Li–Si–Al–O–N and Li–Si–O–N oxynitride glasses study and characterization

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The extent of oxynitride glass regions has been determined within Li–Si–Al–O–N and Li–Si–O–N systems. Physical properties such as density, hardness, elastic moduli and characteristic temperatures have been studied in terms of nitrogen content in the vitreous network. A comparison between the two systems studied enables the role of aluminium in these alumino-silicated glasses to be precisely determined.

1. Introduction
Jack [1] studied the densification of sialons with oxide type additants, and showed the existence of oxynitride glasses in M–Si–Al–O–N systems, where M is magnesium or yttrium. Since then, systematic studies have enabled Verdier *et al.* to determine the extent of vitreous regions within a certain number of M–Si–Al–O–N type systems where M is a bivalent cation: magnesium [2], calcium [3], strontium [4], barium [2] or manganese [3], or a trivalent cation: neodymium [3] or gadolinium [5]. A first study, for which sodium was the monovalent element, has been described (an updated bibliography on oxynitride glasses has been published by Messier). Given the particular chemical behaviour of lithium, compared to the other group I_A elements, we have started the study and characterization of vitreous phases within the Li–Si–Al–O–N system and we have extended it to glasses within the Li–Si–O–N quaternary system.

2. System representation method
The Li–Si–Al–O–N quinary system can be represented within a double triangular pyramid. Cations are located on the equatorial summits and anions are located on the two poles (Fig. 1). Component oxides or nitrides are located on the edges converging towards the poles. The triangular prism which is inscribed in this double pyramid constitutes the diagram of compositions (Fig. 2). Oxides are located on the summits of one of the bases; nitrides are located on the summits of the other base.

Oxynitride glasses which belong to the Li–Si–Al–O–N quinary system and those we have studied are situated within the Li_2O–SiO_2–AlN pseudo ternary cut (plane a, Fig. 2). In order to define more precisely the role of aluminium within these glasses, the vitreous region in the Li–Si–O–N quaternary system has also been studied. These glasses are situated on the Li_2O–SiO_2–Li_3N–Si_3N_4 plane, which constitutes one of the faces of the composition prism (Fig. 2).

3. Experimental conditions
In order to determine the influence of the nitriding agent on the extent of the oxynitrided vitreous region in the Li–Si–Al–O–N diagram, the following compounds were used as a nitrogen source.

(i) Commercial aluminium nitride, obtained by carbonitridation of alumina at 1600° C; we shall refer to this as AlN(C).

(ii) Aluminium nitride, obtained by the reaction of ammonia on alumina at 1300° C [6]; we shall refer to this as AlN(L).

(iii) Lithium and silicium double oxynitride LiSiON [7]. In this case, it is necessary to add alumina to the original mixture, so that the global composition can always be represented by one point of the Li_2O–SiO_2–AlN triangle.

Lithium has been introduced as Li_2SiO_3 silicate. The Li_2SiO_3 silicate has been prepared beforehand in order to avoid the handling of Li_2O, which is hygroscopic.

These pulverulent mixtures have been placed in tubes made of nickel, sealed under a flow of nitrogen, and then heated for 1 h at a temperature of 1300° C. These tubes are internally protected by a molybdenum sheet. Thermal treatment is followed by quenching.

In order to prepare larger samples, we have also used the technique of high frequency heating within molybdenum crucibles, placed in a glove box under nitrogen atmosphere. This technique enables fast increases and decreases in temperature to be obtained.

4. Vitreous region in the Li–Si–Al–O–N system
The compositions which have been studied are located in the Li_2O–SiO_2–AlN triangle. Fig. 3 represents the different regions. The smallest region, indicated by curve 1, is the one which has been obtained with AlN(C). Curve 2 refers to the region which has been obtained with AlN(L) and with LiSiON oxynitride.

These experimental results can be partially interpreted by the following remarks.

(i) The fact that AlN(L) is very pure, that its granulometry is weak and that its preparation temperature is weaker, accounts for its important reactivity compared to AlN(C).
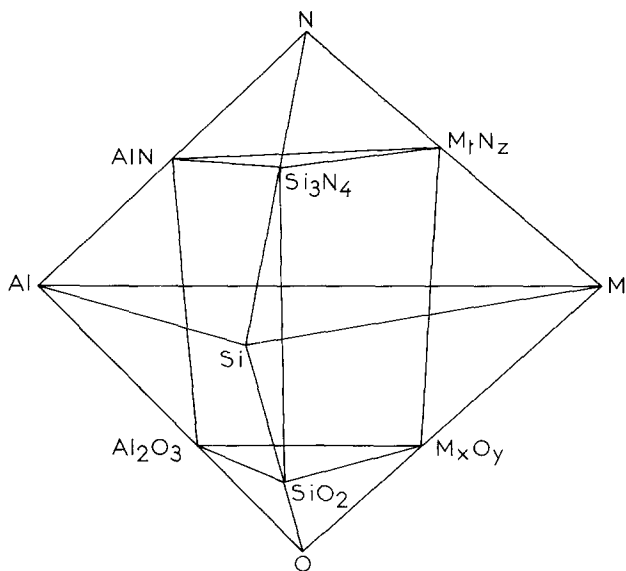
(ii) The preexistence of Li–N or Si–N bounds in the

Figure 1 M–Si–Al–O–N quinary system.

LiSiON oxynitride allows a more important homogeneity of the melted flux. This is a favourable factor for the formation of glasses because it leads to the reduction of the number of crystallization germs.

In order to measure all physical properties on glasses which had undergone the same thermal treatment, it has been necessary to prepare massive blocks, from which samples have been taken for purpose of study.

4.1. Nitrogen measurement

The evolution of physical properties being closely linked to the nitrogen content, this element has been chemically measured. Table I gathers the results of measures made on vitreous compositions, for which only the oxygen to nitrogen ratio varies and for which the cationic composition remains constant. Glasses which have been chosen can be formulated as follows

$$(Li_2O)_{0.30}(SiO_2)_{0.60}(AlN)_{0.10(1-x)}(Al_2O_3)_{0.05x}$$

The values of x being: 0, 0.33, 0.66 and 1.

A loss in nitrogen, of about 14% can be observed. This is explained by the duration of glass fining, which leads to a slight oxidation, and by the fact that chemical measurement of nitrogen is always slightly deficient.
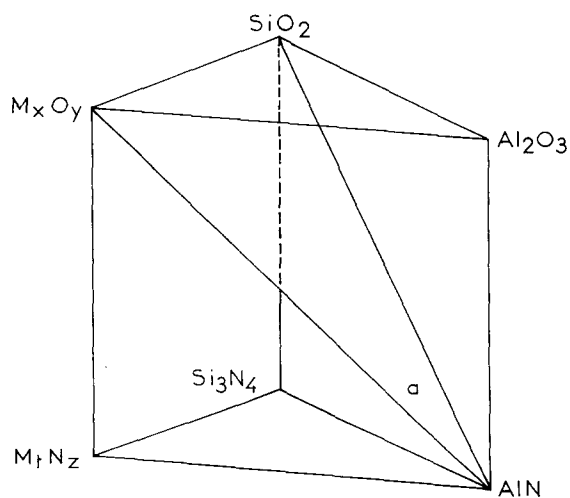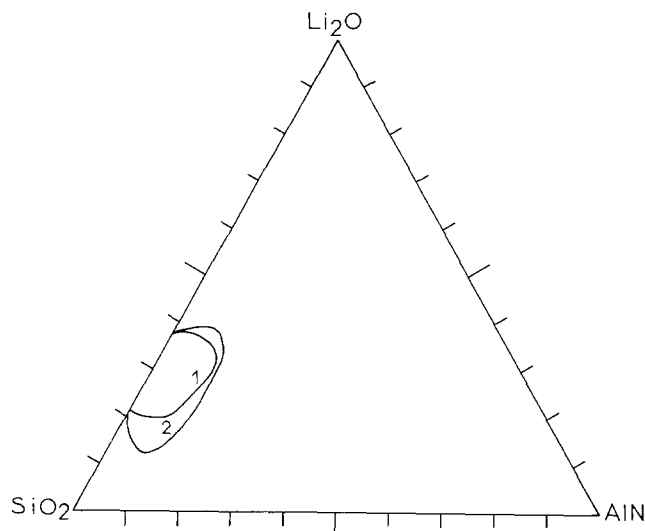

Figure 2 Composition prism.

Figure 3 Vitreous regions within the diagonal plane (a) of Fig. 2 — (mol %) (curve 1: AlN(C); curve 2: AlN(L), LiSiON).

5. Physical properties of Li–Si–Al–O–N glasses

5.1. Densities

Calculated densities are expressed in terms of the compositions of the original mixture, so that a comparison can be made with the experimental density of glasses.

The evolution of densities is represented in Fig. 4. It can be seen that the density of glasses (line 1) increases in terms of the substitution of Al_2O_3 by AlN. This has already been observed in previous work on other systems [2]. This study is, therefore, a confirmation of the hypothesis according to which this densification is not due, for a given system, to the modifier cation, but to the presence of nitrogen in the anionic network. As a matter of fact, the substitution of oxygen by nitrogen in silicium coordination tetrahedra, increases their individual negative charge, which leads to an increase in the coulombic forces between these tetrahedra and the cations, thus enabling a more important compactness of the network to be observed.

5.2. Hardness

A correlation exists between hardness and the number x of anion-g per unit volume. For a given valence for a modifier cation, the more important this number is, the more important measured hardness values of oxynitride glasses are. Moreover, all things being furthermore equal, hardness increases in terms of the substitution rate of oxygen by nitrogen, and this, for a same cation. Fig. 6 represents the evolution of Vickers hardness in terms of the nitrogen content.

The determination of density, as well as the study of its evolution in terms of different parameters, enables global structural data to be obtained directly. As a

TABLE I

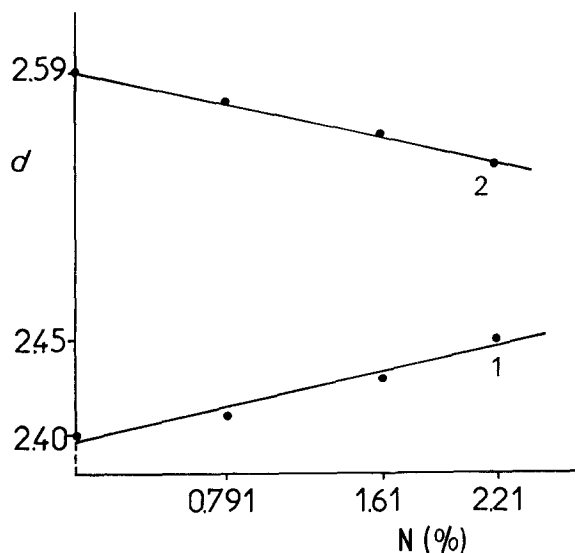| x	N_{cal} (wt %)	N_{exp} (wt %)
1	0	0
0.66	0.94	0.79
0.33	1.88	1.61
0	2.53	2.21

Figure 4 Evolution of densities of the nitrogen content (line 1: experimental densities; line 2: calculated densities).

matter of fact, as vitreous compositions are known, it is possible to calculate the number of anions per unit volume. Each composition is expressed as CA_n, where C represents the total number of cations restored to the unit level, and A_n, the total number of anions. The molecular weight of each glass is thus determined according to

$$M = \sum_{i=1}^{m} x_i M_i$$

where x_i is the molecular fraction of component i, with
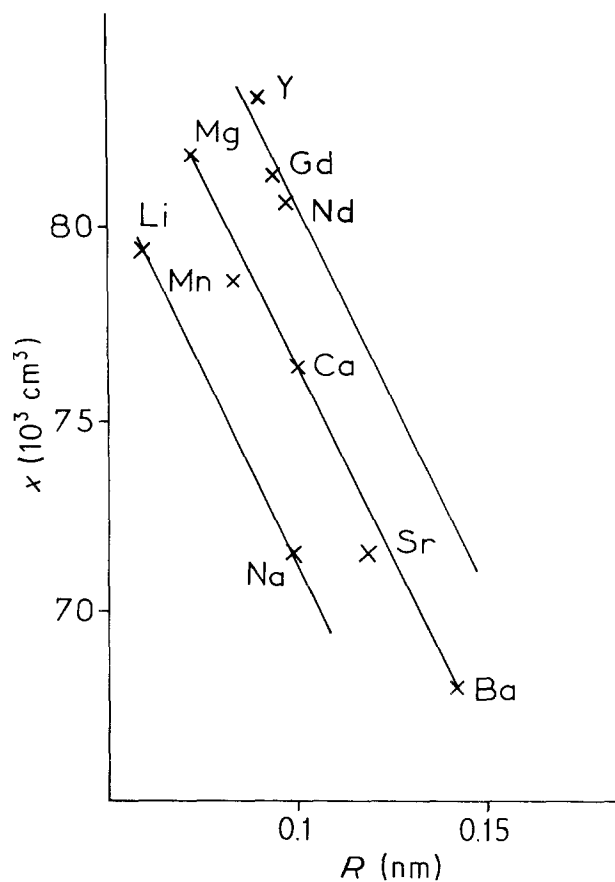

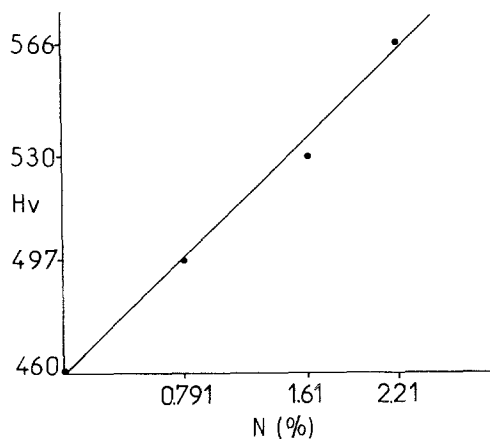Figure 5 x as a function of cation ionic radii.

Figure 6 Evolution of hardness in terms of the nitrogen content.

a molecular weight M_i, and where m is the total number of components. The ratio of measured density on calculated molecular weight for a glass, expresses the number of moles and the number of cations per unit volume. The product of that number of moles and n gives the number of anions per unit volume

$$x = \frac{n \times d}{M}$$

where, for a given glass, d is its experimental density, M its molecular weight and n the number of anions per cation. In the case of lithium oxynitride glasses, the value of x is 79.5×10^{-3} anion g per cm^3.

Fig. 5 represents the variation of x, number of anion g per cm^3, in terms of the radius of the modifier cation. We can see that lithium and sodium form a new line which is parallel to those obtained for bivalent or trivalent elements.

Hardness increases in terms of the rate of substitution of oxygen by nitrogen, and this, for a same cation. Fig. 6 represents the evolution of Vickers hardness in terms of the nitrogen content.

5.3. Characteristic temperatures

In order to avoid the oxidation of glasses during DTA measurement, a constant sweeping of neutral gas, i.e. nitrogen, has been used.

The glass transition (T_g), crystallization (T_c), and fusion (T_f) temperatures are collected together in Table II, along with the Hruby factor (H_r).

We can note the following.

(i) An increase in the glass transition temperature in terms of the nitrogen content. These results are in agreement with those obtained by Loehman [8], when he studied the Y–Si–Al–O–N system.

(ii) An increase in the crystallization temperature in terms of the nitrogen content. The differential thermal analysis curves, obtained with the different samples are represented in Fig. 7. We can note that the

TABLE II

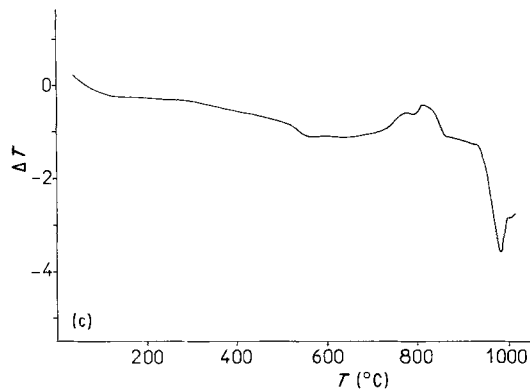| x	N (%)	T_g	T_c	T_f	T_g/T_f	H_r
1	0	485	630	995	0.59	0.40
0.66	0.79	495	676	980	0.61	0.59
0.33	1.61	508	722	965	0.63	0.88
0	2.21	519	737	945	0.65	1.04

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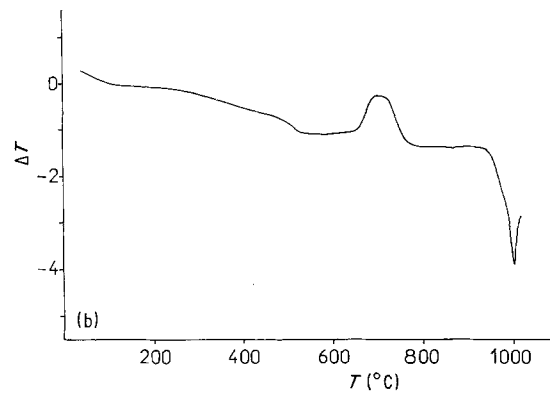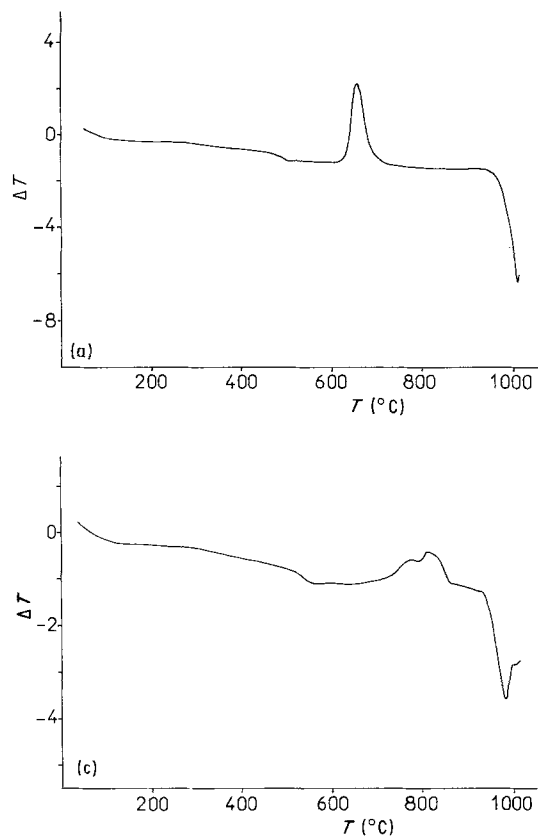
Figure 7 DTA traces of glasses with different oxygen to nitrogen ratios. (a) $Si_{0.6}Li_{0.6}Al_{0.1}O_{1.65}$. (b) $Si_{0.6}Li_{0.6}Al_{0.1}O_{1.575}N_{0.05}$, (c) $Si_{0.6}Li_{0.6}Al_{0.1}O_{1.5}N_{0.1}$.

crystallization becomes weaker as the nitrogen content increases. Moreover, for the most nitrided glass, the formation of two peaks shows the complexity of this phenomenon.

On the other hand, Table II shows that the fusion temperature decreases in terms of the nitrogen content. Anyhow, it remains true that the preparation of oxynitride glasses requires much higher temperatures than those required for pure oxygenated glasses; this is due to their more important viscosity.

Various authors have tried to make a link between some characteristic temperatures. Sakka and Mackenzie [9] have shown that for many glasses, the T_g/T_f ratio is close to 2/3; this empirical value can be found in phases with several constituents. In this work, a value close to 0.60 has been found. It is obvious that this value is not constant in terms of the composition, as T_g values increase whereas T_f values decrease. Moreover, Hruby [10] defines an H_r ratio which is expressed as

$$H_r = \frac{T_c - T_g}{T_f - T_c}$$

The value of this ratio indicates how easy it will be to obtain vitreous phases. High H_r values can be obtained, either when the $T_c - T_g$ difference is important, or when $T_f - T_c$ is weak. It can be noted that in this latter case, the closeness of T_f and T_c enables a rapid crossing of the favourable temperature interval for crystallization; in this case, a vigorous quenching is not necessary.

The values of T_g, T_c and T_f, shown in Table II, indicate that the numerator of the H_r ratio increases, whereas the denominator decreases when the nitrogen content increases. The H_r value, which is equal to 0.40

for an oxide glass, increase to 1.04 for a glass which contains 2.21% of nitrogen by weight. It is possible to compare these values to those of fluoride glasses for example, for which the H_r value, close to 0.20, implies an important quenching speed.

5.4. Thermal expansion

The values of the thermal dilatation coefficient have been determined within an interval of temperatures ranging from 20 to 400° C. Fig. 8 shows the evolution of α in terms of the nitrogen content. A linear decrease of the dilatation coefficient with the increase in the nitrogen content can be observed.

Thermal dilatation coefficient depends on the vibration of particles in terms of temperature. When temperature increases, the distances between two atoms, or between two groups of atoms, can increase, and a dilatation of the material is observed on a macroscopic scale.

The substitution of oxygen by nitrogen within the vitreous network, increases the individual charge of anionic groups. The result is a more important number of links and a more important attraction force between the anionic groups and the cations, which can explain a decrease of α in terms of the composition.

5.5. Elastic moduli

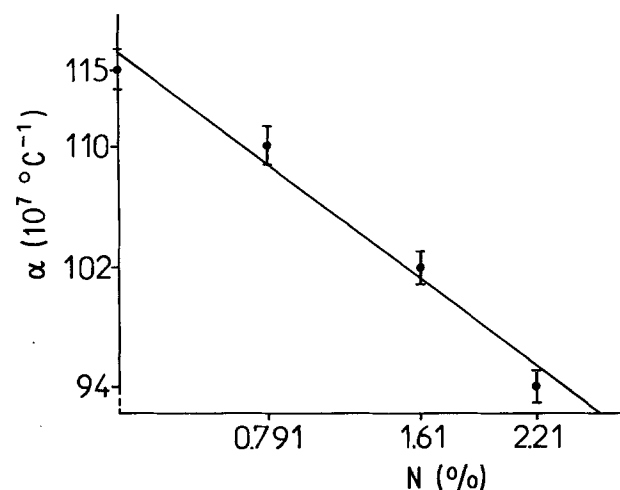In order to determine the value of elastic moduli, it has
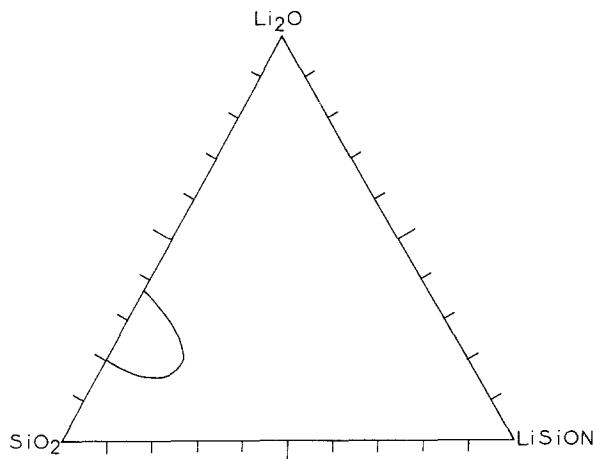

Figure 8 Evolution of α in terms of nitrogen content.

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Figure 9 Vitreous area within the Li_2O–SiO_2–LiSiON triangle (mol %).

been necessary to measure first the refraction index of glasses. The elastic constants C_{11} and C_{12} have been obtained by the study of Brillouin scattering [11]. Table III gathers the values of refraction indexes n, their uncertainty n, and the constants C_{11} and C_{12} for the different studied glasses.

An increase of n, C_{11} and C_{12} in terms of the nitrogen content can be observed. This is in agreement with the results which have been previously obtained in this study of the Ca–Si–Al–O–N system [12].

Elastic constants measured for a given sample, enable the different moduli, defined by the following relations to be evaluated.

Young's modulus E (in GPa)

$$E = C_{11} - \frac{2C_{12}^2}{C_{11} + C_{12}}$$

Shear modulus S (in GPa)

$$S = \frac{C_{11} - C_{12}}{2}$$

Bulk modulus K (in GPa)

$$K = \tfrac{1}{3}(C_{11} + 2C_{12})$$

Poisson's ratio μ

$$\mu = \frac{C_{12}}{C_{11} + C_{12}}$$

The values of E, K, S and μ in terms of the nitrogen content of glasses, are given in Table III.

In general, a significant increase of the different moduli can be observed, when nitrogen is substituted by oxygen: Young's modulus E increases by about 17%, shear modulus S, by about 15% and bulk modulus K, by 22%. These variations show a more important rigidity of the structure. These results are in total agreement with those which have been obtained when

similar systems have been studied with other modifier cations [12–14].

The Poisson's ratio can be calculated from the following relations between the elastic moduli

$$E = 2(1 + \mu) \quad S = 3(1 - 2\mu)K$$

This ratio gives an account for the tridimensional variations of the glass. As a matter of fact, during dilatation, a transversal contraction occurs in the direction which is perpendicular to lengthening. If $\Delta l/l$ represents the relative lengthening and $\Delta d/d$, the relative contraction, then the ratio is defined by the following relation

$$\mu = (\Delta d/d)/(\Delta l/l)$$

Smyth [15] has calculated the value of μ from a theoretical point of view; he has made the supposition that, for silicated glasses, each deformation is only due to silicon–oxygen distance variations. He found a value of 0.25. In the case a deformation of the Si–O–Si angle should occur at the same time, then μ is inferior to 0.25. This is the reason for which silicate glass has a $\mu = 0.17$. The presence of modifier cations in the vitreous network results in an increase in the value of μ, which can reach up to 0.30 for ions with important radii. The value of μ for a lithium oxide glass is 0.22, and increases slightly in terms of the nitrogen content. Furthermore, Makishima and Mackenzie [16] have linked the value of μ to the compactness of the vitreous network. The transverse constraint will be small for a glass with a small compactness, as atoms have more space for re-ordering. Therefore, the value of μ will be smaller. The increase of μ, which has been observed when the nitrogen content increases, can then be explained by the more important compactness of the coordination polyhedra network.

6. Vitreous area in the Li–Si–O–N system

Previous studies have shown that a vitreous area exists in the Li_2O–SiO_2 binary system. Corresponding oxynitride glasses must be located in the Li_2O–SiO_2–Li_3N–Si_3N_4 plane, forming a face of the composition prism (Fig. 2). As these glasses do not contain aluminium, it has not been possible to use AlN as a nitriding agent. In order to avoid the use of Li_3N which is difficult to prepare and to manipulate, and of Si_3N_4 which is less reactive, the LiSiON oxynitride has been chosen. As a matter of fact, this compound which is easy to manipulate, seemed to be very favourable because of pre-existing lithium–nitrogen bonds, and because of pre-existing mixed oxygen–nitrogen tetrahedra around silicon.

The system which has been studied is therefore represented by the Li_2O–SiO_2–LiSiON triangle, which

TABLE III

x	N (%)	n	C_{11} (GPa)	C_{12} (GPa)	E (GPa)	K (GPa)	S (GPa)	
1	0	1.539(5)	97.2	27.5	1	85.0	34.9	0.221
0.66	0.79	1.549(5)	99.2	28.6	86.5	52.1	35.3	0.224
0.33	1.61	1.557(5)	105.1	31.5	90.5	56.0	36.8	0.231
0	2.21	1.569(5)	115.1	35.1	99.9	61.8	40.0	0.234

is part of the $Li_2O-SiO_2-Li_3N-Si_3N_4$ quaternary system. Fig. 9 represents the extent of the vitreous area.

Vitreous transition and crystallization temperatures have been determined for several samples of glasses belonging to the $Li_2O-SiO_2-LiSiON$ system. In order precisely to find the influence of nitrogen, corresponding oxygenated glasses in the Li_2O-SiO_2 binary, have also been prepared. The compositions which have been studied and the results which have been obtained are as follows

		T_g (°C)	T_c (°C)
A	$= Li_{0.55}Si_{0.75}O_{1.70}N_{0.05}$	495	670
A_{OX}	$= Li_{0.55}Si_{0.75}O_{1.775}$	471	642
B	$= Li_{0.50}Si_{0.80}O_{1.70}N_{0.10}$	500	715
B_{OX}	$= Li_{0.50}Si_{0.80}O_{1.85}$	475	621
C	$= Li_{0.55}Si_{0.80}O_{1.65}N_{0.15}$	506	722
C_{OX}	$= Li_{0.55}Si_{0.80}O_{1.875}$	472	635

An increase in these temperatures in terms of the nitrogen content can be observed. Still, it must be noted that these values are systematically inferior to those which have been determined for glasses in the Li–Si–Al–O–N system. It is possible to observe, for example, the results obtained for the following compositions.

		T_g (°C)
− D	$= Li_{0.60}Si_{0.60}Al_{0.10}O_{1.65}$	485
− E	$= Li_{0.60}Si_{0.70}O_{1.70}$	470

7. Conclusion

The study of oxynitride glasses in the Li–Si–Al–O–N and Li–Si–O–N systems enables the influence of aluminium on the characteristics of these glasses to be defined. As aluminium, in an oxygenated environment, can adopt two coordinations, i.e. octahedral and tetrahedral, this element can play different roles within the vitreous network.

For small aluminium concentrations, there would preferably be a formation of octahedra (AlO_6). According to Yoldas [17], this structural hypothesis would be responsible for the decrease in viscosity, and for the decrease of T_g temperatures for alkaline glasses.

This would be correct, only below a certain critical concentration of aluminium (0.5% in weight); up to that limit, Al_2O_3 plays a modifying role. Above, and up to an aluminium to lithium atomic ratio equal to 1, (AlO_4) tetrahedra would predominate. The presence of these tetrahedra, which are analogous to (SiO_4) tetrahedra which constitute the network, confers a new role to aluminium, which becomes a formating agent instead of being a modifying one. The result is a significant increase in viscosity, whereas the thermal dilatation coefficient decreases. In our case, it also leads to the increase in T_g temperatures, as we have observed. The value of the critical concentration, which governs the aluminium coordination change, has not been accurately defined and further studies on the structure of these glasses are necessary.

References

1. K. H. JACK, *J. Mater. Sci.* **11** (1976) 1135.
2. R. PASTUSZAK and P. VERDIER, *J. Non-Cryst. Solids* **56** (1983) 141.
3. P. VERDIER, R. PASTUSZAK and Y. LAURENT, *Verres Réfract.* **36** (1982).
4. P. VERDIER, Personal Communication.
5. J. ROCHERULLE, P. VERDIER and Y. LAURENT, *J. Mater. Sci. Eng.* **2** (1989) 265.
6. J. ROCHERULLE, P. VERDIER and Y. LAURENT, *Rev. Int. Hautes Temper. Refract.* **22** (1985) 83.
7. Y. LAURENT, J. GUYADER and C. ROULT, *Acta Crystallogr.* **B36** (1980) 911.
8. R. E. LOEHMAN, *J. Non-Cryst. Solids* **6** (1983) 123.
9. S. SAKKA and J. D. MACKENZIE, *ibid.* **6** (1971) 145.
10. A. HRUBY and C. CZECH, *J. Phys.* **B32** (1972) 1187.
11. C. ECOLIVET, Thesis, Rennes (1981).
12. C. ECOLIVET and P. VERDIER, *Mater. Res. Bull.* **19** (1984) 227.
13. D. R. MESSIER and A. BROZ, *J. Amer. Ceram. Soc.* **68** (1985) C131.
14. W. K. TREDWAY and R. E. LOEHMAN, *J. Amer. Ceram. Soc.* **68** ((1985) 131.
15. H. T. SMYTH, *J. Amer. Ceram. Soc.* **42** (1959) 276.
16. A. MAKISHIMA and J. D. MACKENZIE, *J. Non-Cryst. Solids* **17** (1975) 147.
17. B. E. YOLDAS, *Physics Chem. Glasses* **12** (1971) 28.