al* (1989) possibility of any silicon inclusion was neglected from electron diffraction pattern of glasses in the Y–Si–Al–O–N system so also presence of any crystalline phase was ruled out (figure 1). The transparency of the glasses has been found to increase by reducing the concentration of precipitates in the glass by selecting compositions which could be melted at low temperature at 1450°C where substantial reduction of decomposition of Si<sub>3</sub>N<sub>4</sub> is expected to occur. The transparency in the glasses of the system CaO–Al<sub>2</sub>O<sub>3</sub>–MgO–SiO<sub>2</sub>–AlN containing a little over 3 wt% silicon synthesized by quenching in liquid nitrogen is considerably better than the commonly made dark green in colour.

Infrared and ultraviolet transmission of Ca–Si–Al–O–N and Li–Si–Al–O–N glasses are affected by incorporation of nitrogen. The absorption band at 2.7  $\mu\text{m}$  characteristic of Si–OH bond are not observed in these glasses suggesting that the incorporation of nitrogen lowers the concentration of structural water by the reaction same as in (10).

## 7. Properties of oxynitride glasses

The finding that incorporation of small amount of nitrogen in a glass alters its properties significantly has encouraged many workers in evaluating different physical and chemical properties of oxynitride glasses and their dependence on nitrogen concentration. But many of the early works on property evaluation suffered from the drawback that the change in properties observed could not be established unequivocally to be due to change in nitrogen in a glass system. For example M–Si–Al–O–N, the ratio of atoms other than O and N i.e. M : Si : Al is to be maintained constant. Such a five-component system can be represented by a model (figure 2) which can be compared with a trigonal–biprism structure. Here the triangle can be considered as a plane of constant M : Si : Al and as the nitrogen content increases one can assume a shift of the triangular plane of constant M : Si : Al vertically upward (M = Mg, Ca, Y, Nd). Most of the property evaluation have been done in the silicate system, some in the phosphate system and very few in borate system.

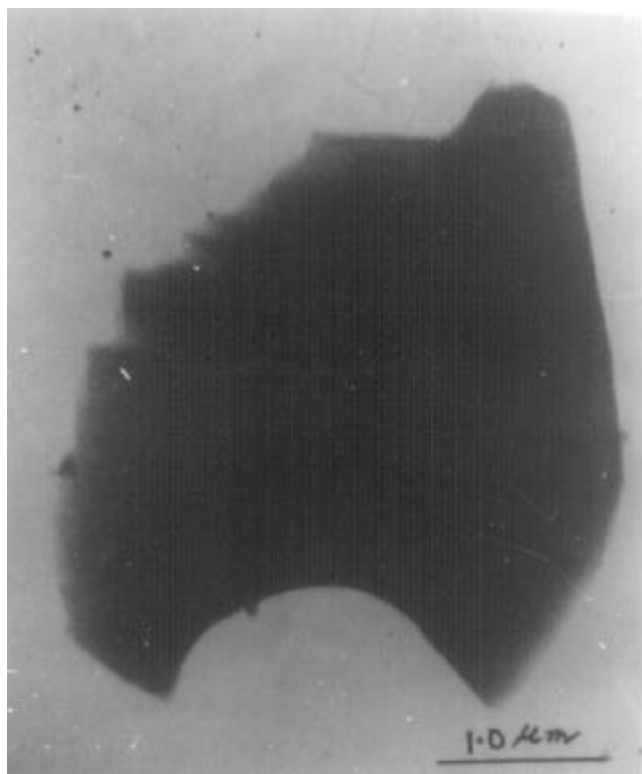


Figure 1. Bright-field TEM image of a glass particle.

### 7.1 Physical properties of oxynitride glasses

Oxynitride glasses have improved physical properties in comparison to their pure oxide glass analogue. Thus glass transition temperature (Elmer and Nordberg 1967; Davies and Meherahli 1971; Jack 1977; Larson and Day 1986), hardness (Elmer and Nordberg 1967; Jack 1977; Marchand 1983; Larson and Day 1986; Rajaram and Day 1986), fracture toughness (Jack 1977; Marchand 1983; Larson and Day 1986), Young's modulus (Elmer and Nordberg 1967; Loehman 1979; Marchand 1983; Frischat *et al* 1984; Rajaram and Day 1986), viscosity (Davies and Meherahli 1971; Frischat *et al* 1984; Rajaram and Davies 1987), flexural strength (Larson and Day 1986), measured in M–Si–Al–O–N system where M = Y, Mg, Ca, Na, Nd etc have all been found to increase with increase in N content starting from a minimum value for the pure oxide glass (figures 3a–d). The variation in thermal expansion coefficient (Jack 1977; Larson and Day 1986) on the other hand follow a reverse trend. Wusirika (1984) found thermal expansion coefficient to be independent of N content. Electrical properties of oxynitride glasses, however, could not be related to the presence of nitrogen in the compositions.

As the trend in the variation of the properties with nitrogen content is always same, description of the properties in each of the glass composition has therefore been omitted, instead some representative curves for the properties are given (figures 3a–d). The figures are self explanatory.

An infrared cut off edge to 6.5  $\mu\text{m}$  can be obtained while the optical energy gap was found to be in the range 2.0–2.5 eV. Most properties are observed to be dependent in a systematic manner on the  $\text{ZnCl}_2$  content (Sahar and Noordin 1995).

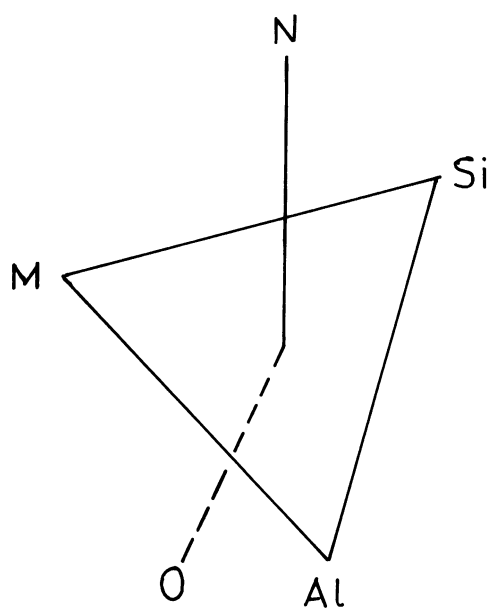


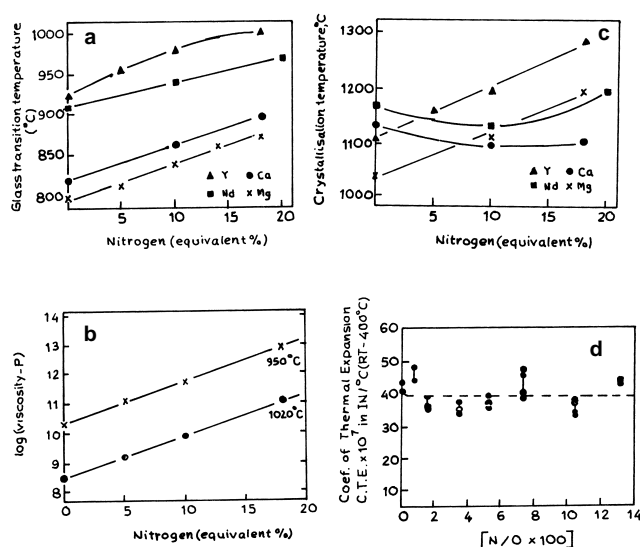
Figure 2. Model of a five-component system diagram.

## 7.2 Chemical properties

**7.2a Leach resistance:** Nitrogen increases the chemical durability of oxynitride glasses. Loss of weight% studied under distillation at 950°C were found to decrease with increasing nitrogen in the glass (Loehman 1979). Improvement in leach rate was achieved (Frischat *et al* 1985) 2/3 times for a Na–O–CaO–SiO glass containing 4 eq% N while it was 1/2 for a Li–Si–Al–O–N glass containing 18 eq% N.

**7.2b Oxidation behaviour of oxynitride glasses:** Oxynitride glasses are very prone to oxidation. When a Y–Si–Al–O–N glass powder, with 8 at% N, was heat treated up to 1200°C in air in a Pt-crucible a foamy white product (figure 4) was obtained which was soft outside while hard inside (Das 1993). The oxidation property (thickness of oxide layer) depends on the composition of such glasses. Berilya glasses are resistant to oxidation (Wusirika 1985). Oxidation behaviour of the glasses in the system Ln–Si–Al–O–N (Ln = Dy, Er, Gd, La, Nd, Sm, Y, Yb) was analysed by assuming that the weight change is proportional to the  $n$ th power of the oxidation time, and it was found that the oxidation exponent,  $n$ , tends to increase with decreasing radius of rare earth ions. Yb–Si–Al–O–N glass had the best oxidation resistance in these rare earths containing oxynitride glasses. The oxidation mechanism of the oxynitride glasses was also discussed (Murakami and Yamamoto 1994).

Elastic moduli and hardness markedly increase with increasing N content. The increase in elastic moduli with increasing N content is attributed to N bonded to three Si. This has been confirmed by a molecular orbital calculation, which shows that the bending force constant for



**Figure 3.** a. Glass transition temperature ( $T_g$ ); b. crystallization temperature ( $T_c$ ); c. viscosity of Y–Si–Al–O–N glasses; and d. thermal expansion coefficient.

model N  $[\text{Si}(\text{OH})_3]_3$  is very large compared with that for  $[\text{Si}(\text{OH})_3]_2$ . It is shown that a drastic improvement in chemical durability by nitriding is seen in some glasses but not in others. Ionic conductivity of alkali silicate glasses increases with N content (Sakka 1995).

Mixed alkali glasses or rather melts of the molar composition  $(74 - 3x)\text{SiO}_2, x\text{Si}_3\text{N}_4, 16(\text{R}_2\text{O} \cdot 10\text{CaO})$  with  $\text{R}_2\text{O} = \text{Na}_2\text{O}, \text{K}_2\text{O}$  show a deviation from linearity of glass transition temperature ( $T_g$ ), thermal expansion, viscosity, and density (Larson and Frischat 1998).

## 8. Crystallization of oxynitride glasses

Oxynitride glasses are very stable to devitrification, withstanding 12 h or more at 1000°C without detectable crystallization in Y–Si–Al–O–N system (Loehman 1980). Crystallization in O–N glasses starts after 1100°C and depends on the composition. Complicated pattern in the X-ray diffraction are usually obtained. Some of the phases which have been identified are Y-disilicate ( $\text{Y}_2\text{Si}_2\text{O}_7$ ),  $\text{Al}_2\text{Y}_4\text{O}_9$ , YAG ( $\text{Y}_3\text{Al}_5\text{O}_{12}$ ),  $\text{YAlO}_3$ , crystoballite, silimanite ( $\text{Al}_2\text{SiO}_5$ ). Some nitrogen containing phases are  $\text{Si}_4\text{Al}_4\text{O}_{11}\text{N}_2$ ,  $\text{Si}_2\text{N}_2\text{O}$ ,  $\text{b-Si}_3\text{N}_4$  etc (Wusirika and Chyung 1980).

## 9. Structure of oxynitride glasses

The present knowledge of oxynitride glass structure is limited, the role of different oxides as modifier or former, in particular. With the aid of different spectroscopic techniques, viz. FTIR, XPS, etc and from some theoretical aspects it has been possible to enlighten some of the areas in this field but the scope of future research is still wide open. In the following section the role of different cations



**Figure 4.** Mass left after oxidation of a Y–Si–Al–O–N glass (Das 1993).

and anions involved in such glass structure will be discussed in the silicate system on the basis of the so far available experimental results so also some theoretical aspects to give some model structure.

### 9.1 Bridging and non-bridging anions, the oxynitride network

The oxynitride glass network in the silica system essentially consists of the basic  $[\text{SiO}_{(4-x)}\text{N}_x]_{x=0-4}$  tetrahedron units polymerized through oxygen/nitrogen atoms. This means some of dibridging oxygens of the silicate network get replaced by the tribridging nitrogen atoms leading to increased amount of crosslinkings in oxynitride network. Thus each nitrogen is shared among three  $\text{Si}(\text{O}, \text{N})_4$  tetrahedra leading to increased compactness and tightening of the glass structure; in addition, the bonds with nitrogen tend to become more covalent causing the material to stiffen with consequent change in properties.

That in case of an oxynitride glass the bridging characteristics increases was proved by Risbud (1981) by a model. Considering oxygen ( $\text{O}^{2-}$ ) and nitrogen ( $\text{N}^{3-}$ ) as the anions and Si and Al as the glass forming cations it was shown that introduction of nitrogen in the aluminosilicate network results in an increase in the average number of bridging anions at the cost of average non-bridging anions. Thus the overall effect of nitrogen incorporation into an oxide glass is the generation of new bridging sites as well as conversion of some non-bridging sites. The three possible modes of nitrogen incorporation are as follows:

- (I)  $-\text{Si}-\text{N}^{2-}$  comparable to non-bridging oxygen  $-\text{Si}-\text{O}$   
(no bridge)
- (II)  $-\text{Si}-\bar{\text{N}}-\text{Si}-$  comparable to a bridging oxygen  
 $-\text{Si}-\text{O}-\text{Si}-$   
(di-bridging)
- (III)  $-\text{Si}-\text{N}-\text{Si}-$  impossible in oxide glass  
          |  
          Si  
(tribridging)

Thus with the mode III which is not possible in oxide glasses the degree of crosslinkings of glass structure get increased.

IR spectroscopic data suggest that 70–80% of the N content is fixed in the structural network of a glass (Budov *et al* 1996).

### 9.2 FTIR analysis

The fourier transform infrared spectra of the glasses in the system  $\text{M}-\text{Si}-\text{O}-\text{N}$  ( $\text{M} = \text{Y}-\text{Al}$ ) (Loehman 1979; Yuquan *et al* 1989),  $\text{Li}-\text{Al}$  (Luping and Quanxin 1983) show two major bands one at around  $470 \text{ cm}^{-1}$  and another at  $920 \text{ cm}^{-1}$ .

The IR spectrum of pure  $\text{SiO}_2$  has absorption at  $460 \text{ cm}^{-1}$  ( $\text{Si}-\text{O}-\text{Si}$  bending) and  $1080 \text{ cm}^{-1}$  ( $\text{Si}-\text{O}-\text{Si}$  stretching) while that of  $\text{Si}_3\text{N}_4$  has a broad absorption at around  $900 \text{ cm}^{-1}$  ( $\text{Si}-\text{N}-\text{Si}$  stretching). A shift in the position of the  $\text{Si}-\text{O}-\text{Si}$  stretching absorption towards lower wavenumber of that of  $\text{Si}-\text{N}$  with increase in nitrogen content occurs which indicates substitution of nitrogen for oxygen in the silicate network. The spectra of oxynitride glasses may be regarded as the spectra of the pure oxide glasses superimposed mainly by the  $\text{Si}-\text{N}$  stretching bands. Again, the oxynitride glass prepared from  $\text{AlN}$  as the nitrogen source shows no or very small absorption around  $700 \text{ cm}^{-1}$  corresponding to  $\text{AlN}$  bonds. These indicate that nitrogen in oxynitride network is an integral part of the structural network.

### 9.3 XPS investigation

Brow *et al* (1984) found in their XPS investigation of the oxynitride glasses that most of them had N 1S spectra with at least two components. One was the primary oxynitride peak around 398 eV and the other peak was smaller having binding energy about 2 eV lower. That the majority of the nitrogen atoms in the glass network was coordinated by three silicon atoms was confirmed by the similarity of the primary N 1S binding energy of the glasses and  $\text{Si}_3\text{N}_4$ . The low energy shoulder of the N 1S spectra was attributed to be due to the presence of non-bridging nitrogen. But only a single photoelectron peak was observed in the XPS spectra by Schrimpf and Frischat (1983) indicating one mode of nitrogen incorporation in these glasses.

Bonding and coordination number N in the glass network has been deduced from NMR, XPS and Raman spectroscopy. Existing evidence show that N replace O in  $\text{PO}_4$  network as doubly ( $=\text{N}$ ) and triply coordinated ( $>\text{N}-$ )  $\text{N}^{3-}$  ions (Reidmeyer and Day 1995).

Neutron diffraction analysis and  $^{29}\text{Si}$  and  $^{27}\text{Al}$  NMR spectroscopy have shown that in  $\text{Na}-\text{Si}-\text{O}-\text{N}$  and  $\text{Y}-\text{Si}-\text{Al}-\text{O}-\text{N}$  oxynitride glasses there exist N-bonded to two Si as well as N-bonded to three Si. It is also shown that N hardly make bonds with Al in glasses containing both Si and Al and that N do not enter into the glass network but form clusters containing  $\text{AlN}_4$  units in aluminate glasses (Sakka 1995).

The glass structure has been studied via  $^{29}\text{Si}$  and  $^{27}\text{Al}$  NMR and by IR spectroscopy. IV, V, and VI coordinated  $\text{Al}_2\text{O}_3$  groups are present for all compositions. The N is incorporated in  $\text{Si}(\text{O}_3\text{N})$  tetrahedral units (McMillan *et al* 1998).

$^{29}\text{Si}$  MAS NMR measurements on glasses of the system  $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2-\text{Si}_3\text{N}_4$  prove that the number of links between the  $[\text{SiO}_4]^{4-}$  tetrahedra increases with increasing N content (Larson and Frischat 1998). With such a discussion a model partial structure of Mg containing (as



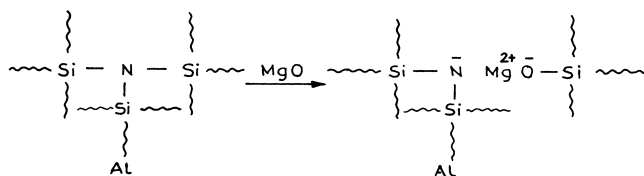


Figure 5. Model structure of a Mg-Si-Al-O-N glass.

modifier) Si-Al-O-N glass is shown in figure 5 (Das *et al* 1994).

On the basis of XRF analysis of the glasses it has been stated that with increasing content of introduced Si<sub>3</sub>N<sub>4</sub> the content of Na<sup>+</sup> in glass decreased. This may be interpreted as a suggestion that sodium cation was bound with reactive N in the form of Na<sub>3</sub>N and deposited on the walls of the heating chamber of the induction heater (Konderatowicz and Wasylak 1995).

#### 9.4 Applications of oxynitride glasses

The ultimate usefulness of oxynitride glasses and fibres depends upon the minimization or elimination of metallic defects that arise during processing. Despite this, the origins and chemistry of such defects in oxynitride glass has received scant attention in the literature. The defects reduce glass transparency and cause oxynitride glass fibres to fail at relatively low stress levels (Messier and Patel 1992). The physicomechanical properties obtained for the synthesized glasses of the above system are indicative of their promise as materials for manufacture of high modulus fibre and other purposes (Budov *et al* 1996). The oxynitride glass has potential applications in metal-metal, metal-ceramic, and ceramic-ceramic joining materials and coatings if composition is properly selected. Due to high leach resistance they can also be used for the containment of high-level nuclear waste for their ultimate disposal. Oxynitride glass fibre is also a promising one to be exploited.

#### References

- Bagaasen I M and Risbud S H 1983 *J. Am. Ceram. Soc.* **66** 69  
 Baik S and Raj R 1985 *J. Am. Ceram. Soc.* **68** C168  
 Brinker C J, Haaland D M and Loehman R E 1983 *J. Non-Cryst. Solids* **56** 179  
 Brow Richard, Pantano K and Carlo G 1984 *J. Am. Ceram. Soc.* **67** C72  
 Budov V V, Bormotunov K A, Sarkisov P D and Medvedev V V 1996 *Glass Phys. Chem.* **22** 378  
 Coon D N, Doyle T E and Weidner J R 1989 *J. Non-Cryst. Solids* **108** 180  
 Coon D N, Rapp J C, Bradt R C and Pantano C G J R 1983 *J. Non-Cryst. Solids* **56** 161  
 Das T 1993 *Diffusion of sodium and iron in oxynitride glasses*, Ph.D. Thesis, Jadavpur University, Jadavpur  
 Das T, Sanyal A S and Mukerji J 1991 *Phys. Chem. Glasses* **32** 180  
 Das T, Sanyal A S and Mukerji J 1994 *Phys. Chem. Glasses* **35** 198  
 Davies M W and Meherahli S G 1971 *Metall. Trans.* **2** 2729  
 Day D E 1989 *J. Non-Cryst. Solids* **112** 7  
 Elmer T H and Nordberg M F 1967 *J. Am. Ceram. Soc.* **50** 275  
 Frischat G H, Krause W and Hubenthal H 1984 *J. Am. Ceram. Soc.* **67** C10  
 Frischat G H, Krause W and Sebastian K 1985 *J. Am. Ceram. Soc.* **68** C305  
 Grande T, Jacob S, Holloway J R, Memillan P F and Angll C A 1995 *J. Non-Cryst. Solids* **184** 151  
 Jack K H 1977 *Nitrogen ceramics* (ed.) F L Riley (Leyden: Noordhoff) **109** 262  
 Jankowski P E and Risbud S H 1980 *J. Am. Ceram. Soc.* **63** 350  
 Jankowski P E and Risbud S H 1983 *J. Mater. Sci.* **18** 2087  
 Konderatowicz J and Wasylak J 1995 *Proc. 17th int. cong. on glass* **5** p. 540  
 Larson R W and Day D E 1986 *J. Non-Cryst. Solids* **88** 97  
 Larson S C and Frischat G H 1998 *Glastech. Ber.* **71** 19  
 Loehman R E 1979 *J. Am. Ceram. Soc.* **62** 491  
 Loehman R E 1980 *J. Non-Cryst. Solids* **42** 433  
 Loehman R E 1985 *Treatise on materials science and technology* (Acad. Press Inc) **26** p. 119  
 Luping Yao and Quanxin Fang 1983 *J. Non-Cryst. Solids* **56** 167  
 Makishima A, Mitomo M, Ii N and Tsutsumi M 1983 *J. Non-Cryst. Solids* **66** C55  
 Marchand R 1982 *CR Acad. Sci. Paris* **294** 91  
 Marchand R 1983 *J. Non-Cryst. Solids* **56** 173  
 Mc Millan P F, Sato R K and Poe B T 1998 *J. Non-Cryst. Solids* **224** 267  
 Messier D R and Deguire E J 1984 *J. Non-Cryst. Solids* **67** 602  
 Messier D R and Patel P J 1992 *Silicon nitride ceramics, Scientific technological advancesymp., Boston* **30** p. 365  
 Murakami Y and Yamamoto H 1994 *J. Ceram. Soc. Jap.* **102** 231  
 Mulfingher H O 1966 *J. Am. Ceram. Soc.* **49** 462  
 Rajaram M and Day D E 1986 *J. Am. Ceram. Soc.* **69** 400  
 Rajaram M and Day D E 1987 *J. Am. Ceram. Soc.* **70** 203  
 Reidmeyer M R and Day D E 1995 *J. Non-Cryst. Solids* **181** 201  
 Risbud Subhas H 1981 *Phys. Chem. Glasses* **22** 168  
 Sahar M R and Noordin N 1995 *J. Non-Cryst. Solids* **184** 137  
 Sakka S 1995 *J. Non-Cryst. Solids* **181** 215  
 Schroeder J, Javk, Joseph J 1988 *J. Non-Cryst. Solids* **102** 181  
 Schrimpf C and Frischat G H 1983 *J. Non-Cryst. Solids* **56** 153  
 Wusirika R R 1984 *J. Am. Ceram. Soc.* **67** C232  
 Wusirika R R and Chyung C K 1980 *J. Non-Cryst. Solids* **38/39** 39  
 Yuquan Ding, Zishang Ding and Zhonghna Jiang 1989 *J. Non-Cryst. Solids* **112** 408