



---

**Título artículo / Títol article:** Factors Controlling Properties of Ca-Mg, Ca-Er, Ca-Nd, or Ca-Y-Modified Aluminosilicate Glasses Containing Nitrogen and Fluorine.

**Autores / Autors** Garcia Bellés, Ángel R. ; Monzó Fuster, María ; Barba Juan, Antonio ; Clausell Terol, Carolina ; Pomeroy, M. J. ; Hanifi, A. R. ; Hampshire, S.

**Revista:** Journal of the American Ceramic Society

**Versión / Versió:** Pre-print

**Cita bibliográfica / Cita bibliogràfica (ISO 690):** GARCÍA - BELLÉS, Ángel R., et al. Factors Controlling Properties of Ca - Mg, Ca - Er, Ca - Nd, or Ca - Y - Modified Aluminosilicate Glasses Containing Nitrogen and Fluorine. Journal of the American Ceramic Society, 2013, vol. 96, no 9, p. 2839-2845.

**url Repositori UJI:** <http://hdl.handle.net/10234/96836>

---

# **Factors controlling properties of Ca- Mg, Er, Nd or Y modified aluminosilicate glasses containing nitrogen and fluorine**

**A. R. García-Bellés, M. Monzó, A. Barba, C. Clausell**

*Instituto Universitario de Tecnología Cerámica (ITC). Universitat Jaume I. Castellón 12071, Spain*

**M. J. Pomeroy, A. R. Hanifi, S. Hampshire**

*Materials and Surface Science Institute, University of Limerick, Limerick, Ireland*

**Keywords:** oxynitride glasses, mixed-modifiers, fluorine, cationic field strength

## **Abstract.**

Glasses with composition (in eq.%) (30-x)Ca: xM: 55Si: 15Al: 80O: 15N: 5F have been prepared with different levels of substitution of Ca<sup>2+</sup> cations by Mg<sup>2+</sup>, Y<sup>3+</sup>, Er<sup>3+</sup> or Nd<sup>3+</sup>. The properties of these glasses are examined in detail and changes observed in molar volume, free volume, fractional glass compactness, Young's modulus, microhardness, glass transition temperature and thermal expansion as a function of M content are presented. Using linear regression analysis, evidence is presented which clearly shows that these glass properties are either solely dependent on the effective cation field strength, if modifier cation valency is the same (e.g. Mg substitution for Ca), or dependent on the effective cation field strength and the number of (Si,Al)(O,N,F) tetrahedra associated with each modifier when Ca is replaced by the trivalent modifiers. Combining these correlations with those observed previously relating glass properties to N and F substitution for O, it becomes apparent that glass properties for Ca-M-Si-Al-O-N-F glasses can be described by correlations which involve independent but additive contributions by N and F substitution levels, effective cation field strength and the number of tetrahedra associated with each modifier ion.

## I. Introduction

Oxynitride glasses are special types of silicate or aluminosilicate glasses in which oxygen atoms in the glass network are partially replaced by nitrogen atoms. They arise as intergranular phases in silicon nitride based ceramics where their composition and volume fraction determine the properties of the material<sup>1</sup>. Numerous studies have focused on formation and properties of oxynitride glasses in different systems<sup>2-11</sup> showing that increases in glass transition temperature, hardness, elastic modulus or viscosity with regard to the corresponding oxide glasses are due to a higher cross-link density provided by nitrogen within the glass network. These changes in properties are explained by the theory of Mulfinger<sup>12</sup> in which oxygen atoms in the SiO<sub>4</sub> tetrahedra within the silicate network are partially replaced by nitrogen atoms. This leads to a higher than average coordination of non-metal atoms since nitrogen is tri-coordinated compared with oxygen which is bi-coordinated, leading to a more rigid glass network as a result of increased cross-linking. The increase in the properties of glasses with increasing nitrogen content reflects an increased compactness of the glass structure as nitrogen, capable of bridging three tetrahedral groups, replaces oxygen, capable of bridging only two of them.

Other reports have presented effects of modifier cations on glass properties for fixed nitrogen content. Rouxel *et al.*<sup>13</sup> confirmed for oxynitride glasses the mixed cation effect between calcium and magnesium, previously found in alkali silicate and aluminosilicate glasses and referred to as the mixed alkali effect<sup>14</sup>. This effect appears as a non-monotonic trend in glass transition temperature as magnesium replaces calcium. Rouxel *et al.*<sup>13</sup> also reported an increase in Young's modulus and microhardness when calcium is substituted by magnesium. NMR experiments carried out in this study<sup>13</sup> revealed that magnesium behaves as an intermediate ion, which means that it can act either as a network modifier or a network

former, depending on the overall glass composition. It was also found that nitrogen can enhance the effect of magnesium in tetrahedral sites, concluding that the environment of the cation determines its effects on the glass properties. In another study, Pomeroy *et al.*<sup>15</sup> showed that for glasses containing mixed rare-earth trivalent modifiers (such as La-Y, La-Er and Nd-Y) properties such as compactness, Young's modulus, microhardness, glass transition temperature and softening point, all increased linearly with increasing effective cationic field strength (ECFS) of the modifiers, while the molar volume and the thermal expansion coefficient decreased. This was consistent with previous findings<sup>16-18</sup> in glasses with constant cation ratio and fixed nitrogen contents, where the modifiers were singular rather than mixed. Because of the linearity of trends observed, it was suggested that all the glasses are comprised of the same Si-Al-O-N tetrahedral network and the only difference, as the modifier substitutions are made, is the attractive forces exerted on non-bridging oxygens and nitrogens linked to the modifier cations. The extent of attractive forces should increase as the average cation field strength increases. Increased attractive forces should be expected to lead to observations of decreased molar volume and increased glass compactness and Young's modulus values. As the attractive forces on the non-bridging anions increase, resistance to segmental motion would be expected as would resistance to relative motion between glass structural units. These two effects would be expected to increase glass transition temperature ( $T_g$ ) and dilatometric softening temperature ( $T_{DS}$ ), respectively. As a conclusion it was suggested that, all other factors being equal, the effective CFS controls the glass properties in rare-earth Si-Al-O-N glasses containing mixed modifier cations.

However, in other studies<sup>19-20</sup> it was shown that this conclusion was only valid with mixed-modifier cations with the same valency. In fact, in mixed modifier systems in which cation valencies are not equal, such as Mg-Y-Si-Al-O-N glasses, other correlations rather than

effective cationic field strength (ECFS) were required to explain property variations with substitutions of a divalent by a trivalent cation. Thus, only linear correlations were obtained when changes in glass transition temperature or dilatometric softening temperature were plotted against the number of tetrahedra per effective modifier cation. Linear increases in  $T_g$  and  $T_{DS}$  with increasing levels of coordination of  $(Si,Al)(O,N)_4$  tetrahedra around effective modifier cations reflect a higher level of cross-linking between the structural units of the Si–Al–O–N glass network<sup>19</sup>.

Fluorine-containing glasses are used for a wide variety of purposes, among them bioglasses and bioglass-ceramics, where fluoride release stimulates hydroxyapatite formation<sup>21</sup> and prevents secondary caries when used in glass-ionomer cements<sup>22</sup>. Monovalent fluorine acts as a network terminator, thus reducing the connectivity of the glass network and causing a marked reduction in  $T_g$  and viscosity as the fluorine content of the glasses is increased<sup>23-24</sup>. The preparation of oxyfluoride silicate glasses results mainly in the formation of Si-F bonds as well as fluorite ( $CaF_2$ ) clusters<sup>25</sup>, whilst in aluminosilicate glasses fluorine is preferentially bonded to aluminium<sup>24,25</sup>. Structural studies of fluorine-containing alumino-silicate glasses have shown the presence of F–Ca(n) and Al–F–Ca(n) species in alumino-silicate glasses<sup>27-28</sup>. Addition of fluorine to oxynitride glasses has been reported recently<sup>29-31</sup> and this shows that the incorporation of fluorine (1) increases nitrogen solubility and extends the range of glass forming compositions, (2) decreases glass melting temperatures, (3) markedly reduces glass transition and dilatometric softening temperatures thus reducing glass working temperatures, and (4) has no effect on the significant increases in elastic modulus or microhardness induced by nitrogen substitution. In another study<sup>32</sup>, the effects of replacing fluorine for oxygen systematically in oxynitride glasses containing mixed modifiers have been investigated and this shows the important effect of fluorine on thermal properties, decreasing dramatically the

values of  $T_g$  or  $T_{DS}$  with relatively low levels of substitution. However, the effect of F on mechanical and physical properties of these glasses is found to be virtually negligible. Effects of fluorine and nitrogen on properties are independent and additive rather than synergistic.

With this background, the work reported here was designed to study systematically the effects of calcium replacement by divalent Mg or trivalent cations (Y, Er, Nd) on the properties of oxynitride glasses containing fluorine with fixed nitrogen and fluorine contents, which has not been reported previously.

## II. Experimental procedure

The generic composition, in equivalent percent, of the seventeen glasses was (30-x)Ca: xM: 55Si: 15Al: 80O: 15N: 5F, where M is Mg, Er, Nd or Y and values for x and the corresponding Ca contents are given in Table I. Table I also gives the nominal glass compositions in atomic percentages. The (Ca:M):Al and Si:Al ratios chosen were expected to maintain Al in four-fold coordination, so that Al atoms all enter the glass network as  $[AlO_4]^-$  tetrahedra. Therefore, formation of volatile  $SiF_4$  with any subsequent fluorine loss is minimized in the experimental design. Ca–Mg glasses were fabricated using  $MgF_2$  as fluorine source so that complete replacement of calcium by magnesium could be achieved. However, for Ca–Er, Ca–Nd and Ca–Y glasses, use of  $ErF_3$ ,  $NdF_3$  or  $YF_3$  was not feasible. These glasses were prepared using  $CaF_2$  as the fluorine source and, as a consequence, only partial replacement of calcium by these trivalent cations was possible up to a maximum of 20 eq. %.

The glass samples were fabricated by wet ball milling the requisite amounts of  $Si_3N_4$  (UBE Industries, Yamaguchi, Japan) and  $CaF_2$  (Aldrich Chemical Company, Milwaukee, WI, USA) or  $MgF_2$  (Fluka Chemical Corp., Ronkonkoma, NY) together with high purity (99.9%)

oxides: CaO (Fisher Scientific Co., Pittsburgh, PA), MgO and SiO<sub>2</sub> (Fluka Chemical Corp., Ronkonkoma, NY), Y<sub>2</sub>O<sub>3</sub>, Er<sub>2</sub>O<sub>3</sub> and Nd<sub>2</sub>O<sub>3</sub> (Alfa Aesar GmbH & Co KG, Karlsruhe, Germany) and Al<sub>2</sub>O<sub>3</sub> (Sumitomo Chemical Co. Ltd, Tokyo, Japan), for 24 h, using Al<sub>2</sub>O<sub>3</sub> milling media, a polyethylene container and isopropanol as the fluid. The mixtures were dried by evaporation in a rotovap. The dried powders were pressed into compacts by cold isostatic pressing at 150 MPa. These were then placed in a BN-lined graphite crucible and melted at 1650°C in a vertical tube furnace under 0.1 MPa flowing nitrogen for 1 h. The melt was then quickly withdrawn and poured into a preheated graphite mould to form large bars followed by annealing at the respective glass-transition temperature (T<sub>g</sub>) for 1 h, to relieve cooling stresses, and then furnace-cooled to ambient temperature. T<sub>g</sub> values were previously determined by differential thermal analysis of smaller samples using a Stanton-Redcroft STA 1640 (Stanton Redcroft Inc., Rheometric Scientific, Epsom, UK) instrument. A heating rate of 10 °C per minute was used.

Effective cationic field strengths (ECFS) of the compositions (see Table I) were calculated using the expression:

$$ECFS = CFS_{M_1} \cdot \frac{C_{M_1}}{C_{M_1} + C_{M_2}} + CFS_{M_2} \cdot \frac{C_{M_2}}{C_{M_1} + C_{M_2}} \quad (1)$$

where CFS<sub>M<sub>1</sub></sub> and CFS<sub>M<sub>2</sub></sub> are the cationic field strengths of the M<sub>1</sub> and M<sub>2</sub> cations (calculated as valency / ionic radii<sup>2</sup>), and C<sub>M<sub>1</sub></sub> and C<sub>M<sub>2</sub></sub> are their respective concentrations in atomic percent. The numbers of tetrahedra per modifier cation (TpM) were calculated from:

$$TpM = \frac{[Si] + [Al]}{[Ca] + [M]} \quad (2)$$

where [X] indicates the atom fraction of ion X in the glass formula.

Specimens of each glass were cleaned and dried and weighed dry and immersed in water to enable glass-density determination ( $\rho$ ) by the Archimedes principle. The molar volume (MV) of each of the glasses was calculated according to the expression:

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

where  $x_i$  is the fraction of ionic species “i”,  $v_i$  the volume of ionic species,  $m_i$  the ionic mass of the species and  $\rho$  the glass density. Glass compactness (C) was calculated according to the expression:

$$C = \frac{\sum_{i=1}^i x_i v_i N}{\sum_{i=1}^i x_i m_i} \cdot \rho \quad (4)$$

where N is Avogadro’s number.

The value of  $v_i$  was calculated using the ionic radii ( $r_i$ ) given by Shannon<sup>33</sup> and the expression:

$$v_i = \frac{4}{3} \pi \cdot r_i^3 \quad (5)$$

Specimens of each glass, 10 mm x 3 mm x 3 mm in size, were cut from the large bars and placed in a dilatometer Netzsch Dil 402-C (Netzsch-Gerätebau GmbH, Selb, Germany). The specimens were then heated under flowing nitrogen, at a rate of 5°C/min, to above the dilatometric-softening point. Thermal expansion coefficients over the temperature range 300 to 600°C were calculated, using the following equation:

$$CTE = \frac{\Delta l / l_0}{\Delta T} \quad (6)$$

where  $l_0$  is the original length at 300°C,  $\Delta l$  the change in length between 300 and 600°C and  $\Delta T$  is the temperature change (i.e. 300°C). 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 inflection point of the expansion curve. Any such decrease in slope would have reflected incomplete glass annealing and, consequently, any glass showing such behaviour should be re-annealed at  $T_g$  for an additional hour.

Specimens of the glass were mounted in a cold setting epoxy resin, polished to a 1  $\mu\text{m}$  finish and subjected to microhardness testing, using a Leco microhardness tester (Leco Corporation, St. Joseph, Michigan), and with a Vickers indenter with a 300 g load for 10 s ( $\mu\text{Hv}$ ). Young's modulus was measured using an ultrasonic pulse-echo-overlap technique<sup>34</sup> in which the velocities of shear waves ( $V_s$ ) and compressional waves ( $V_c$ ) were measured. Four experiments were conducted for each glass. The Young's modulus ( $E$ ) was calculated from the following equation ( $\rho$  is the glass density):

$$E = \frac{\rho \cdot V_s}{3 \cdot V_c^2 - 4 \cdot V_s^2} \quad (7)$$

### III. Results

Table I gives the effective cation field strengths, tetrahedra per modifier, colour and density data for each of the Ca-M-SiAlONF glasses. XRD analyses of each of the as-melted glasses confirmed their amorphous nature. Various bulk colours were observed ranging from black (for Ca-Mg and Ca-Y glasses) through pink/claret (for Ca-Er glasses) to dark blue (for Ca-Nd glasses). 3 mm slices of the glasses were typically transparent. As shown in Table I, only slight decreases in density ( $\rho$ ) occur as calcium is replaced by the lighter element, magnesium, whereas, as expected, density increases arise as calcium is replaced by the heavier elements, yttrium, erbium or neodymium. It must be kept in mind, though, that the substitutions investigated are not solely due to the replacement of one cation by a lighter or

heavier cation, but are also associated with volume changes within the glass structure, expressed as molar volume (MV) and fractional glass compactness (C), values of which are given in Table II along with mechanical and thermal properties for the glasses. As calcium is replaced by any of the other cations, the molar volume of the glass decreases whilst glass compactness increases. This is consistent with the fact that the ion volumes decrease as  $\text{Ca}^{2+}$  is replaced by the other cations due to their smaller individual ion volumes. The increases in compactness must arise from stronger bonding effects related to the substituting modifier cation.

In common with compactness, both Young's modulus (E) and microhardness ( $\mu\text{Hv}$ ) increase when Ca is replaced by any of the other cations. Thus, when Mg substitutes for Ca, E increases from 96 GPa for the glass with only Ca as modifier to 121 GPa for the glass with only Mg as modifier (30 eq.% Mg). For the trivalent cation substitutions, E increases from 96 GPa to ~ 117 GPa for glasses with 20 eq.% Er or Y substitution. Smaller increases from 96 to 110 GPa were observed with 20 eq.% Nd substitution. Substitution effects for microhardness show similar trends with total substitution of Ca by Mg giving a 25% increase in value. Y and Er substitution of 20 eq.% Ca also yielded a 25% increase in microhardness value, whereas substitution of 20 eq.% Ca by Nd gave rise to only a 17% increase in microhardness. CTE values decrease with the introduction of any of the modifiers considered in this study from  $10.4 \times 10^{-6} \text{ K}^{-1}$  for the glass with only Ca as modifier to  $7.7 \times 10^{-6} \text{ K}^{-1}$  for the glass with only Mg as modifier, a 26% decrease. A similar level of decrease in expansion value was observed for the glass containing 20 eq.% Nd. For the 20 eq. % Y and Er substitution levels, the thermal expansion coefficients decreased by 31 to 32%.

Fig. 1 shows that the effect of progressive replacement of Ca by Mg on  $T_g$  is non-monotonic. This effect, previously reported for oxynitride glasses, is well known in alkali silicate glasses and reveals a mixed cation effect between Ca and Mg. In previous work on mixed Ca-Mg oxynitride glasses by Rouxel *et al.*<sup>13</sup>, the minimum in  $T_g$  was situated at the ratio Ca:Mg = 1, whereas in the present study, the minimum in  $T_g$  occurs at ~10 eq.% Mg, that is, at a substitution level of 1 in 3 Ca atoms. Substitution of Ca by a trivalent cation results in a substantial increase in  $T_g$  from 722°C for the glass containing only Ca to 810°C for the glass with 20 eq.% Er, 776°C for the glass with 20 eq.% Nd and 784°C for the glass with 20 eq.% Y.

In summary, increases in fractional glass compactness, Young's modulus and microhardness occur when Ca is substituted by Mg, Er, Nd or Y. These substitutions also cause decreases in molar volume and CTE. Glass transition temperatures of the glasses typically increase except for substitution of Ca by Mg when a mixed alkaline-earth effect is observed.

#### IV. Discussion

If it is assumed that the overall glass network structure, comprising cross-linked (Si,Al)(O,N,F)<sub>4</sub> tetrahedra, must be the same for each composition as the numbers of these ions does not change, then the structural factors controlling glass properties must solely relate to the attractive force with which the modifier cations associate with these tetrahedra. With respect to the substitution of Ca by Mg then the number of modifier ions is the same and thus the only change occurring in the factors controlling bonding would be effective cation field strength. If this bonding characteristic induced stronger association of tetrahedra, then the glass contractions observed (decreasing molar volumes with increasing ECFS) might be expected. However, molar volume comprises ion volume and free volume and, accordingly,

if the free volume decreases with increasing ECFS then this could be taken as clear evidence that this is due to greater association of the network tetrahedra by the modifying cations.

Figure 2 shows the effect of ECFS on free volume for the glasses where Ca is fully substituted by Mg. Regression analysis shows that the correlation coefficient is 0.9933 and, therefore, it can be concluded that ECFS does indeed control free volume which is a measure of the increased association of the glass network by cations with higher charge density. Regression analysis for the effects of ECFS on C, E and  $\mu\text{Hv}$  also indicate strong linear correlation (see table III). Such linear correlations are in total agreement with the work of previous studies<sup>15-18,20</sup> using substitutions of modifier ions of similar valency. These studies endorse the fact that, as ECFS increases, network tetrahedra are more strongly associated with attendant property improvement.

The quality of fit between ECFS and properties, particularly free volume, as Ca is replaced by Mg is clearly indicative of ECFS being the factor controlling the structure of the Ca-Mg modified glasses. This is in contrast to the conclusions of Rouxel et al.<sup>13</sup>, who indicated that, for Ca-Mg modified SiAlO(N) glasses, the substitution of Ca by Mg was associated with a change from a modifier role (Ca) to a former role (Mg) due to a more favourable cation : anion radius ratio. As shown in Figure 3, for the Ca-Mg modified glasses investigated in this work, average cation / anion radius ratios are in the range 0.739 for the glass modified by Ca alone to 0.532 for the glass modified by Mg alone. Based on crystal chemistry, all Ca-Mg modified glasses should have the modifier in VI-fold coordination. Due to the fact that Table III shows that excellent linearity of property - effective cation field strength correlations exist for the Ca-Mg modified glasses, it can be concluded that there is little change in the

coordination state of the modifier cation, although radial distribution function data similar to that obtained by Rouxel et al.<sup>13</sup> would endorse the conclusion made here.

In addition to showing the trend in free volume with ECFS for the Ca-Mg modified glasses, Figure 2 also compares the effect of ECFS on free volume for the Ca-M(III) modified glasses, where M(III) = Er, Nd or Y. While showing a similar negative linear trend, it is clear that the slope for the Ca-M(III) modified glasses is greater than for the Ca-Mg modified glass data points. As indicated in the introduction, for aliovalent modifier ion substitutions it is necessary to invoke a parameter taking into account the proportion of modifying cations in the system<sup>19</sup> in terms of the number of effective modifier atoms per network tetrahedron. In contrast to the method of calculation used in the previous study<sup>19</sup>, this parameter might be better simplified to the number of tetrahedra per modifier (TpM) for the Ca-M-Si-Al-O-N-F glasses discussed here, due to the wide variation in modifier ion electronegativity and the presence of fluorine in the glass. Thus, the number of tetrahedra per modifier (TpM), defined simply in equation 2, would be expected to control how properties vary with cation composition as well as with ECFS.

The only way in which the combined “linear” effects of ECFS and TpM can be assessed for the Ca-Mg, Ca-Er, Ca-Nd and Ca-Y glasses is by using multivariate linear regression analysis using the LINEST function in Microsoft Excel<sup>®</sup>. If the property data for all seventeen glasses is analysed using LINEST, then the effects of ECFS and TpM can be analyzed. The results of the analysis are given in Table IV. It is seen that all properties analysed can be linearly related to ECFS and TpM with an average for coefficients of determination of 0.95 and standard error values which are low with respect to the measurement error values given in Table II. Figures 4 and 5 show the goodness of fit between observed values for Young’s modulus and glass

transition temperature for Ca-M(III) glasses only (where M(III) = Er, Nd or Y) and values calculated using the correlations. The standard error and  $R^2$  data given in Table IV clearly indicate that simple linear relationships exist between glass properties, effective cation field strength (ECFS) and the number of tetrahedra per modifier cation (TpM). This fact endorses the findings referred to in the introduction, based on refs<sup>15-20</sup>, relating to the fact that ECFS and TpM both act to associate structural units in the glass more strongly. Such effects decrease free volume and thus increase glass compactness, modulus and microhardness. The increased strength with which glass units are associated with increasing ECFS and TpM also gives rise to increases in  $T_g$ . In addition, it would be expected that ECFS and TpM would act independently of each other as ECFS reflects the strength of bonding between structural glass units while TpM reflects the average number of tetrahedra associated by each modifier, the higher the number the greater the association.

Following from the analysis above, an additive equation can be written for the various properties (e.g. Molar Volume, MV) in terms of ECFS and TpM as in eq. 8:

$$MV = C + x_1.[ECFS] + x_2.[TpM] \quad (8)$$

where C is the intercept value and  $x_1$  and  $x_2$  are the slopes for ECFS and TpM given in Table IV.

It can be concluded that the effects of effective cation field strength and tetrahedra per modifier have independent and additive effects in terms of glass properties. When this is taken into account along with the clear evidence that nitrogen and fluorine substitution effects on properties are also independent and additive<sup>31,32</sup>, it can be concluded that glass properties can be manipulated by appropriate choice of ECFS, TpM, nitrogen content and fluorine content with each having an independent but additive effect on the chosen property.

## V. Conclusions

For the Ca-M-Si-Al-O-N-F glasses studied here with fixed levels of Si, Al, O, N and F and M = Mg, Er, Nd and Y, the following conclusions can be drawn:

- 1) Replacement of calcium by magnesium (M = Mg) causes a non-monotonic trend in glass transition temperature, due to a mixed alkaline-earth effect.
- 2) When Ca is substituted by Mg, fractional glass compactness, microhardness and Young's modulus values increase, while molar volumes and coefficients of thermal expansion values decrease. These increases / decreases are linearly related to the effective cation field strength of the mixed Ca-Mg modifier atoms.
- 3) When Ca is substituted by higher field strength Mg, the glass free volume decreases linearly with respect to increasing effective cation field strength. This free volume contraction is the result of greater association of network forming tetrahedra by cations with higher cation field strength.
- 4) Due to the significant linearity of property - effective cation field strength correlations for the Ca-Mg modified glasses, it is concluded that there is little change in the coordination state of the modifier cation.
- 5) When calcium is substituted by erbium, neodymium or yttrium, fractional glass compactness, microhardness and Young's modulus values increase, while molar volumes and coefficients of thermal expansion values decrease. These increases / decreases are linearly related to the both the effective cation field strength of the mixed Ca-M(III) (M(III) = Er, Nd, Y) modifier ions and the number of tetrahedra associated with each modifier ion.

- 6) For Ca-M-Si-Al-O-N-F glasses studied here and elsewhere, it is possible to state that effective cation field strength, tetrahedra per modifier, nitrogen substitution level and fluorine substitution level have independent and additive effects on glass properties.

## References

- <sup>1</sup> S. Hampshire and M.J. Pomeroy, "Grain boundary glasses in silicon nitride: A review of chemistry, properties and crystallisation," *J. Eur. Ceram. Soc.*, **32** [9] 1925-1932 (2012).
- <sup>2</sup> S. Hampshire, "Oxynitride Glasses," *J. Eur. Ceram. Soc.*, **28** [7] 1475-1483 (2008).
- <sup>3</sup> R. E. Loehman, "Preparation of oxynitride glasses," *J. Non-Cryst. Solids*, **56** [1-3] 123-134 (1983).
- <sup>4</sup> P. F. Becher, S. B. Waters, C. G. Westmoreland, and L. Riester, "Influence of Composition on the Properties of Si-RE-Al Oxynitride Glasses: RE=La, Nd, Gd, Y or Lu," *J. Am. Ceram. Soc.*, **85** [4] 897-902 (2002).
- <sup>5</sup> P. F. Becher, S. Hampshire, M. J. Pomeroy, M. J. Hoffmann, M. J. Lance and R. L. Satet, "An Overview of the Structure and Properties of Silicon-Based Oxynitride Glasses," *Int. J. Appl. Glass Sci.*, **2** [1] 63-83 (2011).
- <sup>6</sup> K. R. Shillito, R. R. Wills and R. B. Bennett, "Silicon metal oxynitride glasses," *J. Am. Ceram. Soc.*, **61** [11-12] 537 (1978).
- <sup>7</sup> R. A. L. Drew, S. Hampshire, and K. H. Jack, "Nitrogen Glasses"; pp. 119-32 in *Special Ceramics 7*, Vol. 31, Edited by P. Popper. Brit. Ceram. Proc., Stokeon-Trent, UK, 1981.
- <sup>8</sup> S. Hampshire, E. Nestor, R. Flynn, J.-L. Besson, T. Rouxel, H. Lemerrier, P. Goursat, M. Sabai, D.P. Thompson and K. Liddell. "Oxynitride Glasses: Properties and Potential for Crystallisation to Glass Ceramics," *J. Eur. Ceram. Soc.*, **14**, 261-273 (1994).
- <sup>9</sup> Z. H. Lian, S. L. Wang, L. F. Tian and W. Q. Ge, "Preparation and Properties of Alkaline-earth Silicon Oxynitride Glasses," *Adv. Mat. Res.*, [287-290] 819-822 (2011).



<sup>10</sup>E. Dolekcekic, M. J. Pomeroy and S. Hampshire, "Structural characterisation of Er-Si-Al-O-N glasses by Raman spectroscopy," *J. Eur. Ceram. Soc.* **27** [2-3] 893-898 (2007).

<sup>11</sup>S. Ali and B. Johnson, "Compositional effects on the properties of high nitrogen content alkaline-earth silicon oxynitride glasses, AE = Mg, Ca, Sr, Ba," *J. Eur. Ceram. Soc.*, **31** [4] 611-618 (2011).

<sup>12</sup>H. O. Mulfinger, "Physical and chemical solubility of nitrogen in glass melts," *J. Am. Ceram. Soc.* **49** [9] 462-467 (1966).

<sup>13</sup>T. Rouxel, N. Dély, J. C. Sangleboeuf, S. Dériano, M. LeFloch, B. Beuneu and S. Hampshire: "Structure-property correlations in Y-Ca-Mg-Sialon glasses: Physical and mechanical properties," *J. Am. Ceram. Soc.*, **88** [4] 889-896 (2005).

<sup>14</sup>J. O. Isard, "The mixed alkali effect in glass," *J. Non-Cryst. Solids* **1** [3], 235-261, (1969).

<sup>15</sup>M. J. Pomeroy, E. Nestor, R. Ramesh and S. Hampshire, "Properties and crystallisation of rare-earth Si-Al-O-N glasses containing mixed trivalent modifiers," *J. Am. Ceram. Soc.*, **88** [4] 875-881 (2005).

<sup>16</sup>R. Ramesh, E. Nestor, M. J. Pomeroy and S. Hampshire, "Formation of Ln-Si-Al-O-N glasses and their properties," *J. Eur. Ceram. Soc.*, **17** [15-16] 1933-1939 (1997).

<sup>17</sup>S. Hampshire and M. J. Pomeroy, "Effect of composition on viscosities of rare earth oxynitride glasses," *J. Non-Cryst. Solids*, **344** [1-2] 1-7 (2004).

<sup>18</sup>Y. Menke, V. Peltier-Baron and S. Hampshire, "Effect of rare earth cations on properties of sialon glass," *J. Non-Cryst. Solids*, **276** [1-3] 145-150 (2000).

<sup>19</sup>M. J. Pomeroy, C. Mulcahy and S. Hampshire, "Independent effects of nitrogen substitution for oxygen and yttrium substitution for magnesium on the properties of Mg-Y-Si-Al-O-N glasses," *J. Am. Ceram. Soc.* **86** [3] 458-64 (2003).

<sup>20</sup>M. J. Pomeroy and S. Hampshire, "Composition-structure-property relationships for Si-Al-O-N glasses containing mixed modifiers," *Ann. Chim. Sci. Mat.*, **28** [2] 63-70 (2003).

<sup>21</sup>K. T. Stanton, K. P. O'Flynn, S. Kiernan, J. Menuge and R. Hill, "Spherulitic crystallization of apatite–mullite glass-ceramics: Mechanisms of formation and implications for fracture properties," *J. Non-Cryst. Sol.*, **356** [35-36] 1802-1813 (2010).

<sup>22</sup>R. W. Billington, J. A. Williams, A. Dorban and G. J. Pearson, "Glass ionomer cement: evidence pointing to fluorine release in the form of monofluorophosphate in addition to fluoride ion," *Biomaterials* **25** [17] 3399-3402 (2004).

<sup>23</sup>E. De Barra and R. G. Hill, "Influence of glass composition on the properties of glass polyalkenoate cements. Part III: influence of fluorine content," *Biomaterials* **21** [6] 563-569 (2000).

<sup>24</sup>L. J. Lin, G. Z. Ren, M. P. Chen, Y. Liu and Q. B. Yang, "Study of fluorine losses and spectroscopic properties of Er(3+) doped oxyfluoride silicate glasses and glass ceramics," *Opt. Mater.* **31** [10] 1439-1442 (2009).

<sup>25</sup>E. M. Rabinovich, "On the structural role of fluorine in silicate glasses," *Phys. Chem. Glasses* **24** [2] 54-56 (1983).

<sup>26</sup>T. J. Kiczanski and J. F. Stebbins, "Fluorine sites in calcium and barium oxyfluorides: F-19 NMR on crystalline model compounds and glasses," *J. Non-Cryst. Solids*, **306** [2] 160-168 (2002).

<sup>27</sup>A. Stamboulis, R. V. Law and R. G. Hill, "Structural characterisation of fluorine containing glasses by <sup>19</sup>F, <sup>27</sup>Al, <sup>29</sup>Si and <sup>31</sup>P MAS-NMR spectroscopy," *J. Non-Cryst. Solids* **351**, 3289-3295 (2005).

<sup>28</sup>R. G. Hill, R. V. Law, M. D. O'Donnell, J. Hawes, N. L. Bubb, D. J. Wood, C. A. Miller, M. Mirsaneh and I. Reaney, "Characterisation of fluorine containing glasses and glass-ceramics by <sup>19</sup>F magic angle spinning nuclear magnetic resonance spectroscopy," *J. Eur. Ceram. Soc.* **29** [11] 2185-2191 (2009).

<sup>29</sup>A. R. Hanifi, M. J. Pomeroy and S. Hampshire, 2011, “Novel Glass Formation in the Ca-Si-Al-O-N-F System,” *J. Am. Ceram. Soc.*, **94** [2] 455–461 (2011).

<sup>30</sup>A. R. Hanifi, A. Genson, M. J. Pomeroy, S. Hampshire, “Oxyfluoronitride Glasses with High Elastic Modulus and Low Glass Transition Temperatures,” *J. Am. Ceram. Soc.*, **92** [5] 1141-1144 (2009).

<sup>31</sup>A. R. Hanifi, A. Genson, M. J. Pomeroy and S. Hampshire, “Independent but additive effects of fluorine and nitrogen substitution on properties of a calcium aluminosilicate glass,” *J. Am. Ceram. Soc.*, **95** [2] 600-606 (2012).

<sup>32</sup>A. R. García-Bellés, M. J. Pomeroy, A. R. Hanifi, M. Monzó-Fuster, A. Barba-Juan and S. Hampshire, “Independent and additive effects of fluorine and nitrogen on the properties of Si-Al-O-N-F glasses containing mixed modifiers,” In *Proceedings of the 10<sup>th</sup> International Conference and Exhibition of the European Ceramics Society*, Berlin, Germany, June 17-21, 2007.

<sup>33</sup>R. D. Shannon, “Effective ionic radii in oxides and fluorides,” *Acta Cryst., Sect B: Struct. Crystallogr. Chem.* **B25** 751-56 (1969).

<sup>34</sup>H. Lemerrier, T. Rouxel, D. Fargeot, J.-L. Besson, and B. Piriou, “Yttrium Si–Al–O–N Glasses: Structure and Mechanical Properties—Elasticity and Viscosity,” *J. Non-Cryst. Solids*, **201**, 128–45 (1996).

**Table I. Modifier contents in equivalent percent, glass compositions in atomic percent, effective cation field strengths, tetrahedra per modifier, colour and density data for Ca:M- SiAlONF glasses (where M = Mg or Er or Nd or Y).**

modifier contents (eq.%)		composition (at. %)							ECFS	TpM	colour
Ca	M	Ca	M	Si	Al	O	N	F	(Å <sup>-2</sup> )		
<b>Mg</b>											
30	0	17.9	0.0	16.4	6.0	47.8	6.0	6.0	2	1.25	Black-blue
25	5	14.9	3.0	16.4	6.0	47.8	6.0	6.0	2.31	1.25	Black-blue
20	10	11.9	6.0	16.4	6.0	47.8	6.0	6.0	2.62	1.25	Black
15	15	9.0	9.0	16.4	6.0	47.8	6.0	6.0	2.93	1.25	Black
10	20	6.0	11.9	16.4	6.0	47.8	6.0	6.0	3.24	1.25	Black
5	25	3.0	14.9	16.4	6.0	47.8	6.0	6.0	3.55	1.25	Black
0	30	0.0	17.9	16.4	6.0	47.8	6.0	6.0	3.86	1.25	Black
<b>Er</b>											
29	1	17.3	0.4	16.5	6.0	47.9	6.0	6.0	2.04	1.26	Black
27	3	16.2	1.2	16.5	6.0	48.0	6.0	6.0	2.13	1.29	Dark red
25	5	15.1	2.0	16.6	6.0	48.2	6.0	6.0	2.22	1.32	Pink
20	10	12.2	4.1	16.8	6.1	48.7	6.1	6.1	2.47	1.41	Pink
15	15	9.2	6.2	16.9	6.2	49.2	6.2	6.2	2.75	1.5	Claret
10	20	6.2	8.3	17.1	6.2	49.7	6.2	6.2	3.07	1.61	Claret
<b>Nd</b>											
25	5	15.1	2.0	16.6	6.0	48.2	6.0	6.0	2.13	1.32	Grey-blue
20	10	12.2	4.1	16.8	6.1	48.7	6.1	6.1	2.28	1.41	Dark blue
15	15	9.2	6.2	16.9	6.2	49.2	6.2	6.2	2.44	1.5	Dark blue
10	20	6.2	8.3	17.1	6.2	49.7	6.2	6.2	2.63	1.61	Dark blue
<b>Y</b>											
20	10	12.2	4.1	16.8	6.1	48.7	6.1	6.1	2.43	1.41	Black
10	20	6.2	8.3	17.1	6.2	49.7	6.2	6.2	2.97	1.61	Black

**Table II. Property values for the various Ca-M-Si-Al-O-N-F glasses**

	MV (cm <sup>3</sup> .mol <sup>-1</sup> )	FV (cm <sup>3</sup> .mol <sup>-1</sup> )	C	E (GPa)	μHv (GPa)	T <sub>g DTA</sub> (°C)	CTE (10 <sup>-6</sup> K <sup>-1</sup> )
<b>Mg (eq.%)</b>							
0	7.94	3.73	0.5295	96	6.29	722	10.4
5	7.77	3.62	0.5345	101	6.59	710	9.3
10	7.64	3.53	0.5379	106	6.92	707	9.0
15	7.50	3.44	0.5414	111	7.18	711	8.7
20	7.34	3.32	0.5470	115	7.40	713	8.8
25	7.22	3.26	0.5491	117	7.62	716	7.9
30	7.11	3.19	0.5513	121	7.86	739	7.7
<b>Er (eq.%)</b>							
1	8.02	3.81	0.5242	97	6.48	725	9.7
3	7.99	3.78	0.5262	99	6.60	720	9.5
5	7.94	3.73	0.5295	101	6.76	738	9.3
10	7.84	3.64	0.5362	106	7.11	762	8.2
15	7.71	3.51	0.5451	112	7.37	792	7.8
20	7.59	3.38	0.5543	118	7.84	810	7.2
<b>Nd (eq.%)</b>							
5	7.97	3.75	0.5293	100	6.54	726	9.6
10	7.96	3.73	0.5317	102	6.72	738	8.7
15	7.87	3.63	0.5392	106	7.15	761	8.2
20	7.83	3.57	0.5440	110	7.35	776	7.9
<b>Y (eq.%)</b>							
10	7.95	3.74	0.5293	104	6.93	746	8.4
20	7.75	3.54	0.5438	117	7.79	784	7.1
<b>ERROR VALUE</b>	±0.01	±0.01	±0.0005	±2	±0.2	±5	±0.2

MV – molar volume, FV – free volume, C – fractional glass compactness,  
E – Young's modulus, μHv – microhardness, T<sub>g DTA</sub> – glass transition temperature,  
CTE – coefficient of thermal expansion.

**Table III Linear regression analysis data for effect of ECFS on various properties for Ca-Mg modified glasses**

		<b>intercept</b>	<b>slope</b>	<b>standard error</b>	<b>R<sup>2</sup></b>
<b>MV</b>	(cm <sup>3</sup> .mol <sup>-1</sup> )	8.81	-0.45	0.018	0.997
<b>FV</b>	(cm <sup>3</sup> .mol <sup>-1</sup> )	4.31	-0.30	0.018	0.993
<b>C</b>		0.5066	0.0119	0.0011	0.985
<b>E</b>	(GPa)	70.67	13.22	1.04	0.989
<b>μHv</b>	(GPa)	4.67	0.84	0.05	0.994
<b>CTE</b>	(K <sup>-1</sup> )	1.26x10 <sup>-5</sup>	-1.28 x10 <sup>-6</sup>	3.08 x10 <sup>-7</sup>	0.903

**Table IV Linear regression analysis data for effect of ECFS on various properties for Ca-M modified glasses (M = Mg, Er, Nd or Y).**

		intercept	slope for ECFS	slope for TpM	standard error	R <sup>2</sup>
<b>MV</b>	(cm <sup>3</sup> .mol <sup>-1</sup> )	8.32	-0.50	0.53	0.046	0.9737
<b>FV</b>	(cm <sup>3</sup> .mol <sup>-1</sup> )	4.38	-0.35	0.08	0.047	0.9439
<b>C</b>		0.4701	0.0153	0.0203	0.0031	0.8913
<b>E</b>	(GPa)	47.03	13.82	17.42	0.898	0.9879
<b>μHv</b>	(GPa)	2.78	0.82	1.55	0.068	0.9827
<b>TgDTA*</b>	(°C)	542.46	76.11	18.71	8.0	0.9395
<b>CTE</b>	(K <sup>-1</sup> )	1.77x10 <sup>-5</sup>	-1.19x10 <sup>-6</sup>	-4.35x10 <sup>-6</sup>	2.46x10 <sup>-7</sup>	0.9337

\* Analysis for TgDTA does not include Ca-Mg modified glasses

Figure Captions

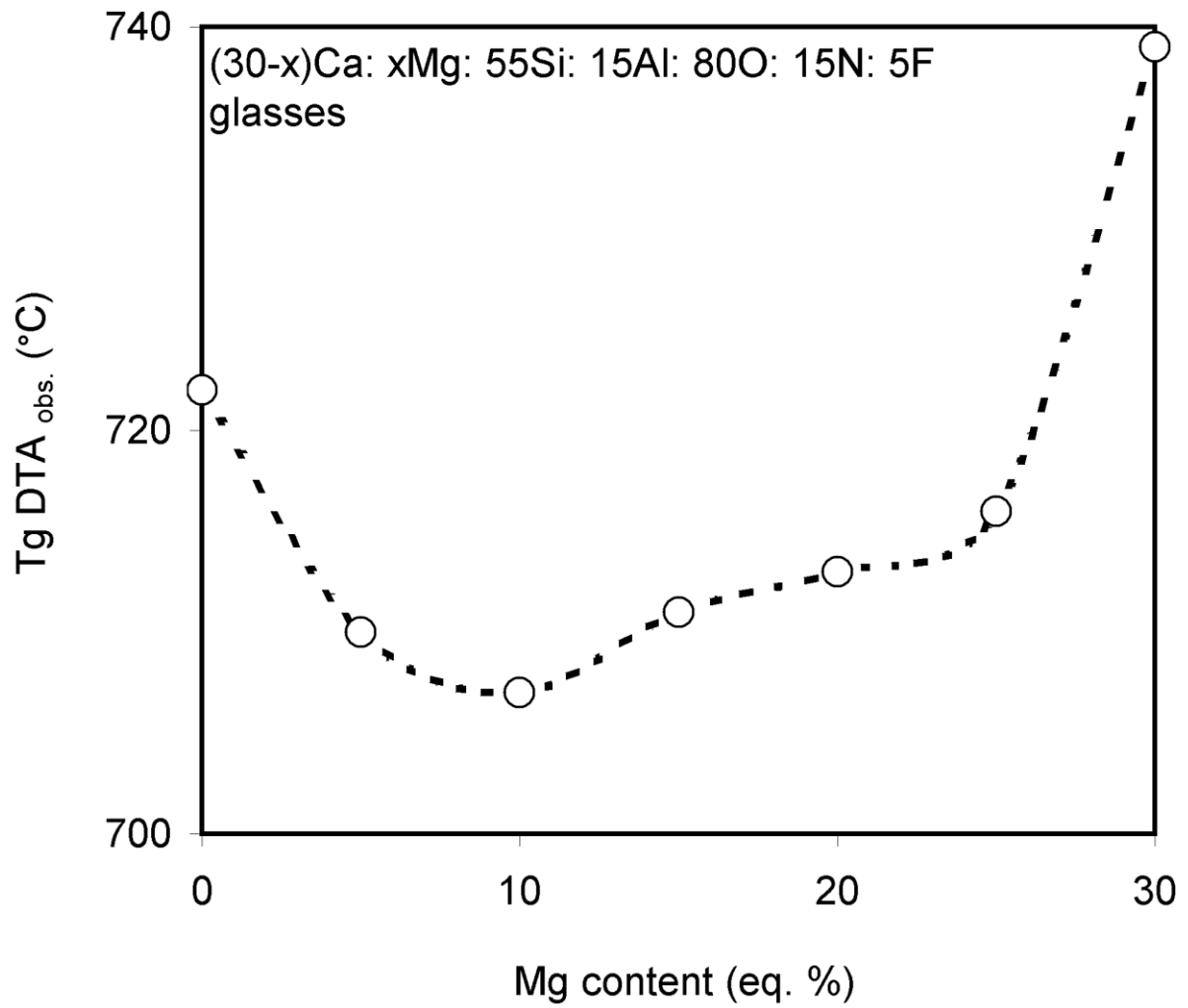
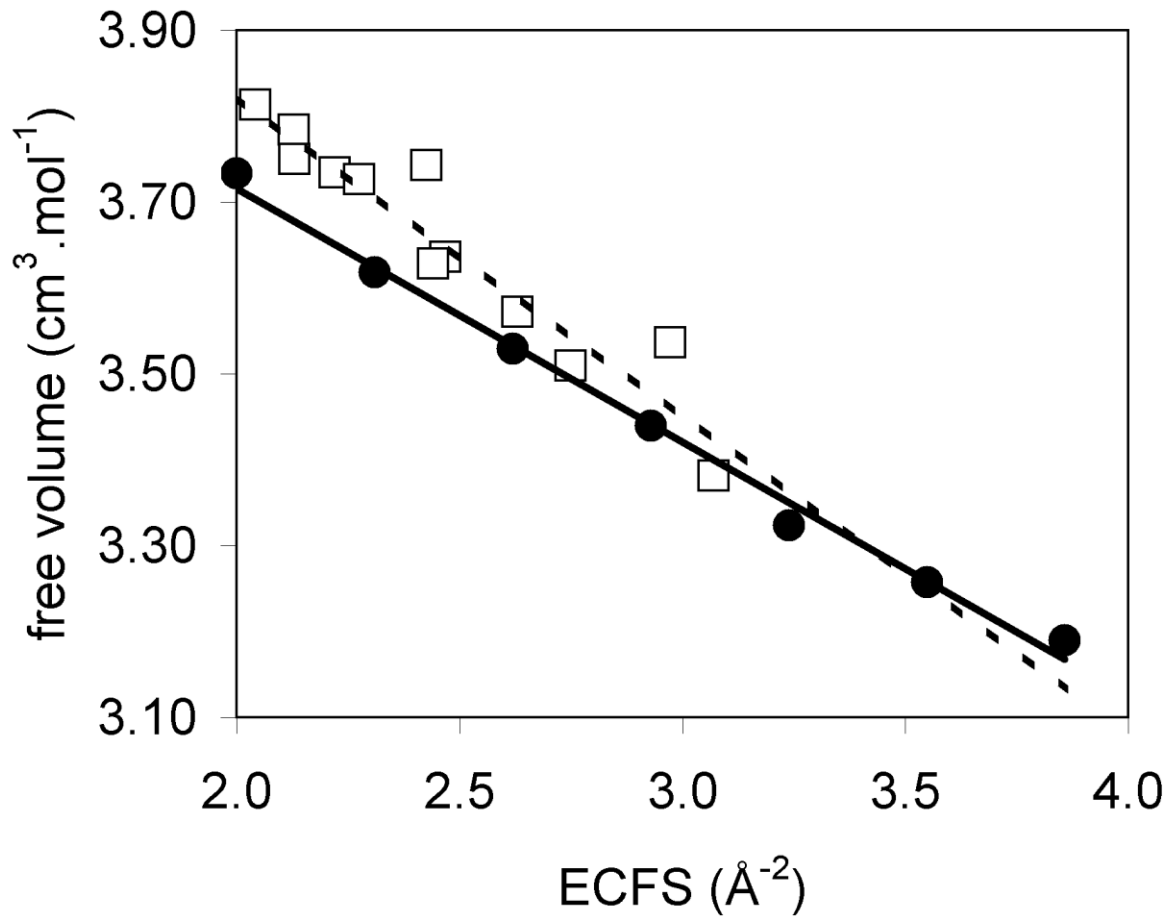


Figure 1. Effect of magnesium substitution level on glass transition temperature of Ca-Mg-Si-Al-O-N-F glasses





● Ca-Mg □ Ca-(Er or Nd or Y)

Figure 2 Effect of effective cation field strength on free volume of Ca-Mg and Ca-M(III)

modified glasses [M(III) = Er, Nd, Y]

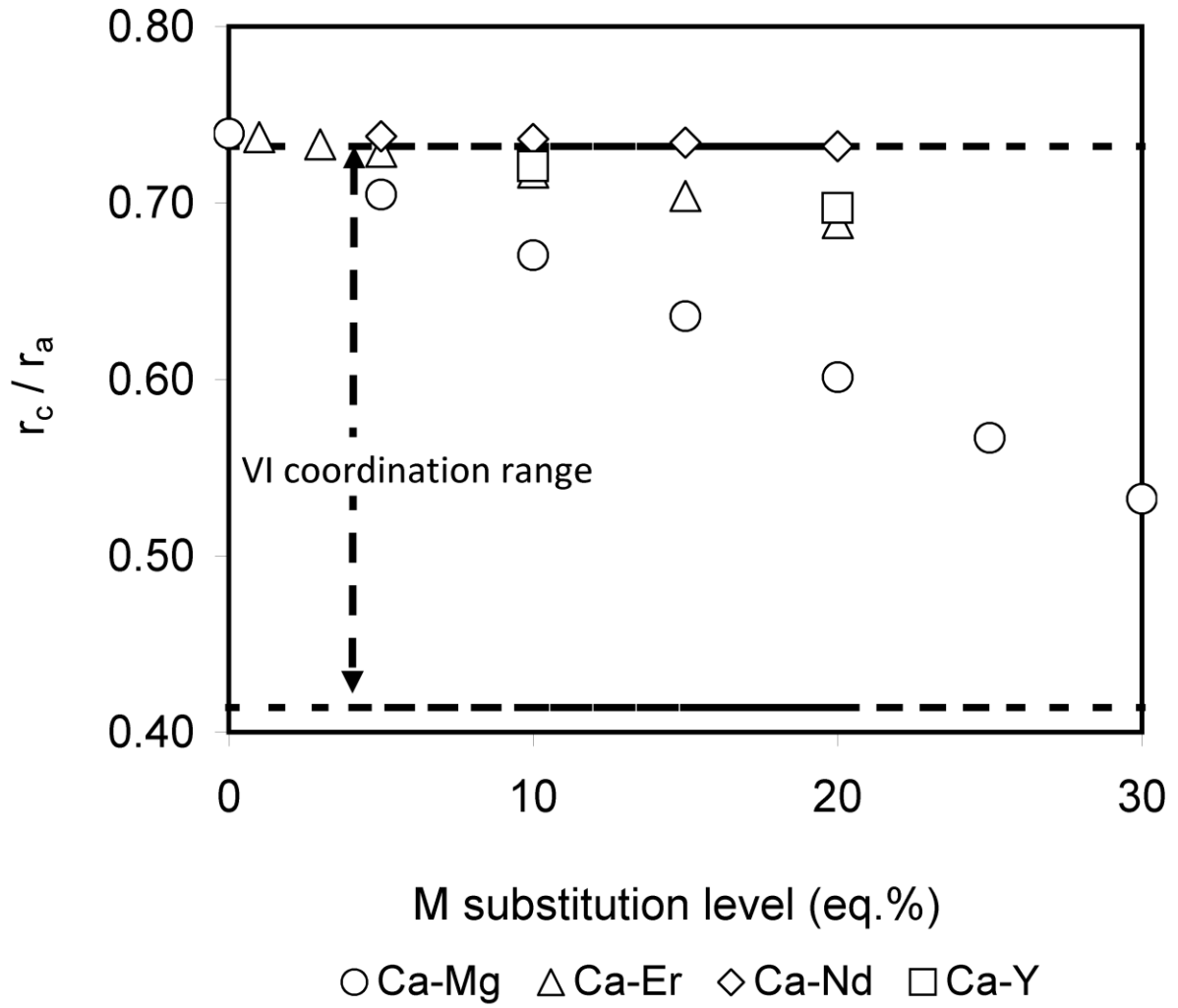
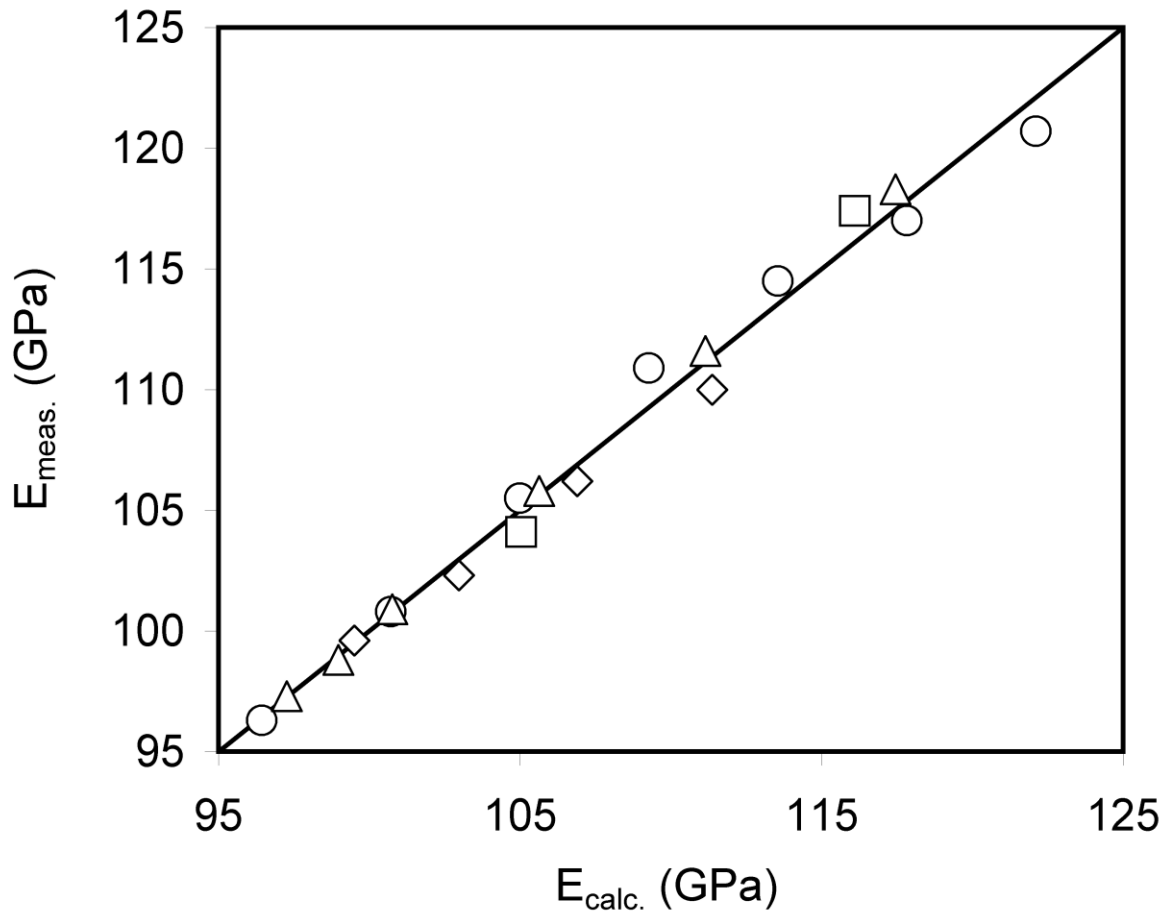
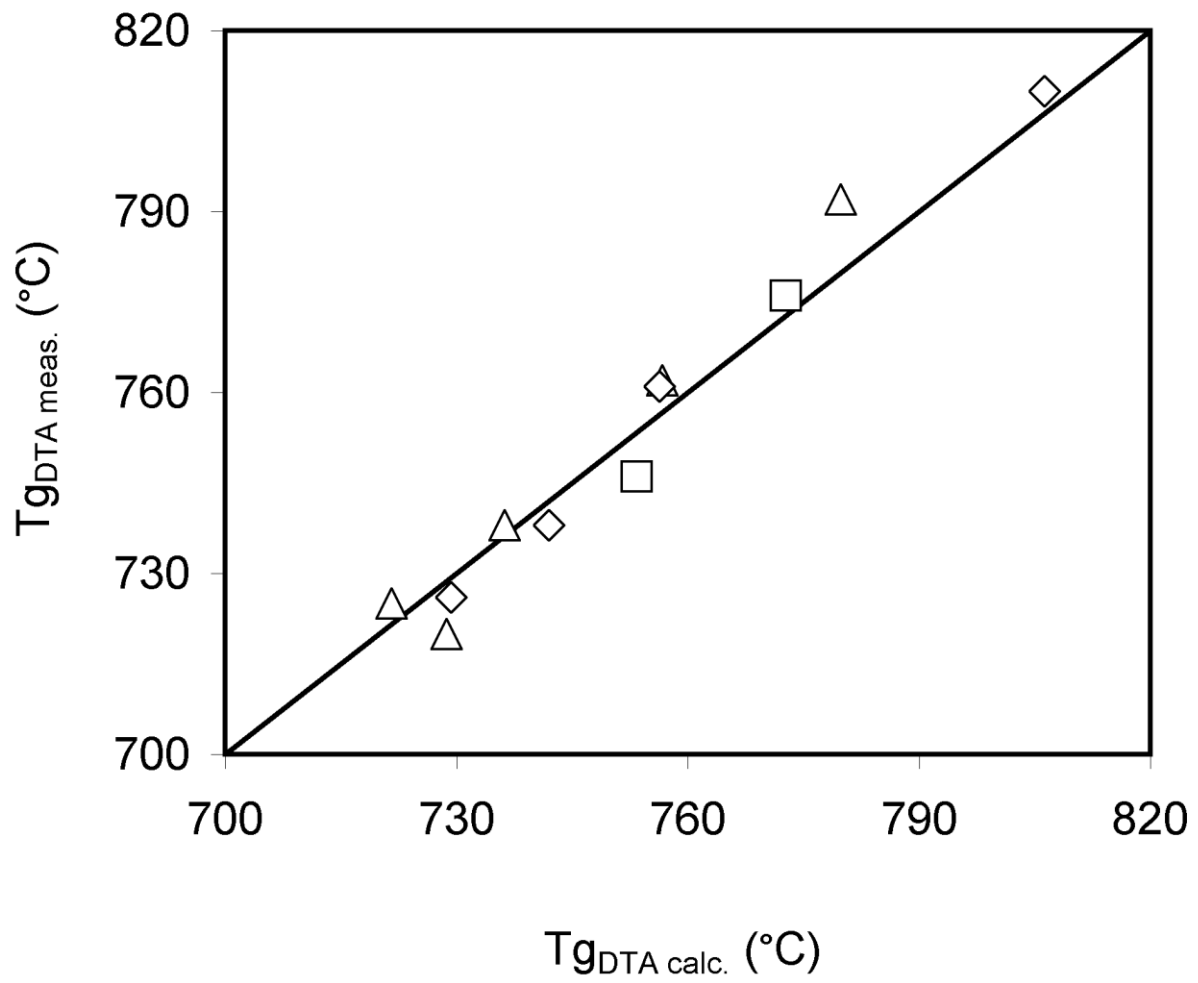


Figure 3. Radius ratio values for average anion and cation radii indicating that values lie in or close to VI coordination values



○ Ca-Mg    △ Ca-Er    ◇ Ca-Nd    □ Ca-Y    — best fit

Figure 4 Comparison of measured values for Young's modulus and those calculated using linear regression data in Table IV



$\triangle$  Ca-Er    $\diamond$  Ca-Nd    $\square$  Ca-Y   — best fit

Figure 5 Comparison of measured values for glass transition temperature and Tg values calculated using linear regression data in Table IV (Ca-(Er, Nd, Y) glasses only)