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# An Introduction of the fluorine and Nitrogen on properties of Ca-Si-Al-O glasses

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## Abstract

Ca-Sialon glasses have been known for some time [1] and they are effectively calciumalumino-silicate glasses containing nitrogen which improves their mechanical properties. Calcium alumino-silicate glasses containing fluorine are known to have useful characteristics as potential bioactive materials [2]. Therefore, the combination of both nitrogen and fluorine additions to these glasses may give useful glasses with enhanced mechanical stability. This paper gives a review of oxynitride glasses and reports glass formation and evaluation of glass properties in the Ca-Si-Al-O-N-F system. Within the previously defined glass forming region in the Ca-Si-Al-O-N system, homogeneous, dense glasses are formed. However fluorine decreases the glass transition temperature, the density and the mechanical properties of the glasses while nitrogen increases them. Therefore, it appears that fluorine acts as a network modifier while, on the contrary, nitrogen acts as a network former even in presence of fluorine.

*Keywords*: Glass, Mechanical properties, oxyfluoronitride, thermal analysis

## 1. Introduction

The substitution of oxygen in silicate glasses by either nitrogen or fluorine has been widely reported. Jack [3] and Loehman [4] were the first to report on the preparation of oxynitride glasses. Over the past 30 years, many studies of M–Si–Al–O–N glass formation and properties have been undertaken and this has recently been reviewed. The role of Al in these glasses is known to expand the compositional range of glass formation, lower the melt temperature, increase nitrogen solubility and, in amounts of only a few atomic percent, suppress the phase separation observed in its absence [5,6,7]. Incorporation of Ca lowers the viscosity sufficiently so that $Si_3N_4$ or other nitride sources can dissolve without decomposition [7]. A study of incorporation of N into a potentially bioactive glass composition has shown that, as expected, nitrogen increases mechanical properties [8]. The main conclusion is that N may be viewed as a network forming anion taking into account that the effects of nitrogen and modifiers on glass properties are independent [9].

The incorporation of fluorine into glasses has been applied in the development of machinable glass ceramics [10] and glass ionomer cements for dentistry [11] While fluorine substitution is known to decrease glass transition temperatures, dilatometric softening temperatures, and glass melting temperatures of aluminosilicate glasses [10,11] its effect on elastic modulus and microhardness has not been studied in depth.

The aim of the current work was to explore a new generation of oxynitride glasses containing fluorine and to develop an initial understanding of the effects of composition on glass formation, structure and properties.

## 2. Experimental Methods

### 2.1. Glass preparation

Three systematic glass compositional series (I), (II) and (III) in weight %, marked GF0Nx, GF12.5Nx and GF25Nx, respectively, were prepared and examined:

$55SiO_2–15Al_2O_3–30CaO–xSi_2N_4$ (I)

$55SiO_2–15Al_2O_3–17.5CaO–12.5CaF_2 –xSi_2N_4$ (II)

$55SiO_2–15Al_2O_3–5CaO–25CaF_2 –xSi_2N_4$ (III)

Where x= 0, 1,2,3 and 4 and 4x is the amount of nitrogen added as $Si_3N_4$. Glass compositions in atomic % of Si Ca, Al, O, F, N are given in Table 1.

**Table 1:** Weight percentages of elements in synthesized GF0Nx, GF12.5 and GF25Nx glasses (T-Theoretical ; E-Experimental).

| **Elements** | **Si** | | **Ca** | | **Al** | | **O** | | **F** | | **N** | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Weight %** | **T** | **E (±0.2)** | **T** | **E (±0.1)** | **T** | **E (±0.1)** | **T** | **E (±0.4)** | **T** | **E (±0.1)** | **T** | **E (±0.1)** |
| GF0N0 | 23.71 | 23.68 | 18.45 | 18.42 | 12.43 | 12.47 | 45.41 | 45.42 | 0 | 0 | 0 | 0 |
| GF0N1 | 23.85 | 23.87 | 18.57 | 18.61 | 12.51 | 12.49 | 44.22 | 44.4 | 0 | 0 | 0.85 | 0.62 |
| GF0N2 | 23.95 | 24.01 | 18.69 | 18.73 | 12.61 | 12.59 | 42.99 | 43.12 | 0 | 0 | 1.76 | 1.28 |
| GF0N3 | 24.15 | 24.36 | 18.80 | 18.93 | 12.67 | 12.92 | 41.76 | 41.83 | 0 | 0 | 2.62 | 1.96 |
| GF0N4 | 24.30 | 24.31 | 18.92 | 18.88 | 12.75 | 12.65 | 40.50 | 41.53 | 0 | 0 | 3.53 | 2.63 |
| GF12.5N0 | 22.09 | 22.08 | 17.21 | 17.23 | 11.58 | 11.59 | 42.34 | 42.33 | 6.78 | 6.77 | 0 | 0 |
| GF12.5N1 | 22.91 | 22.60 | 17.84 | 17.30 | 12.02 | 12.19 | 39.52 | 40.33 | 6.88 | 6.92 | 0.83 | 0.66 |
| GF12.5N2 | 23.01 | 23.61 | 17.91 | 17.41 | 12.07 | 12.28 | 38.26 | 38.34 | 7.08 | 7.01 | 1.67 | 1.35 |
| GF12.5N3 | 23.16 | 23.26 | 18.03 | 18.10 | 12.14 | 12.22 | 37.04 | 37.23 | 7.12 | 7.14 | 2.51 | 2.05 |
| GF12.5N4 | 23.28 | 23.61 | 18.11 | 18.12 | 12.21 | 12.56 | 35.83 | 35.86 | 7.1 | 7.16 | 3.40 | 2.69 |
| GF25N0 | 21.86 | 21.85 | 17.02 | 17.03 | 11.46 | 11.47 | 36.23 | 36.21 | 13.43 | 13.44 | 0 | 0 |
| GF25N1 | 22.05 | 22.01 | 17.16 | 17.19 | 11.56 | 11.59 | 35.16 | 35.15 | 13.28 | 13.32 | 0.80 | 0.74 |
| GF25N2 | 22.10 | 22.16 | 17.20 | 17.29 | 11.60 | 11.61 | 33.89 | 33.91 | 13.60 | 13.60 | 1.61 | 1.43 |
| GF25N3 | 22.22 | 22.32 | 17.31 | 17.37 | 11.66 | 11.71 | 32.71 | 32.76 | 13.68 | 13.69 | 2.42 | 2.15 |
| GF25N4 | 22.36 | 22.55 | 17.40 | 17.47 | 11.73 | 11.78 | 31.51 | 31.56 | 13.76 | 13.86 | 3.24 | 2.78 |

The glasses were prepared in three steps. The first step was the synthesis of Si–Al–Ca–O and Si–Al–Ca–O–F based glasses by reacting and melting $Al_2O_3$ (Merck, purity 99.9%), $CaCO_3$ (Chimie-Plus-Laboratoire, 99%),$SiO_2$ (Merck, pure quartz) in platinum crucibles at 1450 °C in air for 4h for the Si–Al–Ca–O compositions and with addition also of $CaF_2$ (Carlo Erba, 98%) at 1350 °C for 30 mins for the Si–Al–Ca–O–F compositions. Fluorine lowers the melting temperature of the oxide glass and the shorter time used was to avoid the loss of any fluorine during melting. The second step was the milling and mixing of the oxide and oxyfluoride based glasses with varying amounts of silicon nitride ($Si_3N_4$) powder (UBE Indus- tries, minimum purity 99.9%). The oxygen (2 wt%) present as silica on the surface of the silicon nitride particles was taken into account in calculating the correct amount of silicon nitride required for the composition. Samples of 10 g were weighed and mixed in a glass dish using a magnetic stirrer in 50 ml isopropanol and then the alcohol evaporated using a hot plate.

Powder batches were pressed under 300 MPa pressure to form pellets of 10mm height and 26mm diameter. Finally, samples were melted in a boron nitride lined graphite crucible inavertical tube furnace under flowing high purity $N_2$ at 1400 °C for 15min, after which the crucible was with-drawn rapidly from the hot zone. The Si–Al–Ca–O–N and Si– Al–Ca–O–F–N glasses obtained were then annealed at a temperature just below their glass transition temperature for 6 h prior to slow cooling to ambient, to eliminate stresses created by rapid cooling.

### *2.2. Glass Characterization*

### *2.2.1 X-ray Diffraction Analysis*

In order to determine if there were any crystalline phases present, samples were analysed using X-ray diffraction (PanAlytical X-ray diffractometer, The Netherlands) with monochromated CuKα (λ=1.54056 Å) radiation over a range of 2θ of 20º–80º with a speed of 2.4°/min. Data was analysed using X'pert Quantify software.

### *2.2.2. Elemental Analysis by Wavelength Dispersive Spectroscopy, WDS, and EDS*

The nitrogen concentrations retained in the glasses, shown in Table 1 (Exp), were determined by electron probe microanalysis (EPMA) (Cameca SX100 electron probe microanalyser) using wavelength dispersive spectroscopy (WDS). All samples were embedded into an epoxy resin, and then polished using SiC papers down to 0.25 μm to provide a completely flat surface. Quantification of N was carried out at 15 kV, 200 nA. A PC2 (Ni/C) crystal was used to detect the Kα X-rays. The standard used for N quantification was BN. For each glass, 10 measurements were performed to evaluate the nitrogen homogeneity and to calculate the average nitrogen content in the glasses. The background noise used for the calculation of the N Kα peak height on the glass samples was measured on a glass without N. The accuracy and detection limits of this method had previously been assessed by analyses of standard Ca–Mg–alumina-silicate glasses containing up to 6143 ppm nitrogen [12].

The relative contents of Si, Ca, Al, F and O were analysed on similar prepared embedded polished samples using scanning electron microscopy coupled with energy dispersive spectroscopy (SEM–EDS) (Noran System Six-type), the analyzed area being about 1 $\mu m^3$.

### *2.3. Measurement of Density*

The density was measured using a Helium pycnometer. Glasses were crushed before density measurements so that any internal porosity (i.e. bubbles) did not affect the results.

### *2.4. Thermal Analysis*

Differential thermal analysis (DTA) was carried out (Setaram Setsys 16/18 simultaneous TG/DTA analyzer) in order to determine the glass transition temperature, Tg. Samples of 50 mg were heated at 10 °C/min up to 1200 °C in alumina crucibles in a flowing nitrogen atmosphere. $Al_2O_3$ was used as the reference material. The inflexion point of the endothermic drift on the DTA curve is reported as Tg.

### *2.5. Determination of Mechanical Properties*

### *2.5.1. Measurement of Microhardness*

The microhardness of the investigated samples was measured using a standard Vickers hardness tester with a $136^o$ diamond pyramid indenter. The specimens were cut using a low speed diamond saw, dry ground using 1200 grit SiC paper and polished carefully using 6, 3 and 1 μm diamond pastes to obtain smooth glass samples with flat parallel surfaces before indentation. The influence of loading test on hardness (Indentation Size Effect, ISE) was studied for all glasses. Loads were chosen between 25 g and 500 g and the loading time was fixed at 15 s. At least five indentations were measured at each load for each sample. An exception was made at 500 g, where ten indentation measurements were carried out in order to calculate a mean true Vickers hardness number $HV_0$ and standard deviation. Figure 1 shows the effect of load on HV. $HV_0$ is obtained when the measured values of HV are constant with load. The measurements were carried out under normal atmospheric conditions.

The Vickers hardness values (in GPa) were calculated from the following equation:

$$HV=1.8544\frac{P}{d^2} \qquad (1)$$

where P is the applied load and d is the average length of the two diagonals. The eyepiece on the microscope of the equipment allowed measurements with an estimated accuracy of 0.5 μm for the indentation diagonals.

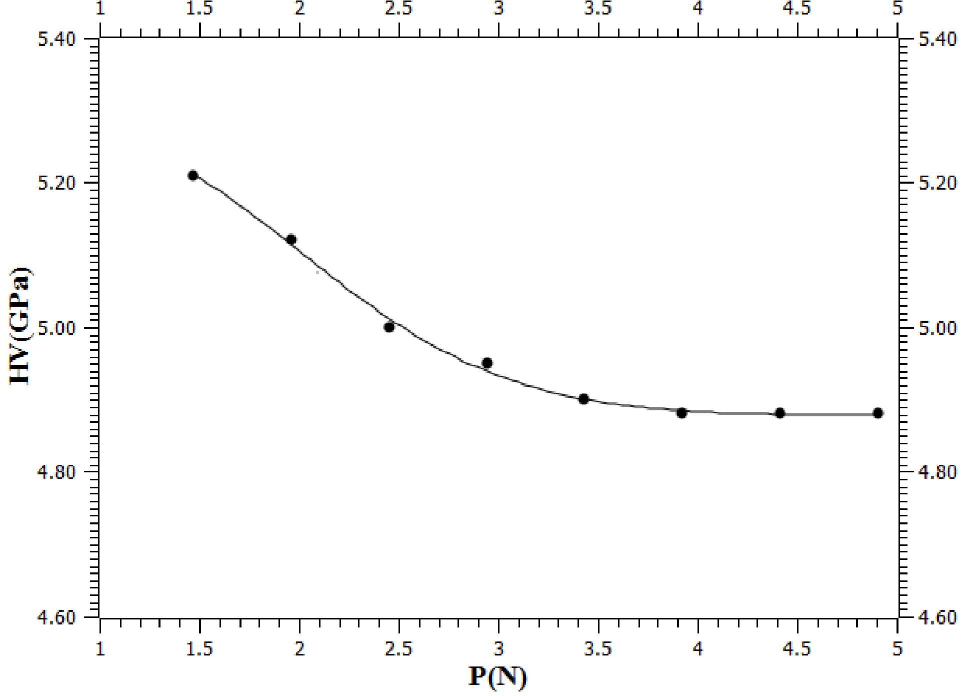


**Figure 1:** Variation of Vickers hardness HV as a function of applied load P

*2.5.2. Measurement of Elastic Modulus*

Elastic modulus was measured using a Knoop indentation method which is based on that given by Marshall et al. [13]. The authors describe a method for calculating the hardness, HK, to elastic modulus, E, ratio (HK/E) of a material from measurements of the Knoop indent diagonals [8]. The decrease in the length of the indent minor diagonal is caused by elastic recovery of the material and, consequently, it can be related to the hardness: modulus ratio by the following equation:

$$\frac{w'}{L'}=\frac{w}{L}-\alpha\frac{HK}{E} \qquad (2)$$

where w′ and L′ are the minor and the major diagonals of the measured Knoop indent, w and L are the minor and major diagonals of the ideal Knoop indent for which L/w=7.11 and α is a constant=0.45 [13].

HK is the Knoop hardness calculated by the relationship:

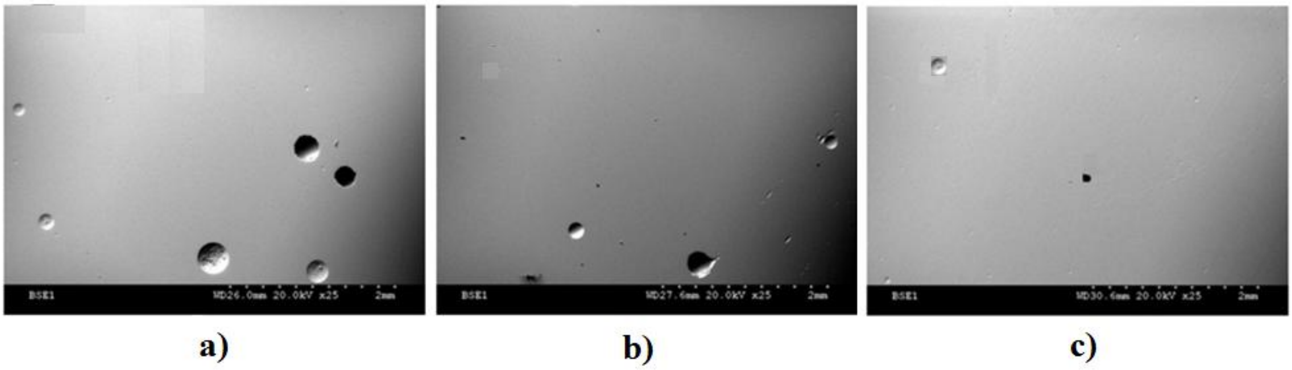
$$HK=14.229\frac{P}{L^2} \qquad (3)$$

where P is the load.

## 3. Results and discussion

*3.1. Appearance of glasses*

X-ray diffraction analysis confirmed that all the glasses are totally amorphous. All the glasses containing nitrogen gray in color. It was observed that the color of the glass is darker when the amount of nitrogen increases. The calculated and analyzed Si, Ca, Na and N contents of glasses are shown in Table 1. Cross sections of the glasses were examined by Scanning Electron Microscopy to analyse homogeneity and the presence of bubbles. Fig. 2 shows the state of GF0N4, GF12.5N4 and GFN4 maximum nitrogen content glasses. Glasses without N, containing F, were free of bubbles but those without F contained some fine residual bubbles from loss of $CO_2$ during melting [14]. F reduces melting temperatures and viscosities thus allowing easier gas release during melting. Glasses containing N always contained evidence of bubbles, both from$CO_2$ loss and from some loss of N, leaving macroporosity in the glasses. This has implications for further characterization of mechanical properties.



**a)** **b)** **c)**

**Figure 2:** Low magnification SEM micrographs of cross sections of glasses: (a) GF0N4, (b) GF12.5N0, (c) GF25N4, showing presence of bubbles

*3.2. Density and molar volume*

The effects of replacing oxygen with both nitrogen and fluorine on the density of the GNx, GF12.5Nx and GF25Nx glasses are shown in Fig. 3. A large increase in density is observed as oxygen is replaced by nitrogen, from 2.8649 g.cm$^{-3}$ at 0 wt% N to 2.9012 g cm$^{-3}$ at 2.63 wt% N for the GF0Nx series, to 2.9029 g.cm$^{-3}$ at 2.69 wt% N for the oxyfluoronitride GF12.5Nx series and to 2.9028 g.cm$^{-3}$ at 2.78 wt% N for the GF25Nx series. As can be seen, very little change in density is observed as oxygen is replaced by fluorine.

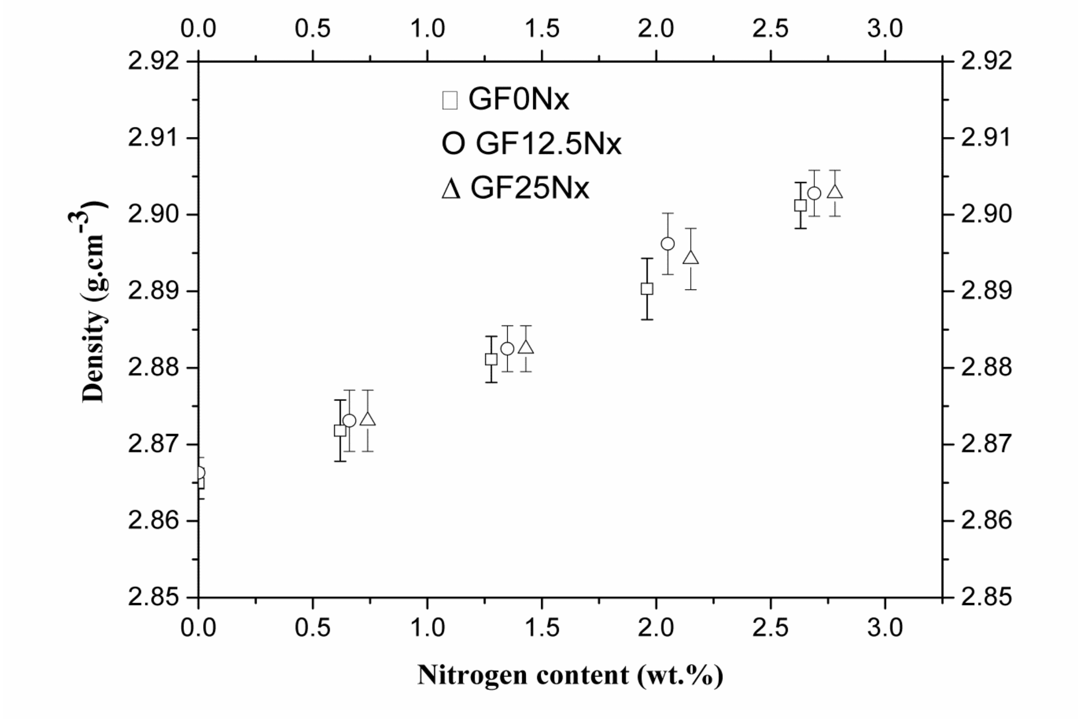


**Figure 3:** Density of Si-Al-Ca-O-N and Si-Al-Ca-O-F-N glasses as a function of nitrogen content

As density increases, then there is a decrease in glass molar volume, with a corresponding increase in glass compactness or atomic packing density. These results confirm previous findings [15] which confirm that addition of nitrogen increases cross-linking of oxynitride glasses since nitrogen is mainly tri-coordinated, whereas oxygen links to only two tetrahedral units. For each percentage of oxygen replacement by nitrogen, an equal number of additional cross-links should be introduced into the glass network and, thus, properties that are dependent on increased crosslinking of the glass network should show a linear dependence with nitrogen. This is discussed in the following sections.

### *3.3. Glass transition temperature Tg*

Glass transition temperatures were determined from the DTA experiments and as can be seen in Fig.4, there is a linear increase in glass transition temperature, Tg , as nitrogen content increases where as Tg decreases as fluorine content increases in the glass. As oxygen is replaced by nitrogen, Tg increases from 630 °C at 0 wt%N to 670 °C at 2.63 wt%N for the GF0Nx series, from 609°C to 649°C for the oxyfluonitride GF12.5Nx series and for GF25Nx series from 588°C at 0 wt% N to 628°C at 2.78 wt.

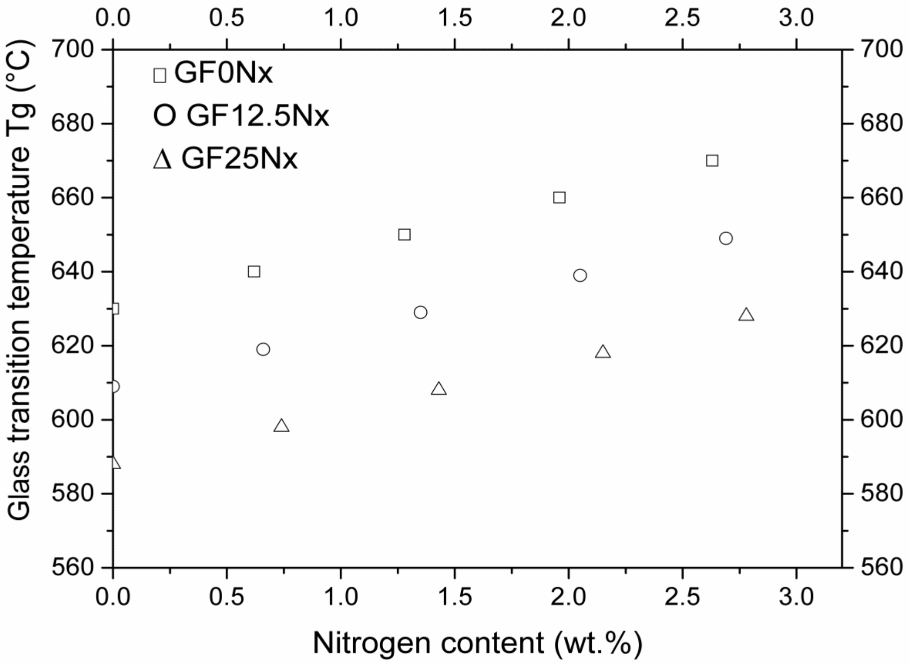


**Figure 4:** Glass transition temperature of Si-Al-Ca-O-N and Si-Al-Ca-O-F-N glasses as a function of nitrogen content

Similar behaviour has also been reported previously for oxyfluoride glasses [16] and for oxyfluoronitride glasses [17]. Non-bridging fluorine ions disrupt the glass structure and the presence of these weaker bonds is responsible for the reduction in Tg. The increase in Tg with N is consistent with previous studies of oxynitride glasses [18] which have shown that N creates extra cross-linkages and stiffens the glass network. The decrease in Tg with F suggests that lower viscosity melts can be synthesized at lower temperatures making it easier for glass production.

### *3.4. Microhardness and elastic modulus*

The Vicker's microhardness (HV) as a function of N content for GF0Nx, GF12.5Nx and GFNx glasses is shown in Fig. 5. HV increases linearly with nitrogen content as reported previously for oxynitride glasses [18-19]. For oxyfluoride glasses, microhardness does not vary with fluorine content, taking into account the error range. For oxyfluoronitride glasses, microhardness increases with increasing nitrogen content as found previously for oxynitride glasses.

These results also show that the addition of fluorine has no significant effect on microhardness as shown previously for oxyfluoronitride glasses [20-21].

Microhardness increases with nitrogen content from 6.86±0.04 GPa for 0 wt %N (with and without F) to 6.69±0.03 GPa at 2.63 at wt% N for the GF0Nx glass series, to 6.70±0.03 GPa at 2.69 wt% N for the GF12.5Nx glass series and to 6.72±0.04 GPa at 2.78 wt% N for the GF25Nx glass series. When the standard deviations are considered, it is observed that as nitrogen content increases, so the standard deviations increase. This result is attributed to bubbles trapped within the glasses and these increase with nitrogen content. Although care is taken to undertake the indentation tests away from surface bubbles, it is possible that some interactions between trapped bubbles and the indentation deformation zone may have taken place.

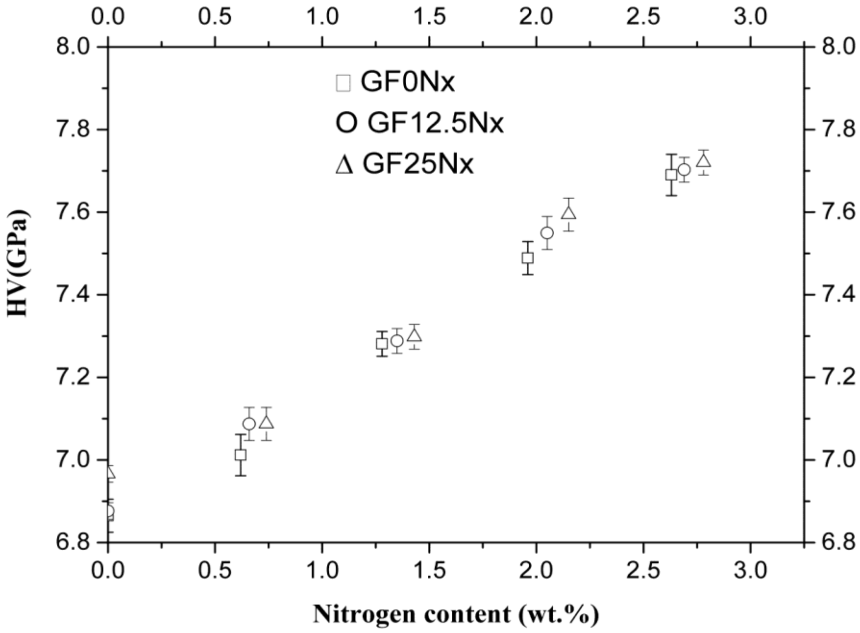


**Figure 5:** Vickers hardness of GF0Nx, GF12.5 and GF25Nx glasses as a function of nitrogen content.

Values for elastic modulus measured by both indentation (Knoop) and an ultrasonic method are given in table 2. Fig. 6 plots these values of elastic modulus (E) as a function of N content for GF0Nx, GF12.5Nx and GF25Nx glasses. As can be seen, E (from both methods) increases linearly with nitrogen content as found in previous studies of oxynitride glasses [17-18, 22-24]. It was difficult to obtain a value for the GF0N4 glass by the ultrasonic method and this may be because of the larger quantity of bubbles present in the oxynitride glasses compared with the oxyfluoronitide glasses. Elastic modulus values measured by the ultrasonic method are within the standard deviation bars of the values obtained by the indentation method which highlights the fact that the two methods are equivalent. However, data for GF0Nx glasses measured using the ultrasonic method deviate much more. Also, the experimental errors are much higher for the data from the GF0Nx glass series which may be attributed to the greater volume of bubbles in the glasses. It can be seen that the standard deviations for elastic is attributed to the difficulty in accurately measuring the smaller diagonal on some Knoop indents seen by microscopy even using image analysis.

**Table 2:** Values of elastic modulus (E) measured by Knoop indentation and an ultrasonic method for GF0Nx, GF12.5Nx and GF25Nx glasses.

| Glasses GF0Nx | GF0N0 | GF0N1 | GF0N2 | GF0N3 | GF0N4 |
|---|---|---|---|---|---|
| E Knoop (GPa) | 88.6±0.6 | 90.2±0.5 | 92.1±0.4 | 93.9±0.6 | 95.2±0.7 |
| E Ultrasonic (GPa) | 87.5±0.9 | 89.7±0.8 | 91.8±0.6 | 92.7±0.7 | 94.6±0.9 |
| Glasses GF12.5Nx | GF12.5N0 | GF12.5N1 | GF12.5N2 | GF12.5N3 | GF12.5N4 |
| E Knoop (GPa) | 88.7±0.6 | 90.5±0.5 | 92.3±0.4 | 93.9±0.6 | 95.5±0.7 |
| E Ultrasonic (GPa) | 88.1±0.8 | 89.9±0.7 | 92.1±0.8 | 92.8±0.7 | 94.9±0.9 |
| Glasses GNx | GF25N0 | GF25N1 | GF25N2 | GF25N3 | GF25N4 |
| E Knoop (GPa) | 88.9±0.8 | 90.8±0.9 | 92.5±1 | 94.1±0.9 | 95.8±0.7 |
| E Ultrasonic (GPa) | 87.7±0.7 | 89.7±0.9 | 91.7±1 | 93.8±0.9 | 95.1±0.7 |

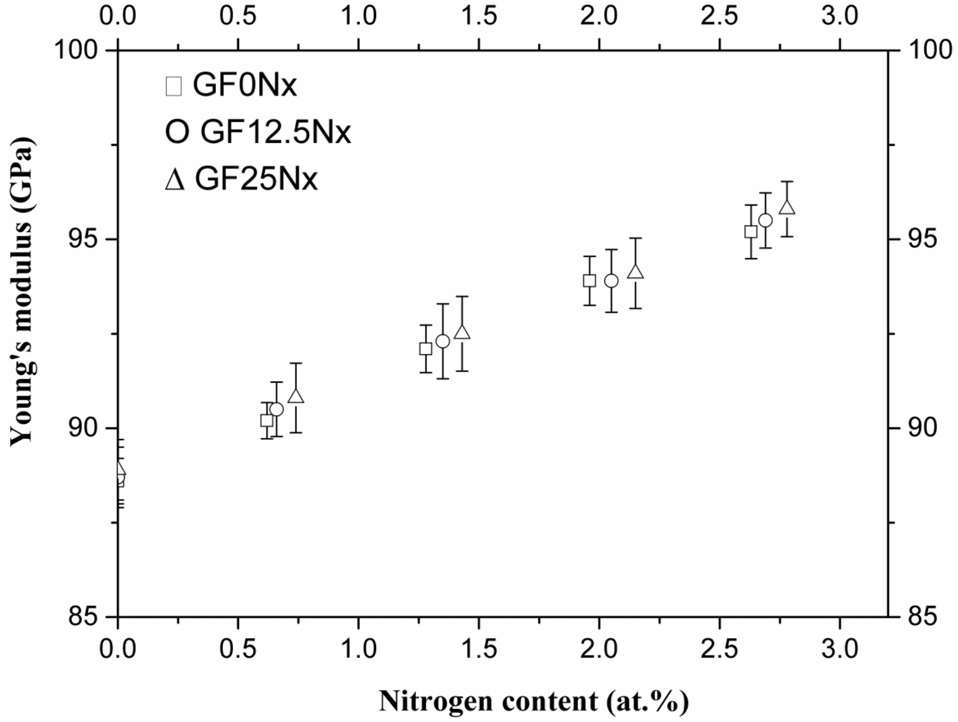


**Figure 6:** Elastic modulus of GF0Nx, GF12.5Nx and GF25Nx glasses as a function of nitrogen content.

The show that the substitution of fluorine for oxygen has negligible effects. The property variations are within the experimental errors associated with glass making consistency, specimen preparation, and property measurement. Thus, at ambient temperatures, these properties arise as a result of the average bond strengths within the glass structure and the effects of fluorine are negligible.
Rouxel [25] has recently shown that virtually all glasses, indeed all silicate and aluminosilicate glasses and their oxynitride analogues, exhibit an empirical decrease in Young's modulus with decreasing glass transition temperature. However, oxyfluoronitride glasses show anomalous trends in that elastic modulus values are not affected by fluorine substitution even though glass transition temperatures markedly decrease.

## Conclusions

The addition of fluorine to alumino-silicate glasses has little effect on density, compactness, Young's modulus, shear modulus or microhardness with increasing fluorine content. Fluorine decreases the glass transition temperature to such an extent that this cannot be linked only to the replacement of oxygen by fluorine. Fluorine acts as a network "modifier" replacing a bridging oxygen ion by two non bridging fluorine ions. On the contrary, nitrogen acts as a network “former” even in presence of fluorine with an increase in all properties with increasing nitrogen content. The fact that elastic moduli do not vary with fluorine inclusion is promising as it is possible to make oxynitride glasses at much lower temperatures while the mechanical properties are not affected. Consequently when glasses with high mechanical properties are required to be formed at lower temperatures, it is recommended to incorporate N and F simultaneously in the glasses, as nitrogen increases the cross-link density and forms more rigid glass and fluorine assists in lowering the melting temperatures.

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