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Properties of Ca-(Y)-Si-Al-O-N-F glasses: independent and additive effects of fluorine and nitrogen

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Abstract

Thirty glasses of composition (in equivalent percent) $Ca_{20-x}Y_xSi_{50}Al_{30}O_{100-y-z}N_yF_z$, with x = 0, 10; y = 0, 10, 20 and z= 0, 1, 3, 5, 7 were prepared by melting and casting. All glasses were X-ray amorphous. Glass molar volumes decreased with nitrogen substitution for oxygen for all fluorine contents and, correspondingly, glass fractional compactness increased. Fluorine substitution of oxygen had virtually no effect on molar volume or fractional glass compactness for the three nitrogen contents tested. Young's modulus and microhardness were virtually unaffected by fluorine substitution for oxygen while nitrogen substitution for oxygen caused increases in these two properties. Glass transition temperature and dilatometric softening point values all decreased with increasing fluorine substitution levels, whilst increasing nitrogen substitution caused values for these thermal properties to increase. Correspondingly, the thermal expansion coefficient increased with fluorine and decreased with nitrogen substitution levels. Using property value differences between glasses containing fluorine and the corresponding glass containing 0 eq. % F enabled 24 data points to be used to determine the effect of fluorine on $T_{g,dil}$ and T_{DS}. The trends were linear with a gradient for both properties of the order of $-22ºC\cdot(\text{eq. \% F})^{-1}$. For the nitrogen effect, 20 data points were analysed for trend effects. As expected from earlier work, all trends had good linearity. Gradients were for $T_{g,dil}$ and T_{DS} $+2.5ºC\cdot(\text{eq. \% N})^{-1}$, which are fairly similar to previous results in oxynitride systems. All of the data collected and its analysis clearly shows that the substitution effects of fluorine for oxygen and nitrogen for oxygen are independent and additive with the fluorine substitution. The property trends of the glasses are discussed in terms of their implications for glass structure.

Keywords: oxynitride glasses, oxyfluoronitride glasses, fluorine.

I. Introduction

Fluorine-containing glasses are used for a wide variety of purposes, among them bioglasses and bioglass-ceramics, where fluoride release stimulates hydroxyapatite formation [1], which bonds to human bone due to similar phase structure [2, 3, 4]. Fluorine is also introduced into ionomer glasses which are used for glass polyalkenoate dental cements, where fluorine atoms are added to lower the refractive index of the glass as well as to enable fluoride ion release from the set cement [5] in order to prevent secondary caries [6]. Fluorine ions in human saliva and plasma also play an important role in development of hard tissues in the body [7].

It is well-known that fluorine facilitates melting of glass at lower temperatures and acts as a powerful network-disrupter [8, 9], creating a marked reduction in the glass transition temperature (T_g), viscosity and refractive index as the fluorine content of the glasses increases. These effects are explained on the basis of replacing bridging oxygens by non-bridging, terminating fluorines, thereby reducing the network connectivity and facilitating network mobility at lower temperatures. Fluorine also aids crystallisation and increases the potential for phase separation [10, 11, 12]. The electrical conductivity and the thermal expansion coefficient of oxyfluoride glasses are raised as the fluorine content increases [13]. It has been suggested that fluorine can exist as fluorite (CaF_2) clusters in calcium-modified glasses [14], bound to silicon as Si-F or bound to Al as Al-F species [9, 15, 16]. Si-F bonding can lead to formation of volatile SiF_4, which must be avoided as it is associated with both fluorine loss and an environmental problem as the SiF_4 produced will hydrolyse in the presence of water to hydrofluoric acid and silica. Some studies have been carried out on the structural role of fluorine in glasses [9, 10, 15, 17]. Despite evidence of Si-F bonds in silicate or alumino-silicate glasses, it has been suggested [14] that fluorine loss as SiF_4 could be suppressed completely from fluoro-alumino-silicate glasses by appropriate choice of composition and the incorporation of sufficient basic network modifying oxide. The ratios between Si:F and Al:F are important in determining the existence of Si-F bonds, with only small quantities forming when Al:F $\geq$ 1 (i.e. when there are enough Al atoms to satisfy all fluorine atoms). Structural studies of fluorine-containing alumino-silicate glasses have shown the presence of F-Ca(n) and Al-F-Ca(n) species in these glasses [10, 17].

On the other hand, numerous investigations have been carried out on glass formation and properties in a wide range of M-Si-O-N and M-Si-Al-O-N glasses, where "M" is typically an alkali, alkaline-earth or rare-earth metal and a comprehensive review is given by Becher et al. [18]. In the initial studies [19-22] correlations between the amount of silicon nitride dissolved into oxynitride glasses and changes in their physical properties were reported. Glass transition temperature, microhardness and relative fracture toughness all increased with increasing nitrogen content while the thermal expansion coefficient decreased. IR spectroscopic analyses [21] indicated that the incorporated nitrogen became chemically bonded to silicon in the glass network and, by substitution for oxygen, produced a more tightly and highly linked structure. However, the cation ratios for these glasses were variable and it was not possible to say unequivocally that the improvements in properties observed were solely due to the increased nitrogen concentration in the glass. In contrast, Drew [23, 24] and Hampshire [25-27] carried out extensive studies on glasses in M-Si-O-N and M-Si-Al-O-N (where M = Ca, Mg, Y and Nd) systems with varying nitrogen:oxygen ratios and fixed cation compositions (i.e. M:Si:Al) to allow direct comparison between systems with different modifiers and also the effect of replacing oxygen by nitrogen within each system. Subsequent studies [28-31] confirmed that when bridging and non-bridging oxygens are replaced by nitrogen, T_g, viscosity, hardness, Young´s modulus, fracture toughness and chemical durability increase linearly with nitrogen content, while the thermal expansion coefficient decreases.

Addition of fluorine to oxynitride glasses has been reported by Hanifi *et al.* [32-34], introducing a new family of Ca-Si-Al-O-N-F glasses. The present work involves a systematic investigation of the effects of oxygen replacement by fluorine and nitrogen simultaneously on the properties of calcium- and calcium-yttrium-modified alumino-silicate glasses with a constant cation composition.

II. Experimental

The compositions of thirty glasses in the Ca-(Y)-Si-Al-O-N-F system that were used in this study are given in Table I. The Ca:Al and Al:Si ratios chosen are expected to maintain Al in 4-fold coordination since they are >1:2 and < 1:1, respectively [33, 35]. Therefore, Al atoms are expected to enter the glass network as $[AlO_4]^-$ tetrahedra leading to preferential formation of Al-F bonds over the undesired Si-F bonds, which can lead to fluorine loss as volatile SiF_4. Furthermore, maximum nitrogen and fluorine substitution levels for oxygen were

chosen so that they were both similar (~8.4 at. %). Glass batches were prepared by wet ball milling the requisite amounts of Si_3N_4 (UBE) and CaF_2 (Aldrich) together with high purity (99.9%) oxides (CaO (Fisher), Y_2O_3 (Alfa Aesar), SiO_2 (Fluka Chemika), Al_2O_3 (Sumitomo)) for 4 h, using Al_2O_3 milling media, a polyethylene container and isopropanol as the fluid. The mixtures were then dried by evaporation in a rotovap. The dried powders were then pressed into compacts by cold isostatic pressing at 150 MPa. These were then placed in a BN-lined graphite crucible and fired at 1650°C in a vertical tube furnace under flowing nitrogen at 0.1 MPa for 1 h. The melt was then quickly withdrawn and poured into a preheated graphite mould to form glass bars followed by annealing at the respective glass-transition ($T_{g,DTA}$) temperature for 1 h, to relieve cooling stresses, and then slow furnace-cooled to ambient temperature. $T_{g,DTA}$ values were determined by thermo-gravimetric analysis using a Stanton-Redcroft STA 1640 instrument.

Specimens of each glass were cleaned and dried and then weighed dry and immersed in water to enable glass-density determination by the Archimedes principle. Glass compactness (C) was calculated according to the expression:

$$C = \frac{\sum_{1}^{i} x_i v_i N}{\sum_{1}^{i} x_i m_i} \cdot \rho \quad (1)$$

where x_i is the fraction of ionic species "i", v_i the volume of ionic species and m_i the ionic mass of the species; N the Avogadro´s number and ρ the glass density. The value of v_i was calculated using the ionic radii given by Shannon [36] and the expression:

$$\upsilon_i = \frac{4}{3}\pi r_i^3 \quad (2)$$

The molar volumes (MV) of the glasses were calculated according to the expression:

$$MV = \frac{\sum_{1}^{i} x_i m_i}{\rho} \quad (3)$$

Specimens of each glass, 10 mm x 3 mm x 3 mm in size, were cut from the large bars and located in a dilatometer, Netzsch Dil 402-C. The specimens were then heated under flowing nitrogen, at a rate of 5°C/min, to above the dilatometric-softening point (T_{DS}). The inflection point of the expansion curve was taken as the glass-transition temperature ($T_{g,dil}$) while the maximum was taken as the T_{DS}. The thermal expansion coefficient ($\alpha_{300-600}$) was calculated between 300 and 600ºC using the following equation:

$$\alpha_{T_1-T_2} = \frac{\Delta l / l_0}{\Delta T} \quad (4)$$

Where l_0 is the original length, Δl is the change in length of the specimen and ΔT is the temperature change. From equation (4) $\alpha_{T_1-T_2}$ is defined in ($ºC^{-1}$).

Dilatometry curves for each glass were examined to ensure that there was no decrease in the $\Delta l/l_0$-temperature slope before the rapid increase in gradient above the $T_{g,dil}$. Any such decrease in slope would have reflected incomplete glass annealing and, consequently, any glass showing such behaviour should be re-annealed for an additional hour.

Specimens of the glass were mounted in a cold setting resin, polished to a 1 μm finish and then subjected to microhardness testing (Leco microhardness tester) using a Vickers indenter with a 300 g load for 10 s. Young´s modulus (E) was measured using the ultrasonic pulse-echo-overlap technique.

III. Results

(1) General observations

The physical, mechanical and thermal properties of the Ca-(Y)-Si-Al-O-N-F glasses investigated are given in Table I. As shown, all glasses were X-ray amorphous after melting, quenching and annealing. This was expected beforehand since the cation composition lies inside the glass forming region for 20 eq.% nitrogen (0 eq.% fluorine) reported by Drew et al. [23] for calcium-sialon glasses and also within the glass forming region for 20 eq.% nitrogen and 5 eq.% fluorine reported by Hanifi *et al.* [33] for Ca-Si-Al-O-N-F glasses. Replacement of 10 eq.% Ca by Y also resulted in amorphous specimens. Nitrogen-free specimens where colourless, while nitrogen-containing glasses were black or dark grey in colour as previously reported for oxynitride glasses [19,

20, 27, 37], and this can be explained by the presence of both $FeSi_2$ and a smaller number of Si particles [37]. These precipitates also contain other metals such as chromium or nickel. Most glasses prepared as slides with thickness of 1.5mm were transparent to light.

(2) Oxygen replacement by fluorine

As shown in Table I, density, molar volume and compactness remain unaltered as fluorine replaces oxygen. In fact, the effect of fluorine on these properties is virtually negligible and changes observed when 7 eq.% oxygen are replaced by fluorine are within experimental range of error. In the case of density, two factors must be analyzed as this property is influenced by the mass and the volume of the atoms in the glass. The introduction of fluorine into the glass network comprises the replacement of one atom of oxygen (O^{2-}) by two of fluorine (F^-). This leads to a higher mass of the atoms in the glass, since the molar weight of oxygen is 15.9994 g/mol and that of fluorine is 18.9984 g/mol. Since fluorine and oxygen have similar ionic radii (135 pm for oxygen versus 131 pm for fluorine), it must be also considered that those two atoms of fluorine will occupy approximately double the space as that occupied by the oxygen atom. It is deduced, then, that the volume of the glass increases to the same extent as does the mass and keeps the density value constant. However, the molar volume does not change with replacement of oxygen by fluorine. Although fluorine and oxygen have different values of m_i, the value of x_i for all the species is modified in such a way that the formula weight ($\sum x_i m_i$) remains unaltered. According to expression (3), since density does not change with fluorine, the molar volume also remains constant. This is of interest since the replacement of one O^{2-} (ionic radius 135 pm) by two F^- ions (ionic radius 131 pm) should lead to a greater molar volume or an increase in compactness, which is demonstrated, to some extent, by the increases in compactness with fluorine content shown in figure 1. Investigation of the data given for Young's modulus and microhardness presented in table I shows that values are virtually unaffected as fluorine is introduced into the glass composition at the expense of oxygen. Only the microhardness of the glasses containing 20 eq.% nitrogen seem to follow a slight decreasing trend with increasing fluorine substitution. It could be suggested that this decrease could be due to a higher nitrogen loss for these glasses, but such nitrogen loss should also be reflected in a reduction in the Young's modulus values and this is not the case. Therefore, it seems that fluorine addition has just a slight influence on microhardness of the compositions containing the highest nitrogen content, but even this decrease is within the experimental range of error and, therefore, it is not considered significant. The data for Young's modulus for the Ca-modified glasses is represented in Figure 2, while the change in

microhardness with fluorine is shown in figure 3. These negligible effects of fluorine substitution arise for all nitrogen contents examined and for the two different modifier types (Ca- and Ca-Y-). In contrast, the substitution of oxygen by fluorine in the glasses had a considerable effect on glass transition temperature and dilatometric softening temperature and also on the thermal expansion coefficient. For each of the different glass series, reasonably linear correlations with similar gradients were observed with respect to fluorine substitution levels. Variation of the thermal expansion coefficient with fluorine content is presented in figure 4.

In accordance with previous studies [28], incremental property changes (Δ_{prop}, i.e., property values for 0, 1, 3, 5 and 7 eq. % fluorine minus the property value for 0 eq. % fluorine) for each nitrogen content (0, 10 and 20 eq. %) enabled 30 data points to be used to determine the effect of fluorine on T_g and T_{DS}. These values of Δ_{prop} were plotted as a function of fluorine content (see Figure 5 for ΔT_g data). As R^2 values were 0.96 for T_g and 0.95 for T_{DS} data and nearly all data points were located within the ± 1.5 x standard error values, for both ΔT_g and ΔT_{DS}, it was concluded that both data sets fitted a linear correlation. For $T_{g,dil}$ the gradient was $-22.9°C\cdot(\text{eq. \% F})^{-1}$ and for T_{DS} it was $-21.8°C\cdot(\text{eq. \% F})^{-1}$. Using this slope data, average intercept values were calculated for each nitrogen content for both the Ca and Ca-Y series of glasses. The intercept data is given in table II and best fit lines using the slope and average intercept data for the Ca- series of glasses are shown in Figure 6 for T_g data points and Figure 7 for T_{DS} data points. Both of these figures show that the method of data analysis gives a reasonable fit for the data points.

(3) Oxygen replacement by nitrogen

Analysis of the data given in Table I shows that for a fixed modifier type (Ca or Ca-Y), substitution of oxygen by nitrogen results in increases in density, glass compactness, Young's modulus, microhardness, glass transition temperature and dilatometric softening temperature for all fluorine contents. Molar volumes and thermal expansion coefficient both decrease with increasing nitrogen content (see figure 8 for molar volume). Such effects have previously been noted for other oxynitride glass systems not containing fluorine [18-31, 38, 39]. The increases in property values are also similar to those previously recorded with the substitution of 1 eq. % O by N giving rise to increases in Young's modulus of about 1 GPa and an increase in microhardness of about 0.1

GPa. Given the broad similarity in change in property values with nitrogen substitution, it is reasonable to assume that fluorine does not affect the manner in which nitrogen changes the glass network.

Using the same data treatment methods for glass transition and dilatometric softening temperatures, gradients were calculated for $\Delta T_{g,dil}$ and ΔT_{DS} as functions of N or F content and the error values and average intercepts calculated. The results of these analyses are given in table III. Figure 9 shows the data points for $T_{g,dil}$ data for the Ca modified glasses against nitrogen content superimposed upon the lines of best fit derived from the data given in table III. It is seen from table III that the gradients for $T_{g,dil}$ and T_{DS} are 2.4 and 2.8°C·(eq. % N)$^{-1}$, respectively, which are somewhat lower than the 3.3 and 3.5°C· (eq. % N)$^{-1}$ observed by Pomeroy *et al.* [28] for Mg-Y-Si-Al-O-N glasses but similar to the values reported by Dolekcekic *et al.* [38] for Er-Si-Al-O-N glasses. What is clear from the slope data presented in table III is that nitrogen has a positive effect on glass transition temperature, which would be expected due to the extra connectivity it brings to the glass network. Comparison of the gradients obtained for fluorine and nitrogen substitution leads to the observation that the increase on these properties produced by the introduction of 1 eq. % nitrogen is around 9 times smaller than the decrease resulting from the addition of 1 eq. % fluorine. Therefore, it is possible to state that the effect of the introduction of 20 eq. % nitrogen on $T_{g,dil}$ or T_{ds} can be "neutralized" with the replacement of only 2 or 2.5 eq. % oxygen by fluorine.

(4) Effect of glass compactness on Young´s modulus

Figure 10 plots Young's modulus data points against their corresponding compactness values for the two series of glasses analysed in this study and clearly shows that these are reasonably linear as previously observed [28] for fluorine-free oxynitride glasses. A similar figure can also be plotted for microhardness. In fact, both properties are strongly correlated to glass compactness and, in the case of Young's modulus, this can be explained on the basis that Young´s modulus is related to average bond strength and increased average bond strength should be reflected in increased glass compactness. Figure 6 also shows that whilst nitrogen content and modifier cation type(s) have a major effect on compactness and elastic modulus, fluorine contents do not, as the family of points for each nitrogen content are clustered closely together. This is of major significance as it means that modulus and microhardness can be controlled by nitrogen substitution and modifier cation selection in glasses containing up to 7 eq. % fluorine.

IV. Discussion

The data presented above for the effect of fluorine on molar volume, Young's modulus and microhardness indicate that they are virtually unaffected. These findings are consistent with those reported for other Ca-Si-Al-O-N-F glasses by Hanifi et al.[34] who clearly showed that the apparent lack of change in property value with increasing fluorine content was due to negligible changes in free volume and thus glass compactness. The effect of nitrogen on glass properties is wholly different. Thus, this substitution increases Young's modulus, microhardness, glass transition and dilatometric softening temperatures as a result of increases in glass compactness brought about by decreases in glass free volume as argued by Hanifi et al.[34].

With respect to glass transition and dilatometric softening temperatures, there are clear differences between the effects of nitrogen and fluorine substitution for oxygen. Given that the gradients for these thermal properties in terms of nitrogen are comparable with previous work it appears that the effect of nitrogen is independent of fluorine content. This might be expected since the replacement of oxygen by nitrogen yields additional crosslinks between $(Si,Al)(O,N)_4$ tetrahedra as indicated by the work of Sakka [39]. Thus, tri-coordinated nitrogen (i.e. $N\equiv(SiO_3)_3$ bonding) causes greater crosslinking thus reducing segmental motion (increasing T_g) and the relative movement of the structural units in the glass (increasing T_{DS}). The linear variations of both thermal and mechanical properties with nitrogen content are consistent with those obtained previously for oxynitride glasses [23-31, 38, 39]. The addition of fluorine has completely the opposite effect as the replacement of an O-Al-O linkage by two Al-F terminations (see [9, 17, 40]) reduces the connectivity of the network thus facilitating the segmental motion and relative movement of the structural units in the glass and lowering T_g and T_{DS} as also observed by Hill *et al.* [9]. In addition to reducing network connectivity via the introduction of Al-F terminations, fluorine also reduces the need for Ca to charge balance (AlO_3F) tetrahedra as they have the same charge as SiO_4 tetrahedra. This therefore increases the number of non–bridging oxygens in the system and, thus, on a comparative atom for atom basis, fluorine would be expected to more significantly disrupt the glass network than nitrogen would crosslink it. It must be assumed that fluorine has a preference to be bonded to aluminium atoms as suggested in the literature [9, 17, 40], in particular, since the Ca:Al and Al:Si ratios were chosen suitably to achieve this purpose. It has been suggested that fluorine can also be bonded to calcium [10, 17], this will also result in a decrease of the cross-linking of the network, as species formed, such as CaF^+, will ionically

bond with only one non-bridging oxygen (NBO) or nitrogen, compared to a fluorine-free glass, where Ca^{2+} ionically bonds two NBOs. However, this kind of bonding is expected to have a much lower effect on the T_g or T_{DS} than the Al-F bonding has. As the effect of fluorine on these properties is fairly linear, it can be suggested that the extent to which each type of bonding (Al-F or Ca-F) takes place is constant and independent of the fluorine content. It is thought, in the absence of MAS-NMR analysis, that increasing fluorine content will induce changes in the ratio of aluminium species in a modifier or network dwelling role, as previously discussed by Hanifi et al.[34] and that this effect as well as additional fluorine terminations of the network is responsible for inducing such large decreases in Tg and T_{DS} per unit change in fluorine content.

Direct comparison of the changes in property values for the glasses with two different modifier types, as reported here, and data reviewed and reported by Hanifi et al.[34] clearly show similar numerical trends. Such similarity in property value changes with nitrogen content endorses the fact that fluorine has no effect on the manner in which nitrogen affects glass structure. In addition, the fact that the variation in glass transition temperature and dilatometric softening temperature with fluorine content for the Ca- and Ca-Y modified glasses and the Ca-modified glasses of Hanifi et al.[34] strongly suggests that for glasses of cation composition (in equiv. %). 20Ca:50Si:30Al, 10Ca:10Y:50Si:30Al and 28Ca:57Si:15Al, the effects of nitrogen content and fluorine content on property values is the same, thus indicating that the roles played by these anions are the same for the range of compositions investigated.

V. Conclusions

Observation and analysis of the effects of various physical, thermal and mechanical properties of oxygen substitution by nitrogen and fluorine in calcium and calcium-yttrium alumino-silicate glasses leads to the following conclusions:

1) Substituting oxygen by fluorine has virtually no effect on glass molar volume, compactness, Young's modulus or microhardness and these effects are independent of nitrogen content.
2) Substituting nitrogen for oxygen decreases molar volume and increases glass compactness, Young's modulus and microhardness by increments, which are independent of fluorine content.
3) The effects of N and F substitution on Young's modulus and microhardness can be explained in terms of relevant glass compactness values.
4) Fluorine substitution for oxygen decreases glass transition and dilatometric softening temperatures by $22.9^{o}C\cdot(\text{eq. \%F})^{-1}$ and $21.8^{o}C\cdot(\text{eq. \%F})^{-1}$ respectively and there is good agreement with these slopes for each nitrogen content.
5) Nitrogen substitution for oxygen increases glass transition and dilatometric softening temperatures by $2.4^{o}C\cdot(\text{eq. \% N})^{-1}$ and $2.8^{o}C\cdot(\text{eq. \% N})^{-1}$ respectively. Again there is reasonable agreement with these slopes for each fluorine content.
6) Fluorine causes significant network disruption by the introduction of Al-F terminations and additional non–bridging oxygens whilst nitrogen substitution for oxygen causes increased network connectivity. These structural effects cause the changes in glass transition and dilatometric softening temperatures and to some extent explain the differences in magnitude of the slopes.
7) The data presented show that the effects of oxygen replacement by fluorine (for fixed nitrogen content) and oxygen replacement by nitrogen (for fixed fluorine content) on physical, thermal and mechanical properties are independent and additive, rather than synergistic.
8) The independent and additive effects of fluorine and nitrogen content on property values are very similar for the two different modifier compositions investigated and thus roles played by these anions in changing glass structure and property values are unaffected by these modifier differences.

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List of captions of tables and figures:

Table I. Effect of nitrogen and fluorine content on physical, thermal and mechanical properties of glasses of cation composition $Ca_{20}Si_{50}Al_{30}$ and $Ca_{10}Y_{10}Si_{50}Al_{30}$.

Table II. Least squares slope, error band and average intercept values for effect of fluorine contents on $T_{g,dil}$ and T_{DS}.

Table III. Least squares slope, intercept and error band values for effect of nitrogen on $T_{g,dil,}$ and T_{DS}.

Fig 1. Effect of fluorine content on compactness of Ca series glasses at fixed nitrogen contents ((○) 0 N (△) 10 N (◇) 20 N); (lines represent average values for all fluorine contents).

Fig 2. Effect of fluorine content on Young´s modulus of Ca series glasses at fixed nitrogen contents ((○) 0 N (△) 10 N (◇) 20 N); (lines represent average values for all fluorine contents).

Fig 3. Effect of fluorine content on microhardness of Ca series glasses at fixed nitrogen contents ((○) 0 N (△) 10 N (◇) 20 N); (lines represent average values for all fluorine contents).

Fig 4. Effect of fluorine content on thermal expansion coefficient for Ca glasses for fixed nitrogen contents ((○) 0 N (△) 10 N (◇) 20 N) (lines represent average values for all fluorine contents).

Fig 5. Effect of fluorine on change in glass transition temperature for Ca (open symbols) and Ca-Y (filled symbols) glasses for each nitrogen content ((○) 0 N (△) 10 N (◇) 20 N); full line – least-squares fit for all data, dashed lines ± 1.5 x standard error).

Fig 6. Effect of fluorine content on glass transition temperature for Ca series of glasses at fixed nitrogen contents ((○) 0 N (△) 10 N (◇) 20 N); (lines are best fits using data in table II).

Fig 7. Effect of fluorine content on dilatometric softening temperature for Ca series of glasses at fixed nitrogen contents ((○) 0 N (△) 10 N (◇) 20 N); (lines are best fits using data in table II).

Fig 8. Effect of nitrogen content on molar volume for Ca series of glasses at fixed nitrogen contents (0 F (●) 1 F(▲) 3 F(◇) 5 F (□) 7 F (×); (lines are best fits using data in table II).

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Table I. Effect of nitrogen and fluorine content on physical, thermal and mechanical properties of glasses of cation composition $Ca_{20}Si_{50}Al_{30}$ and $Ca_{10}Y_{10}Si_{50}Al_{30}$.

Glass composition (eq. %) Ca:Y:Si:Al:O:N:F	Bulk Color	Density (g/cm^3)	Molar volume (cm^3/mol)	Fractional Compactness	E (GPa)	Microhardness (Gpa)	$T_{g,DTA}$ (°C)	$T_{g,dil}$ (°C)	T_{DS} (°C)	$\alpha_{300-600}$ ($°C^{-1}$)
Ca series		*0 N series*								
20:0:50:30:100:0:0	Colorless	2.76	7.99	0.521	90	6.1	837	778	818	7.62
20:0:50:30:99:0:1	Colorless	2.76	8.01	0.520	91	6.1	826	774	809	7.65
20:0:50:30:97:0:3	Colorless	2.77	7.98	0.523	92	6.2	759	689	727	7.84
20:0:50:30:95:0:5	Colorless	2.77	7.98	0.525	91	6.3	726	650	692	7.97
20:0:50:30:93:0:7	Colorless	2.76	7.99	0.526	89	6.0	695	624	662	8.56
		10 N series								
20:0:50:30:90:10:0	Black	2.81	7.87	0.532	99	6.8	868	812	832	7.19
20:0:50:30:89:10:1	Black-Grey	2.81	7.86	0.533	100	7.0	822	767	813	7.20
20:0:50:30:87:10:3	Black-Grey	2.80	7.90	0.532	99	6.8	805	707	754	7.44
20:0:50:30:85:10:5	Black-Grey	2.81	7.86	0.536	99	6.6	756	697	740	7.71
20:0:50:30:83:10:7	Black	2.82	7.86	0.538	96	6.6	735	645	687	7.66
		20 N series								
20:0:50:30:80:20:0	Black	2.86	7.75	0.543	108	7.9	889	840	879	6.81
20:0:50:30:79:20:1	Black	2.85	7.78	0.542	109	7.7	862	802	841	6.86
20:0:50:30:77:20:3	Black	2.86	7.76	0.546	107	7.5	825	750	799	7.25
20:0:50:30:75:20:5	Black	2.86	7.75	0.548	110	7.4	788	706	751	7.17
20:0:50:30:73:20:7	Black-Grey	2.86	7.75	0.549	105	7.1	749	665	712	7.36
Ca-Y series		*0 N series*								
10:10:50:30:100:0:0	Colorless	3.01	7.87	0.547	100	6.6	876	810	844	6.64
10:10:50:30:99:0:1	Colorless	3.00	7.89	0.546	102	6.5	837	778	820	6.71
10:10:50:30:97:0:3	Colorless	3.00	7.91	0.547	98	6.5	799	731	770	6.66
10:10:50:30:95:0:5	Colorless	2.99	7.90	0.548	97	6.5	752	690	734	6.81
10:10:50:30:93:0:7	Colorless	2.99	7.91	0.549	96	6.4	710	652	699	7.26
		10 N series								
10:10:50:30:90:10:0	Black	3.08	7.73	0.561	109	7.5	878	828	876	6.72
10:10:50:30:89:10:1	Black	3.06	7.76	0.559	110	7.4	848	783	823	6.21
10:10:50:30:87:10:3	Black	3.08	7.73	0.563	110	7.5	812	740	793	6.81
10:10:50:30:85:10:5	Black	3.07	7.72	0.565	114	7.5	792	712	763	6.95
10:10:50:30:83:10:7	Black	3.07	7.74	0.565	109	7.3	760	674	724	6.76
		20 N series								
10:10:50:30:80:20:0	Black	3.12	7.64	0.572	120	8.4	921	865	919	6.45
10:10:50:30:79:20:1	Black	3.11	7.67	0.571	120	8.3	892	815	867	6.73
10:10:50:30:77:20:3	Black	3.12	7.65	0.574	119	8.4	840	782	841	7.20
10:10:50:30:75:20:5	Grey	3.14	7.59	0.579	119	8.0	807	723	773	7.19
10:10:50:30:73:20:7	Grey	3.13	7.60	0.579	116	7.5	779	700	756	6.65
Experimental error		± 0.01	± 0.01	± 0.001	± 1.9	± 0.12	± 3	± 3	± 3	±0.10

Table II. Least squares slope, error band and average intercept values for effect of fluorine contents on $T_{g,dil}$ and T_{DS}.

Property	Gradient ($°C.\ (eq.\ \%F)^{-1}$)	Error band (°C)
$T_{g,dil}$	-22.9	± 18.6
T_{DS}	-21.8	± 19.8

	Intercept values (°C)					
	Ca series			CaY series		
	0 N	10 N	20 N	0 N	10N	20N
$T_{g,dil}$	776	799	826	805	821	850
T_{DS}	811	835	866	843	866	901

Table III. Least squares slope, intercept and error band values for effect of nitrogen on $T_{g,dil,}$ and T_{DS}.

Property	gradient (°C. eq. %$^{-1}$)	error band (°C)
$T_{g,dil}$	2.4	± 16.5
T_{DS}	2.8	± 17.1

	intercept values (°C)				
property	0 F	1 F	3 F	5 F	7 F
$T_{g,dil}$ Ca	785	756	691	660	620
$T_{g,dil}$ Ca-Y	812	777	719	686	653
T_{DS} Ca	816	794	733	700	660
T_{DS} Ca-Y	851	808	772	728	697

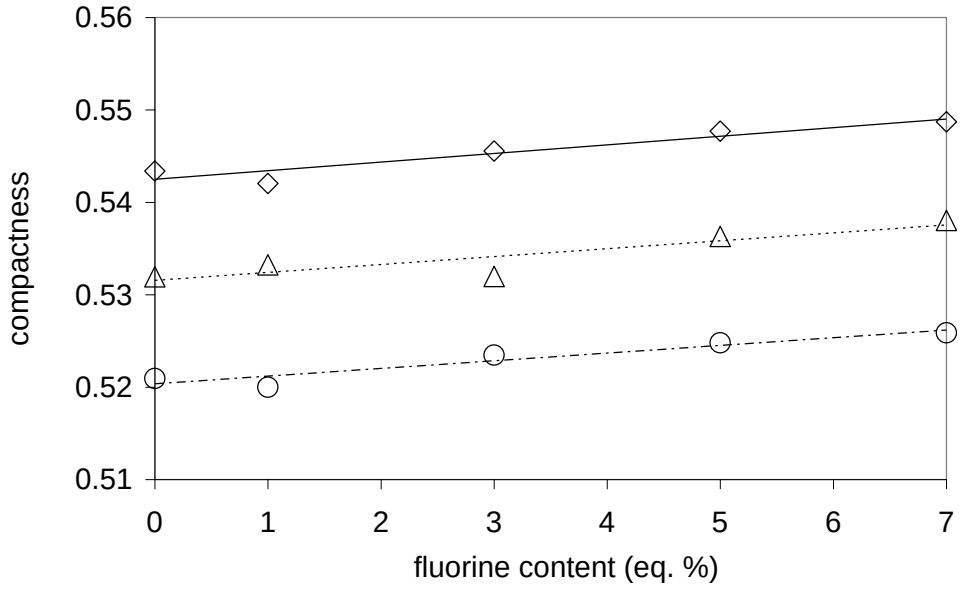


Fig 1. Effect of fluorine content on compactness of Ca series glasses at fixed nitrogen contents ((○) 0 N (△) 10 N (◇) 20 N); (lines represent average values for all fluorine contents).

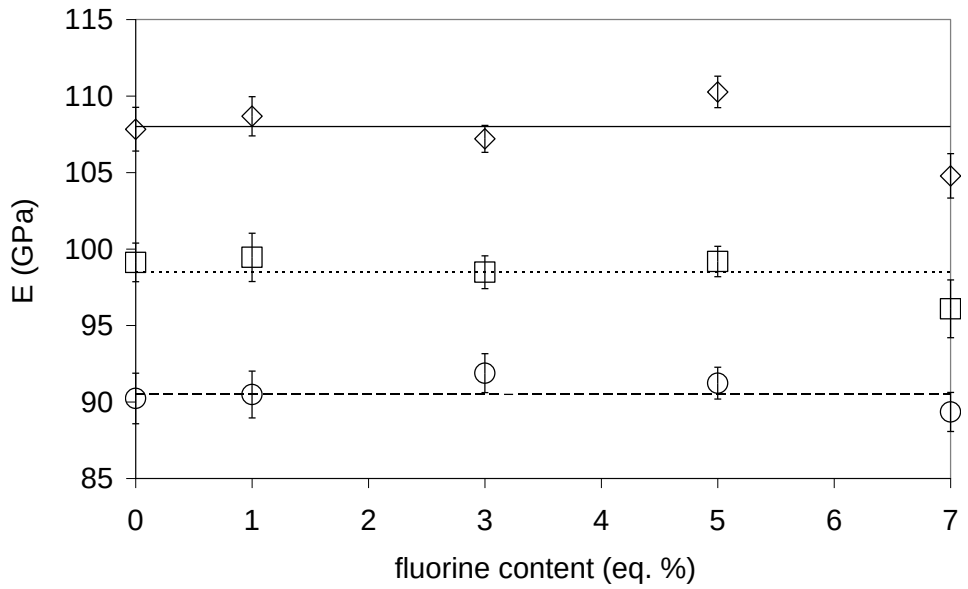


Fig 2. Effect of fluorine content on Young´s modulus of Ca series glasses at fixed nitrogen contents ((○) 0 N (△) 10 N (◇) 20 N); (lines represent average values for all fluorine contents).

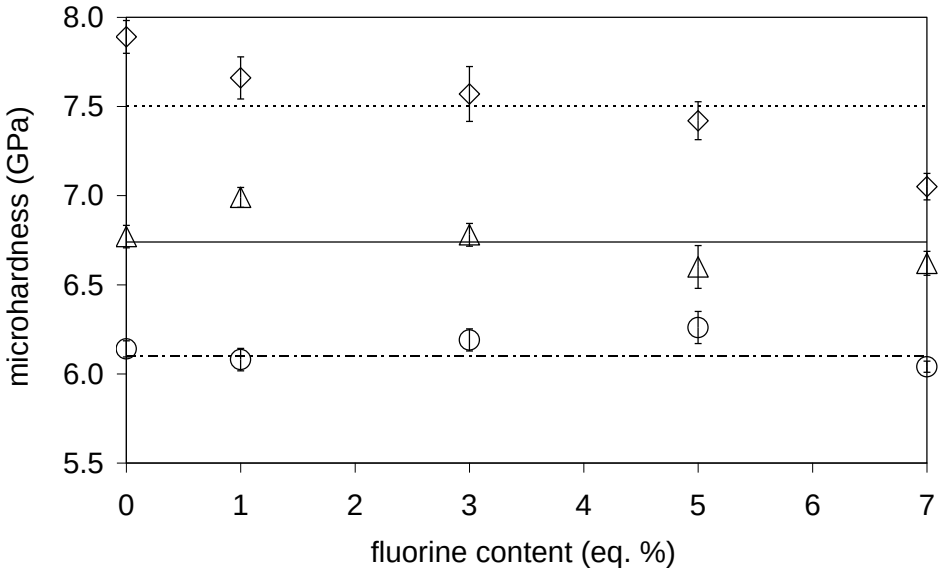


Fig 3. Effect of fluorine content on microhardness of Ca series glasses at fixed nitrogen contents ((○) 0 N (△) 10 N (◇) 20 N); (lines represent average values for all fluorine contents).

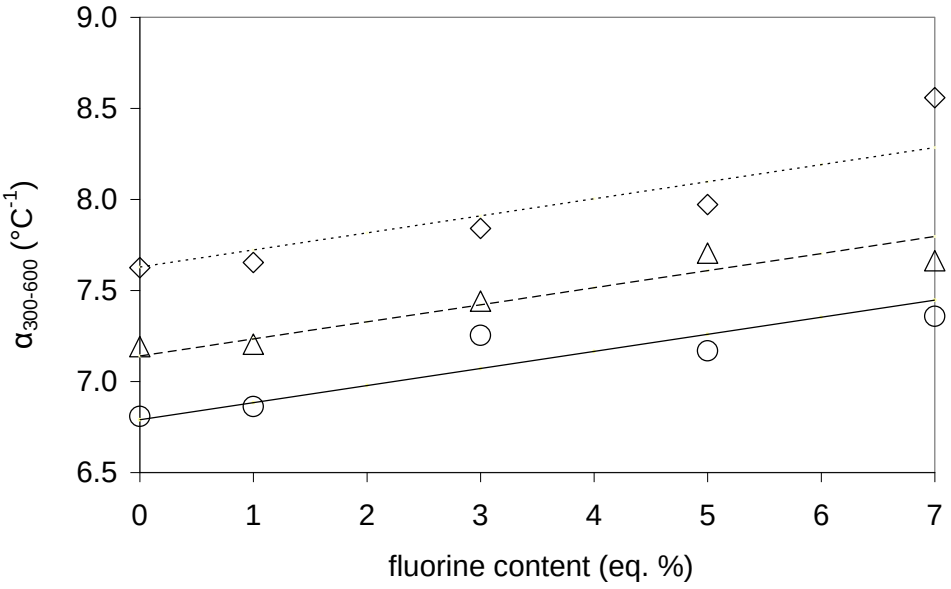
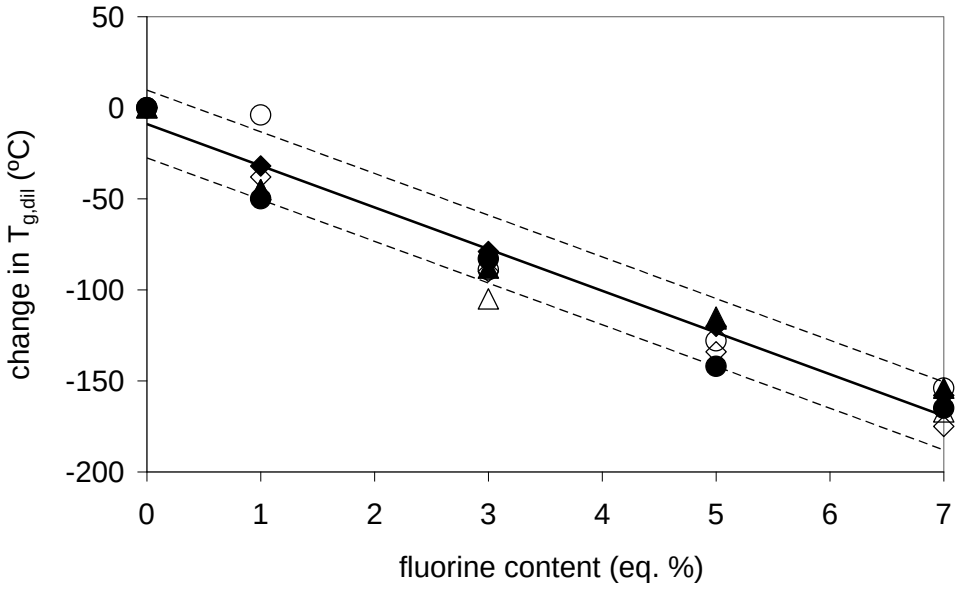


Fig 4. Effect of fluorine content on thermal expansion coefficient for Ca glasses for fixed nitrogen contents ((○) 0 N (△) 10 N (◇) 20 N) (lines represent average values for all fluorine contents).



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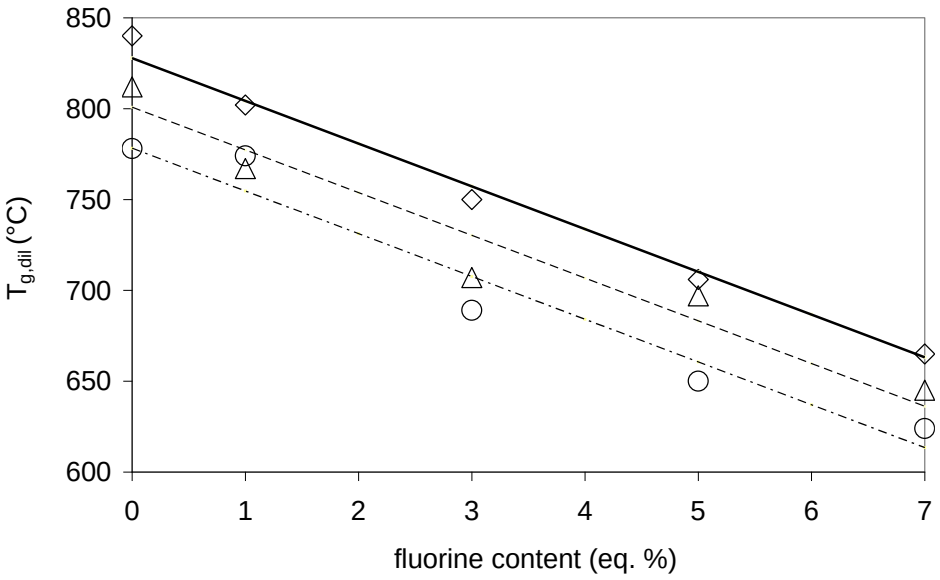

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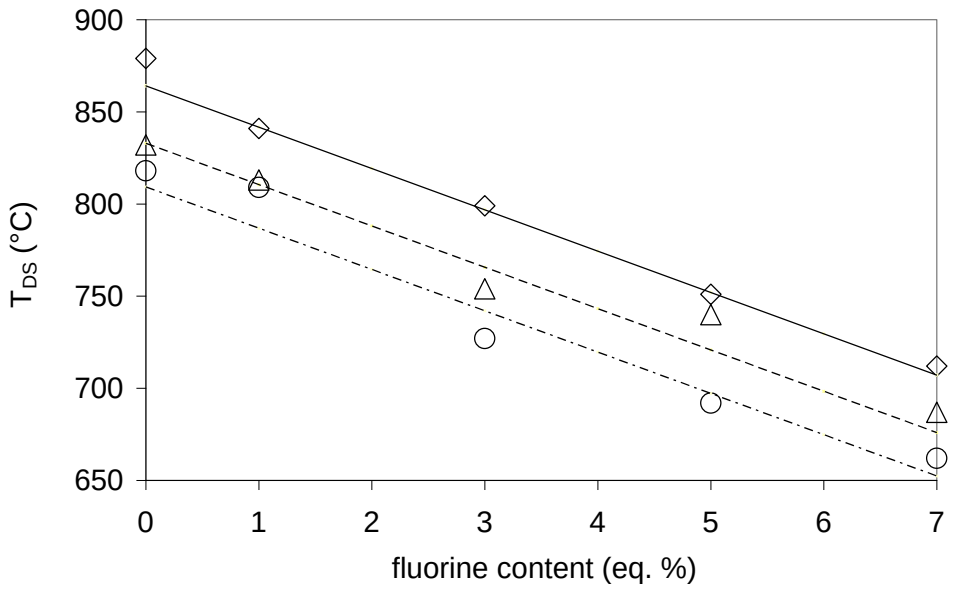
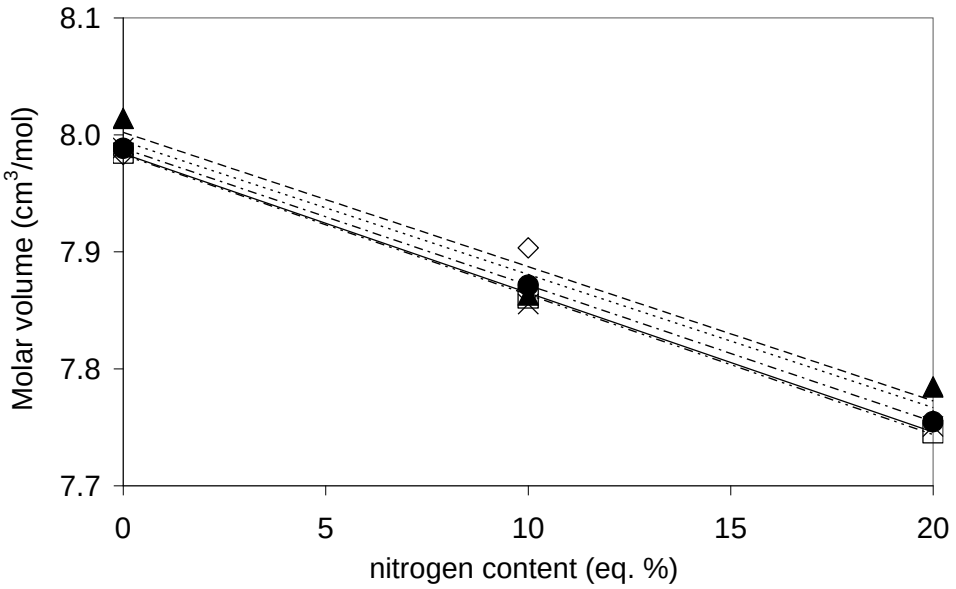


Fig 7. Effect of fluorine content on dilatometric softening temperature for Ca series of glasses at fixed nitrogen contents ((○) 0 N (△) 10 N (◇) 20 N); (lines are best fits using data in table II).



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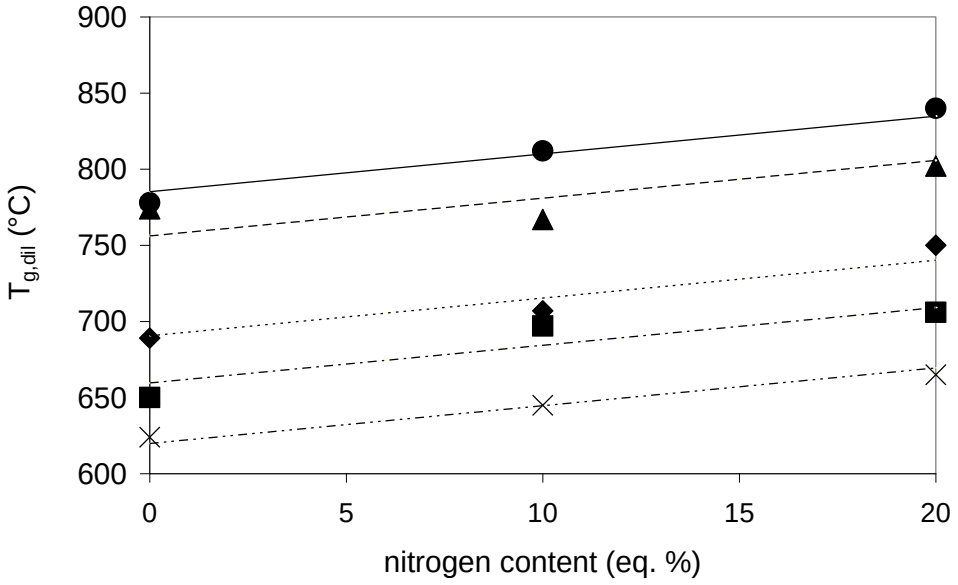

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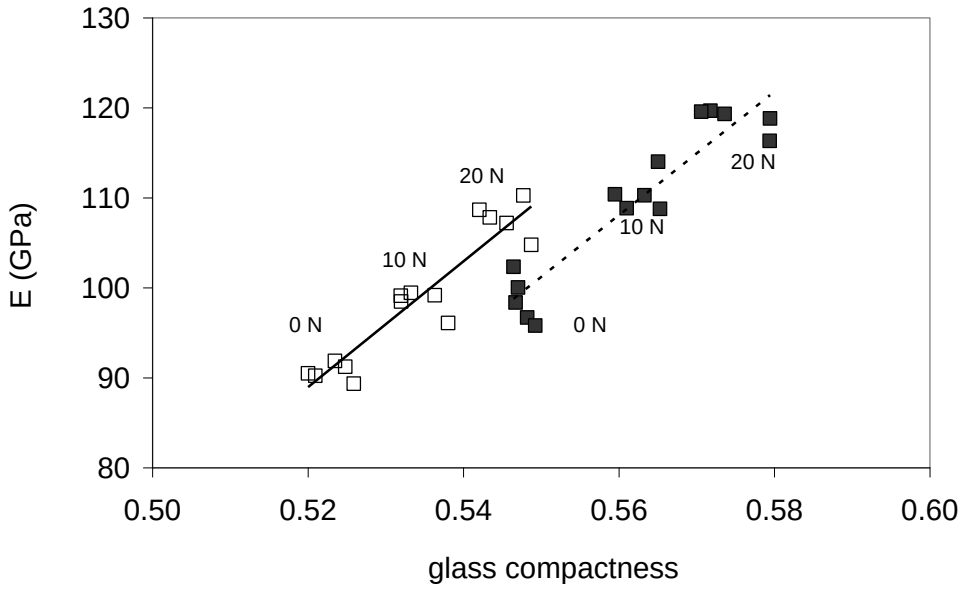

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