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Effect of Fluorine and Nitrogen Anions on Properties of Ca-Si-Al-O Glasses

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Abstract. The preparation of bulk glasses in Ca-Si-Al-O-N-F system with the composition in equivalent % of 28e/oCa:56e/oSi:16e/oAl:100-X-Ye/oO:Xe/oF:Ye/oN are reported. The glass formation behaviour and properties of this new range of glasses are examined in detail. 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.

Introduction

Studies have shown that when oxygen is replaced by nitrogen in alumino-silicate glasses, glass transition temperature, elastic modulus and hardness increase linearly with nitrogen content [1-4]. The main conclusion is that N may be viewed as a network forming anion considering the fact that the effects of nitrogen and modifiers on glass properties are independent [5]. Investigations on the effect of fluorine in alumino-silicate glasses have shown that fluorine reduces the glass transition temperature [6, 7] and this anion may be viewed as a network modifying anion. Fluoro-alumino-silicate glasses are mainly used in biomaterials applications as bone substitutes or dental restoratives. The addition of nitrogen could lead to higher mechanical properties for these biomaterials. Shimada et al. [8] made an attempt to prepare a Ca-Si-Al-O-N-F ceramic using a mixture of α-Si_3N_4, Al_2O_3 and AlN (to form a SiAlON with high N content) with CaF_2. The results from X-ray diffraction suggest that CaF_2 did not react with the SiAlON and is stable at this composition at a temperature of 1700ºC in a closed system under 150 MPa pressure.

In the present work, the formation and stability of glasses in the oxyfluoride (Ca-Si-Al-O-F) and the oxyfluoronitride (Ca-Si-Al-O-N-F) systems have been investigated in order to study the effect on glass formation and thermal and mechanical properties of replacing oxygen by both F and N.

Experimental Procedures

Glass synthesis. The starting materials were commercial powders, CaO (99.9% purity, BDH Chemicals), SiO_2 (99.9% purity, Fluka Chemicals), Al_2O_3 (99.995% purity, Sumitomo Corporation Europe Ltd), Si_3N_4 (99.9% purity, UBE) CaF_2 (99.9% purity, Aldrich Chemicals). The chemical compositions are shown in Table 1 in equivalent percent [e/o], which has been explained in previous publications [1, 3, 4] and in atomic ratios. The equivalent compositions for all Ca-Si-Al-O-N-F glasses were calculated assuming that Ca, Si, Al, O, N, F were in their "normal" +2, +4, +3, -2, -3, -1 oxidation states, respectively. The mixed powders were wet ball milled in isopropanol for 24 h, and then dried again. The O-F series described in Table 1 was directly melted in an alumina crucible in air atmosphere at 1470ºC for 1h after which the melts were poured into a graphite mould and annealed. The O-F-N series powders were first isostatically pressed under 150 MPa and then melted at 1740ºC for 1h under 0.1MPa N_2 in a BN-lined graphite crucible to avoid any contamination between the glass and the crucible. Melts were poured into a graphite mould and annealed. After the determination of the glass transition temperature (Tg) by differential thermal

analysis, both series were annealed in air at Tg-50ºC or Tg for 1h and then cooled slowly to room temperature.

Table 1. Compositions of glasses studied

O-F series	Equivalent %						Atomic ratios					
	Ca	Si	Al	O	F	N	Ca	Si	Al	O	F	N
F0	28	56	16	100	0	0	14	14	5.33	50	0	0
F1	28	56	16	99	1	0	14	14	5.33	49.5	1	0
F2	28	56	16	98	2	0	14	14	5.33	49	2	0
F3	28	56	16	97	3	0	14	14	5.33	48.5	3	0
F4	28	56	16	96	4	0	14	14	5.33	48	4	0
F5	28	56	16	95	5	0	14	14	5.33	47.5	5	0
F5.3	28	56	16	94.7	5.3	0	14	14	5.33	47.35	5.3	0
O-F-N series	Equivalent %						Atomic ratios					
	Ca	Si	Al	O	F	N	Ca	Si	Al	O	F	N
N0	28	56	16	95	5	0	14	14	5.33	47.5	5	0
N5	28	56	16	90	5	5	14	14	5.33	45	5	1.67
N10	28	56	16	85	5	10	14	14	5.33	42.5	5	3.33
N15	28	56	16	80	5	15	14	14	5.33	40	5	5
N20	28	56	16	75	5	20	14	14	5.33	37.5	5	6.67
N25	28	56	16	70	5	25	14	14	5.33	35	5	8.33

Materials characterization. X-ray analysis was carried out using a Philips X'pert PRO Multi Purpose Diffractometer (Cu-Kα radiation) in order to confirm that the glasses were totally amorphous.

The bulk densities of samples of both series were measured by an Archimedean displacement technique using distilled water as the working fluid at a measured ambient temperature. The errors were calculated on more than three values of density. The standard normal distribution Student's t was applied to find the 95% confidence limit coefficient [9]. These density values were used to calculate the molar volume (MV) of these glasses using the relationship:

$$MV = \{\sum_i (x_i M_i)\} / \rho_{glass} \quad (1)$$

where x_i and M_i are respectively the fraction and ionic mass of the ionic species i, and ρ_{glass} is the measured glass density [$g.cm^{-3}$]. Glass Compactness values (C) were calculated according to the expression:

$$C = \{\sum_i (x_i V_i)\} N / MV \quad (2)$$

where N is Avogadro's number and Vi the volume of the ionic species calculated using ionic radii given by Shannon [10] for the various ions. The Young's moduli for the glasses were determined at room temperature from measurements of the longitudinal, v_l, and transverse, v_t, ultrasonic wave velocities with a better than 10^{-3} accuracy. These velocities are determined using two specially designed 10MHz piezoelectric transducers. The measurements are taken on parallel surface samples, each between 2.4 and 2.7 mm in width, using a Panametrics Pulse/Receiver Model 5072PR and a Hitachi VC6045 Digital Storage Oscilloscope. The longitudinal velocities (v_l) and the transverse velocities (v_t) were determined using the expression:

$$v_i = (2\ d) / t_i \quad (3)$$

where d is the width of the sample, t_i is the length of the period for longitudinal or transverse sine wave, v_i is the resulting ultrasonic velocity in m/s. Young's Modulus (E) in GPa for each sample was calculated using the expression:

$$E = \rho (3\ v_l^2 - 4\ v_t^2) / ((v_l / v_t)^2 - 1) \quad (4)$$

where ρ is the density of the material. Shear Modulus (G) and Bulk Modulus (B) were then calculated using the following expressions:

$$G = \rho\ v_t^2 \quad (5)$$

$$B = E\ G / \{3\ (3\ G - E)\} \quad (6)$$

The hardness measurements were made using a LECO Microhardness indenter (M400-G1) with a 136º Vickers diamond indenter. A load (P) of 0.3 Kg was applied during 10 seconds. The indentation half-diagonals were measured using Buehler Imaging Enterprise Software (Buehler, USA). The indentation impression sizes and the Vickers indentation crack lengths were measured immediately after unloading. Only perfect indentation crack lengths, those with clearly symmetrical indentations and with symmetrical crack patterns, were used in the final calculations. A total of 10 perfect indentations were made at each load with the Vickers indenter. The microhardness was calculated using the following equation:

$$H_v = 1854.4\ P / d^2 \qquad (7)$$

where H_v = Vickers Hardness [Kg/mm^2], P = applied load [Kg], d = average length of indentation diagonals [μm].

Differential Thermal Analysis (DTA) was carried out using a Stanton Redcroft STA 1640 series, simultaneous thermogravimetric differential thermal analyser. 50 mg glass powder samples were placed in a BN-lined platinum crucible to prevent any reaction between the platinum and the sample. Boron nitride is stable under a nitrogen pressure and does not induce any significant deviation of the temperature trace. Each sample was heated from 100 to 1300°C at a rate of 10°C/min against an alumina reference and under a flowing nitrogen environment to prevent oxidation of the sample. Three different points within the glass transition range were determined from Tg_{onset}, corresponding to the first endothermic change to Tg_{offset}, which is the last point along the range and Tg is the mid-point of the transition range. Measurement errors in this study are ± 2ºC. During the DTA experiment, the weight of the oxyfluoronitride samples was measured versus the temperature.

Results and Discussion

Glass formation and stability. XRD analyses of each of the fired glasses confirmed their amorphous nature. Transparent glasses were obtained for all the O-F series and the visual appearance suggested that they are homogenous. O-F-N glasses varied in colour from light grey and green to dark green as O was replaced by N (cf. Table 1) but they did not appear as homogeneous as the O-F series. From the thermogravimetric measurements, these glasses are stable with negligible weight loss up to 700ºC. For higher temperatures, at low nitrogen contents, there is weight loss which must be due to loss of fluorine from the O-F-N glasses, whereas eventually, as nitrogen increases, weight loss is converted into a weight gain due to the oxidation of the glass and the loss of some nitride species.

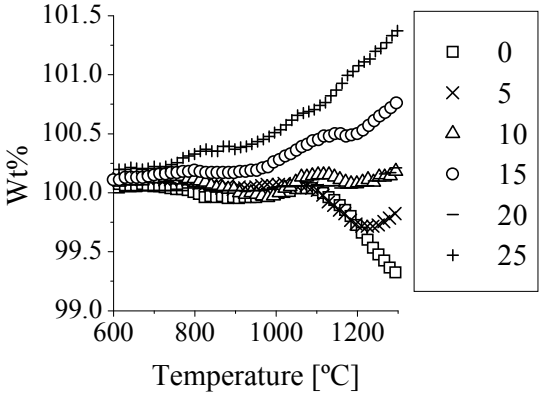
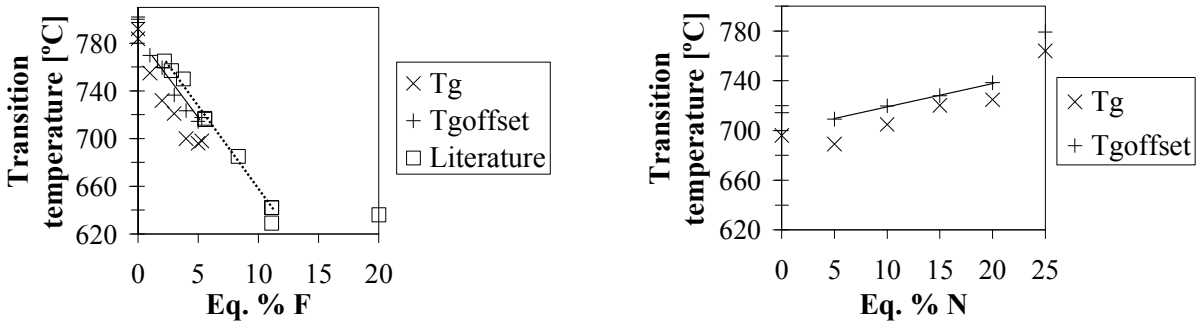


Fig. 1. Effect of nitrogen content on the weight measured during TGA/DTA experiments on the oxyfluoronitride glasses.

From the DTA experiments, the glass transition temperatures were determined. As can be seen from Fig. 2, glass transition offset temperature decreases roughly linearly with increasing fluorine

content in the glass structure, whereas, there is a linear increase in Tg when nitrogen content increases. Similar behaviour has also been reported previously [6, 7, 14]. The Tg v. nitrogen gradient is similar to that observed by Dolekcekic [14]. The Tg v. F gradient is very large in comparison but comparable to the results of Griffin et al. [6, 7]. Those results, obtained on glasses with composition $Ca_{22}Si_{44}Al_{33}O_{100-x}F_x$ are plotted in figure 2a and the slope observed is similar to the current results, even with different cation ratios. When fluorine is added, there is substitution of a bridging oxygen by a non-bridging fluorine and the removal of a network bridging anion. This means that the nitrogen anion contributes to the formation of the network and the fluorine tends to modify it.



a) b)

Fig. 2. Effect of fluorine and nitrogen content on the glass transition temperature of (a) oxyfluoride and (b) oxyfluoronitride glasses.

Table 2. Properties of O-F glasses (annealed at Tg) and O-F-N glasses (annealed at Tg-50K)

O-F series	Properties						
	Colour	Density [$g.cm^{-3}$]	MV [$cm^3.mole^{-1}$]	C	E [GPa]	G [GPa]	Hv [$Kg.mm^{-2}$]
F0	transparent	2.829	8.05	0.5385	92.2	36.0	633
F1	transparent	2.841	8.02	0.5411	92.9	36.2	627
F2	transparent	2.837	8.03	0.5405	94.3	36.8	635
F4	transparent	2.837	8.02	0.5410	91.4	35.8	622
F5	transparent	2.823	8.06	0.5386	92.2	36.2	632
F5.3	transparent	2.832	8.03	0.5404	91.5	35.6	626
Experimental error	-	±0.008	±0.02	-	± 0.7	± 0.9	± 18
O-F-N series							
N0	transparent	2.823	8.06	0.5386	92.2	36	632
N5	non-uniform grey and light green	2.856	7.98	0.5458	98.7	39	648
N10	non uniform dark green	2.863	7.97	0.5484	96.8	38	656
N15	non uniform dark green	2.873	7.95	0.5515	100.5	39	663
N20	non uniform grey and green	2.865	7.98	0.5511	99.0	39	663
Experimental error		±0.010	±0.03	-	± 0.6	± 2	± 17

Physical properties. Variations in glass density as a result of replacing oxygen by both fluorine and nitrogen are given in table 2. Very little change in density is observed as oxygen is replaced by fluorine whereas a small increase in density is observed as oxygen is replaced by nitrogen as shown in previous studies [1-4].

The value of density for the $Ca_{28}Si_{56}Al_{16}O_{100}$ glass is lower than reported by Rouxel et al. [11] for the same composition glass but differences in the rate of cooling and the annealing temperature

may result in density variations. $Ca_{28}Si_{56}Al_{16}O_{80}N_{15}F_5$ glass has a slightly lower density than $Ca_{28}Si_{56}Al_{16}O_{85}N_{15}$ [12, 13] showing that F decreases the density although the differences in values are $\pm$ 0.01-0.02, similar to the error range. Similar densities were also noted for $Ca_{28}Si_{56}Al_{16}O_{100}$ and $Ca_{28}Si_{56}Al_{16}O_{95}F_5$ glasses. It is to be noted that the changes in density may be due to the different anions of different coordination number and also changes in weight of the anions. The role of the different anions can be elucidated from the values of compactness in table 2. Fluorine anions have little effect on the network volume while nitrogen anions result in a more compact network.

The effect of fluorine and the nitrogen on Young's modulus and shear modulus for the oxyfluoride and oxyfluoronitride glasses are given in table 2. The moduli decrease with increasing fluorine content and increase with increasing nitrogen content confirming previous results [2] for Ca-Sialon glasses. The values of Young's modulus for the $Ca_{28}Si_{56}Al_{56}O_{100}$ glass varies with annealing treatment [3, 11] and reaches a maximum of 103.5 GPa when annealed at Tg-50K. Similar values were found for a $Ca_{28}Si_{56}Al_{16}O_{85}N_{15}$ glass [12, 13] and the $Ca_{28}Si_{56}Al_{16}O_{80}N_{15}F_5$ glass. The addition of nitrogen to an oxyfluoride glass increases the mechanical properties.

Microhardness values for oxyfluoride and oxyfluoronitride glasses are shown in table 2. 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.

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.

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