Available online at www.sciencedirect.com

SciVerse ScienceDirect

Journal of the European Ceramic Society 32 (2012) 849–857

www.elsevier.com/locate/jeurceramsoc

Effects of nitrogen and fluorine on crystallisation of Ca–Si–Al–O–N–F glasses

Amir Reza Hanifi, Annaïk Genson, Wynette Redington, Michael J. Pomeroy, Stuart Hampshire*

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

Received 20 May 2011; received in revised form 10 October 2011; accepted 17 October 2011
Available online 23 November 2011

Abstract

The effect of nitrogen and fluorine substitution on the crystallisation of a new generation of oxyfluoronitride glasses in the Ca–Si–Al–O–N–F system has been studied. Glasses were nucleated for 5 h at the nucleation temperature of Tg + 50 °C and crystallised for 10 h at the maximum crystallisation temperature (900–1050 °C depending on the glass composition) determined from differential thermal analysis. For the oxide glass, crystallisation results in formation of wollastonite ($CaSiO_3$), gehlenite ($Ca_2Al_2SiO_7$) and anorthite ($CaAl_2Si_2O_8$) along with a small amount of residual glass. For crystallisation of oxyfluoride glasses (0 equiv.% N), when fluorine content increases, cuspidine ($Ca_4Si_2O_7F_2$) is the major crystalline phase at the expense of gehlenite while in oxyfluoronitride glasses containing 20 equiv.% N, gehlenite is always the dominant crystalline phase at different fluorine contents. At constant fluorine content (5 equiv.%), an increase in nitrogen content favours the formation of gehlenite rather than anorthite or wollastonite suggesting that this phase may be able to accommodate N into its crystal structure. While a small amount of nitrogen substitution for oxygen can be assumed in the gehlenite structure, the residual glass in the glass-ceramic is expected to be very N-rich. In terms of properties, hardness is shown to be more sensitive to changes in microstructure, phase morphology and crystal size compared with elastic modulus which is related to the amounts of constituent phases present.

© 2011 Elsevier Ltd. All rights reserved.

Keywords: C. Mechanical properties; D. Glass ceramics; D. Sialon

1. Introduction

Oxynitride glasses are silicates and alumino-silicates in which nitrogen atoms substitute for oxygen in the glass network and their glass formation, properties and crystallisation have been the subject of extensive research over many years.[1–12] Nitrogen incorporation enhances glass formation and results in increases in properties such as elastic moduli, microhardness, glass transition and softening temperatures, viscosity, glass density and fractional compactness because of extra cross linkages in the glass network.

Fluorine as a non-bridging anion in calcium alumino-silicate glasses[13] acts as a powerful network disrupter which substitutes for bridging oxygen ions and thus reduces glass transition temperature and viscosity. When fluorine is introduced into Ca–Si–Al–O–N glasses, it extends the glass forming region in the Ca–Si–Al–O–N–F system[14] and considerable reductions in liquidus temperatures are observed (up to ~800 °C at more Ca-rich compositions). Fluorine also facilitates the solution of higher amounts of nitrogen (up to 40 equiv.% N) into glasses compared with the Ca–Si–Al–O–N system.[15] Fluorine has the effect of lowering glass transition temperature and melting temperatures of these glasses but has no effect on the elastic modulus or microhardness.[15]

As with other silicate glasses, oxynitride glasses may be heat treated at the appropriate temperatures to crystallise as glass–ceramics and many studies of crystallisation of these types of glasses have been reported[16–25], particularly in the Y–Si–Al–O–N system. In general, nitrogen increases the stability of oxynitride glasses. The conventional process to produce a glass-ceramic involves two steps: a lower temperature heat treatment of glasses, generally just above the glass transition temperature, to induce nucleation followed by heating to a second higher temperature, the so-called crystallisation temperature, to allow growth of the pre-formed nuclei.[24] The crystalline phases formed depend on both the composition of the parent

---

* Corresponding author. Tel.: +353 61 202640; fax: +353 61 202967.
E-mail address: stuart.hampshire@ul.ie (S. Hampshire).

0955-2219/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2011.10.026

Table 1
Thermal properties of Ca–Si–Al–O–N–F glasses as a function of fluorine or nitrogen contents.

Ca (equiv.%)	Si (equiv.%)	Al (equiv.%)	O (equiv.%)	N (equiv.%)	F (equiv.%)	Tg_{DTA} (°C)	Tc_1 (°C)	Tc_2 (°C)	Tc_3 (°C)	Tm (°C)
28	57	15	100	0	0	810	1090	–	–	1269
			99	0	1	773	1020	–	–	1235
			97	0	3	736	1013	–	–	1192
			95	0	5	698	907	–	–	1173
			80	20	0	848	1043	–	–	1261
			79	20	1	829	996	–	–	1212
			77	20	3	781	922	1027	–	1175
			75	20	5	756	925	999	1050	1173
			95	0	5	698	907	–	–	1173
			90	5	5	707	1014	–	–	1177
			85	10	5	713	897	1034	–	1171
			80	15	5	734	883	1041	–	1174
			75	20	5	756	925	999	1050	1173

glass and the heat-treatment process but in many cases, oxide phases form first leaving the residual glass more N-rich.

Fluorine addition to alumino-silicate glasses[26] tends to cause phase separation and aids bulk crystallisation by lowering viscosity and results in glass–ceramics with controlled microstructures and related beneficial mechanical properties. The current study was undertaken to investigate the effects of both nitrogen and fluorine on crystallisation of calcium alumino-silicate glasses and to compare some properties of the resulting glass–ceramics.

2. Experimental procedure

Compositions for oxynitride glasses are usually expressed in equivalent percent (equiv.%).[1,2] A base calcium alumino-silicate glass was prepared with a cation composition (in equiv.%) of 28Ca:57Si:15Al and 100 equiv.% oxygen. A range of glasses was prepared in which this cation composition was maintained constant while anion compositions were varied as shown in Table 1. In two series of glasses with, respectively, 0 and 20 equiv.% N, 0, 1, 3 and 5 equiv.% F was substituted for oxygen in order to evaluate the effects of fluorine on crystallisation of oxide and oxynitride glasses. In a further series of glasses with a constant fluorine substitution of 5 equiv.% for oxygen, 0, 5, 10, 15 and 20 equiv.% N were substituted for oxygen in order to evaluate the effects of nitrogen on crystallisation of oxide and oxyfluoride glasses.

Glasses were prepared by mixing SiO_2 (99.9% purity, Quartz, Fluka Chemika, Buchs, Switzerland), Al_2O_3 (99.995% purity, AKP53, Sumitomo Chemical, Tokyo, Japan) and CaO (99.9% purity, Fisher Scientific, Dublin, Ireland) powders with additionally silicon nitride (99.9% purity, SNE-10, UBE, Tokyo, Japan) and/or CaF_2 (99.9% purity, Aldrich Chemicals, Dublin, Ireland) as appropriate, in isopropanol in a ball mill with alumina milling media for 5 h. The alcohol was then evaporated in a rotary evaporation unit for a further 1 h. The mixed powders were then isostatically pressed into pellets under a pressure of 150 MPa and subsequently melted in a boron nitride lined graphite crucible at 1650 °C under flowing nitrogen for 1 h in a sealed vertical alumina tube furnace (lanthanum chromite heating elements). The crucible was then removed quickly from the furnace and the melt poured into a pre-heated graphite mould (~900 °C). The glass was then annealed for 1 h in a muffle furnace at the glass transition temperature, which had been previously determined on a smaller test glass batch of the same composition, and then furnace cooled slowly to ambient temperature. In the case of glasses not containing nitrogen, melting was carried out at 1400 °C in a carbolite BLF 1800 furnace under air for 1 h. The same casting and annealing conditions were used as for the glasses containing nitrogen. Glasses were cut into specimens with dimensions 15 mm × 10 mm × 3 mm for heat treatment.

In order to determine glass transition temperature (Tg), crystallisation temperature (Tc) and melting point (Tm), differential thermal analysis (DTA) was carried out on dry glass powders of particle size in the range 45–106 μm heated at 10 °C/min to 1350 °C under flowing nitrogen in a Stanton-Redcroft STA 1640 instrument (Polymer Labs, Rheometric Scientific, Epsom, UK) using Al_2O_3 as a reference material. The onset point of an endothermic drift on the DTA curve corresponding to the beginning of the glass transition range is reported as Tg while the peak of the exotherm is taken as Tc. The final endotherm corresponds to Tm. Errors in measurement are ±2 °C.

Glasses were heat treated in a Lenton horizontal furnace under flowing nitrogen with a heating rate of 20 °C/min to the nucleation temperature of Tg + 50 °C, with a hold for 5 h followed by heating at 10 °C/min to the crystallisation temperature Tc with a hold for 10 h followed by removal from the furnace. The crystallised glass–ceramics were cleaned in distilled water and dried in an oven at 100 °C for subsequent analysis. X-ray diffraction (XRD) analysis was carried out on crushed powder samples (<45 μm) mixed with KCl as an internal standard using a Philips X'pert MPD PRO X-ray diffractometer (PANalytical, Almelo, The Netherlands) with Cu-Kα_1 X-radiation, 40 kV and 35 mA, in the range $2\theta = 10–70°$. To identify the crystalline phases, XRD patterns were analysed by X'pert High Score software using ICDD database.

To determine the effect of nitrogen on the lattice parameters of gehlenite ($Ca_2Al_2SiO_7$), two compositions were prepared using (1) SiO_2, Al_2O_3, CaO and (2) SiO_2, Al_2O_3, CaO with Si_3N_4 and fired at 1600 °C for 1 h as follows:

(1) “pure” gehlenite of composition 28.57Ca:28.57Si:42.86Al:100O (in equiv.%) fired under air;
(2) “N-gehlenite” with the same cation composition and substitution of 20 equiv.% N for oxygen (28.57Ca:28.57Si:42.86Al:80O:20N equiv.%) fired under 0.1 MPa nitrogen.

Samples were cooled at 1 °C/min to room temperature. XRD analysis was carried out on crushed powder samples as described. The corrected *d*-spacings of the (0 0 2) and (3 1 0) peaks of tetragonal gehlenite were taken into account to determine “c” and “a” parameters, respectively.

Scanning Electron Microscopy (SEM) was carried out on cut samples of glass–ceramics mounted in epoxy resin and polished to 1 μm with diamond slurries. The mirror surfaces of specimens were sputtered with a gold coating and a JEOL JSM-840 scanning electron microscope was employed for observing the crystal morphology and Energy Dispersive X-ray analysis (EDX) was used to obtain chemical analysis of particular crystals or regions.

The elastic moduli of glasses and glass–ceramics were measured using specimens of 15 mm × 10 mm × 3 mm. Longitudinal, v_l, and transverse, v_t, ultrasonic wave velocities were determined by means of 10 MHz piezoelectric transducers. The Young’s modulus (*E*) was calculated using Eq. (1).

$$E = \rho \cdot \left\{ \frac{3v_l^2 - 4v_t^2}{(v_l/v_t)^2 - 1} \right\} \tag{1}$$

Microhardness tests were carried out using a LECO (M400 G1) microhardness tester with a 136° diamond pyramid indenter. The load used was 300 g and it was applied for 10 s indentation to glass surfaces polished to a 1 μm diamond finish. The results given represent the mean of microhardness obtained from 20 indentations.

3. Results

Weight change measurements carried out show that there was less than 1% weight loss following glass melting indicating that N losses as SiO/N_2 or F losses as SiF_4 were insignificant. This was confirmed for glasses containing 20 equiv.% N and 5 equiv.% F by careful energy dispersive X-ray analysis using $CaMoO_4$, SiO_2, Al_2O_3, BN and SmF_3 to generate Ca, Si, Al, O, N and F standards under the same analysis conditions as the glasses.

The glass transition, crystallisation and melting temperatures of the glasses studied are presented in Table 1. The base oxide glass melts at 1269 °C (Tm), has a glass transition temperature (Tg) of 810 °C and a crystallisation temperature (Tc) of 1090 °C. Substitution of 1 equiv.% F results in significant decreases of Tm by 34 °C, Tg by 37 °C and Tc by 70 °C. Further reductions occur as 3 and 5 equiv.% F are substituted with Tm decreasing to 1192 °C and 1173 °C and Tc to 1013 °C and 907 °C, respectively. The change in Tg from 1 to 5 equiv.% F is linear at −19 °C per equiv.% F.

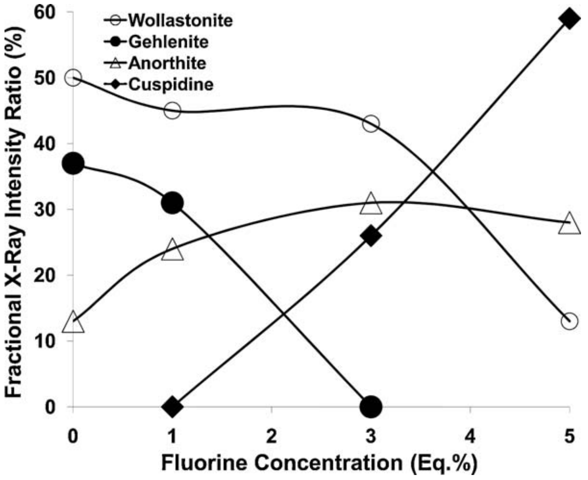

Fig. 1. Effect of fluorine content on crystallisation products of Ca–Si–Al–O–F glasses (0 equiv.% N).

With addition of 20 equiv.% N to the oxide and oxyfluoride glasses, melting temperatures reduce slightly while Tg increases by 38 °C with 0 equiv.% F and by 45–58 °C when F is present. Crystallisation temperatures also decrease with N for 0–3 equiv.% F by 24–47 °C and at this level of fluorine, two crystallisation peaks are observed at 922 and 1027 °C. At 5 equiv.% F, the initial Tc is at a slightly higher temperature (927 °C) than for the oxyfluoride glass without N but two more crystallisation peaks are observed at 999 and 1050 °C which means that inclusion of both N and F leads to crystallisation of three phases in distinct steps.

It should be noted that all the glasses at different nitrogen contents have similar melting points to the oxyfluoride glasses, indicating that in the presence of the powerful network disrupter, fluorine, nitrogen has virtually no effect on melting temperature.

Following heat treatment of the glasses under flowing nitrogen at Tg + 50 °C for 5 h and at Tc for 10 h, the glass–ceramics produced were analysed by XRD and SEM. Figs. 1–3 and Table 2 present the changes in phase assemblages and proportions of crystalline phases in oxyfluoride

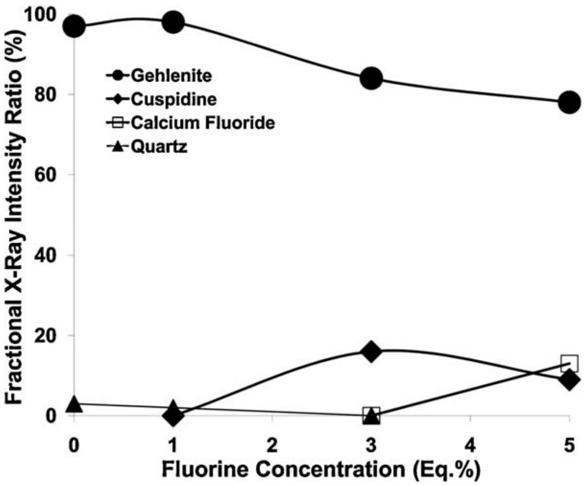

Fig. 2. Effect of fluorine content on crystallisation products of Ca–Si–Al–O–N–F glasses containing 20 equiv.% N.

Table 2
Crystalline products from oxyfluoride and oxyfluoronitride glasses as a function of fluorine or nitrogen contents (PW, pseudo-wollastonite; W, wollastonite; G, gehlenite; A, anorthite; P, cuspidine; Q, quartz; F, calcium fluoride).

Ca (equiv.%)	Si (equiv.%)	Al (equiv.%)	O (equiv.%)	N (equiv.%)	F (equiv.%)	Phase 1 (equiv.%)	Phase 2 (equiv.%)	Phase 3 (equiv.%)
28	57	15	100	0	0	PW (50%)	G (37%)	A (13%)
			99	0	1	W (45%)	G (31%)	A (24%)
			97	0	3	W (43%)	P (26%)	A (31%)
			95	0	5	W (13%)	P (59%)	A (28%)
			80	20	0	G (97%)	Q (3%)	–
			79	20	1	G (98%)	Q (2%)	–
			77	20	3	G (84%)	P (16%)	–
			75	20	5	G (78%)	P (9%)	F (13%)
			95	0	5	W (13%)	P (59%)	A (28%)
			90	5	5	W (13%)	P (51%)	A (36%)
			85	10	5	W (8%)	P (58%)	A (34%)
			80	15	5	G (60%)	P (30%)	A (10%)
			75	20	5	G (78%)	P (9%)	F (13%)

JCPDS of the crystalline phases; PW, PDF 74-0874; G, PDF 79-1725; A, PDF 41-1486; W, PDF 84-0654; P, PDF 11-0075; Q, PDF 83-2469; F, PDF 87-0971.

glass–ceramics as a function of fluorine content (Fig. 1) and oxyfluoronitride glass–ceramics as a function of fluorine content (Fig. 2) and nitrogen content (Fig. 3). It should be emphasised that some residual glass is also present in different proportions depending on the composition. XRD patterns of the crystallised oxide (28Ca:57Si:15Al:100O equiv.%), oxyfluoride (28Ca:57Si:15Al:95O:5F equiv.%), oxynitride (28Ca:57Si:15Al:80O:20N equiv.%) and oxyfluoronitride (28Ca:57Si:15Al:75O:20N:5F equiv.%) glass–ceramics are compared together in Fig. 4. It is noted that the parent glasses studied are well crystallised and some similar phases present in them.

The base oxide glass crystallised to form 50% pseudo-wollastonite ($CaSiO_3$), the synthetic high temperature form, 37% gehlenite ($Ca_2Al_2SiO_7$) and 13% anorthite ($CaAl_2Si_2O_8$) along with a small amount of residual glass. The microstructure of the glass-ceramic formed from the oxide glass is shown in Fig. 5(a). Flower shaped crystals of pseudo-wollastonite can be seen as the major crystalline phase. Addition of 1 equiv.% fluorine results in similar crystalline phases obtained compared with the oxide glass but a network of wollastonite crystals is formed rather than pseudo-wollastonite and the amount is reduced as is also the amount of gehlenite while anorthite increases and these two phases appear among the wollastonite as shown in Fig. 5(b). Fluorine remains in the residual glassy phase of this glass-ceramic. Increasing the fluorine content further to 3 equiv.% leads to the appearance of cuspidine ($Ca_4Si_2O_7F_2$), which are the very light grey crystals shown in the micrograph in Fig. 5(c). Gehlenite has disappeared, while the amount of wollastonite (light grey crystals) decreases slightly and anorthite (dark grey crystals) reaches its maximum (~30%). The black matrix is the residual glassy phase which does not tend to crystallise further. The size of the crystals is very large, of the order of 100 μm or greater. Disappearance of gehlenite provides the required concentrations of Ca and Si for precipitation of the cuspidine phase. At 5 equiv.% fluorine, there is sufficient F present to allow the glass to crystallise more readily to cuspidine, the major phase shown as very light grey dendritic crystals in Fig. 5(d). This

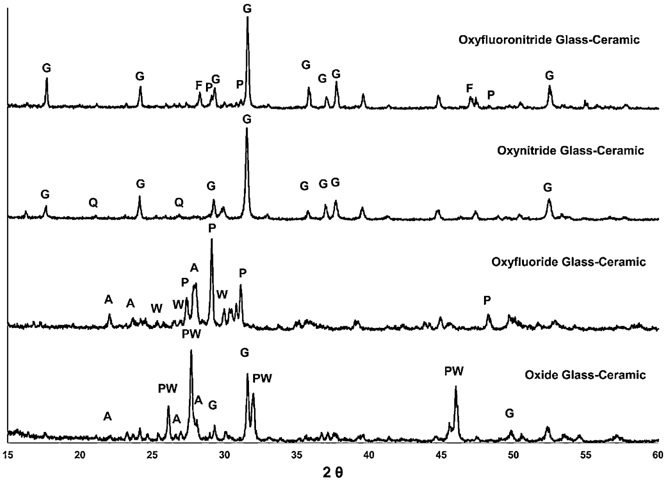

Fig. 4. XRD patterns of the crystallised oxide (28Ca:57Si:15Al:100O equiv.%), oxyfluoride (28Ca:57Si:15Al:95O:5F equiv.%), oxynitride (28Ca:57Si:15Al:80O:20N equiv.%) and oxyfluoronitride (28Ca:57Si:15Al:75O:20N:5F equiv.%) glass–ceramics (PW, pseudo-wollastonite; W, wollastonite; G, gehlenite; A, anorthite; P, cuspidine, Q; quartz; F, calcium fluoride).

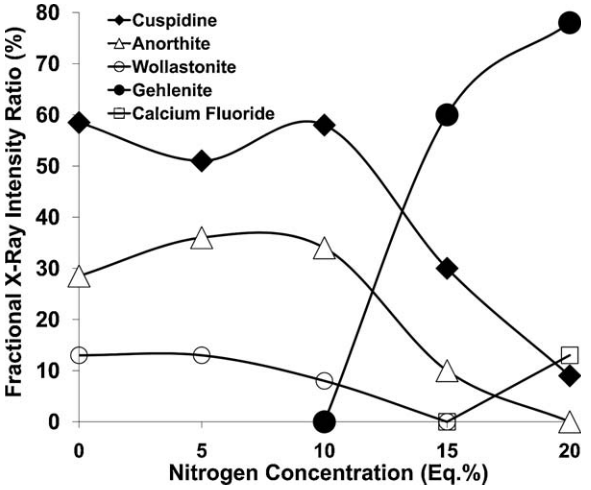

Fig. 3. Effect of nitrogen content on crystallisation products of Ca–Si–Al–O–N–F glasses containing 5 equiv.% F.

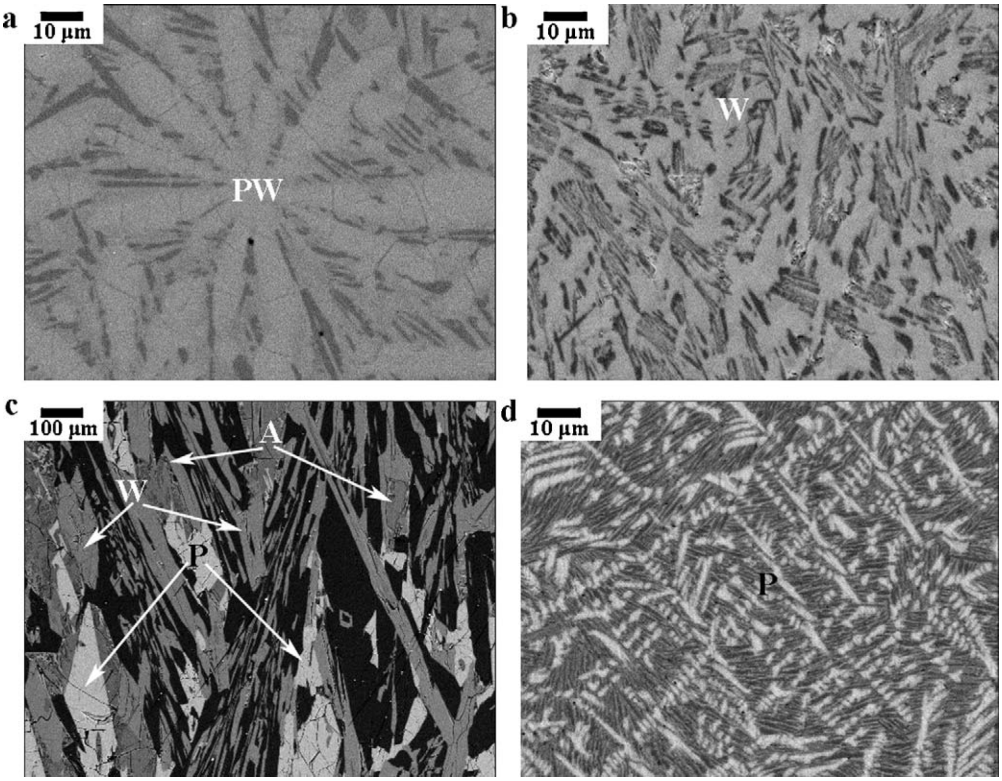

Fig. 5. Back scattered SEM micrographs of oxyfluoride glass–ceramics. (a) 28Ca:57Si:15Al:100O equiv.%, (b) 28Ca:57Si:15Al:99O:1F equiv.%, (c) 28Ca:57Si:15Al:97O:3F equiv.% and (d) 28Ca:57Si:15Al:95O:5F equiv.% (PW, pseudo-wollastonite; W, wollastonite; G, gehlenite; A, anorthite; P, cuspidine).

reduces the amounts of Ca and Si available to form wollastonite, in particular, and so its content decreases considerably. Wollastonite and anorthite crystals have grown in the intervening spaces between the cuspidine dendrites.

The phase assemblages for the oxyfluoronitride glasses containing 20 equiv.% N as a function of F content (see Table 2) are quite different when compared with the oxyfluoride glasses, as gehlenite is the dominant phase at all fluorine contents. Fig. 6 shows the microstructures of these oxyfluoronitride glass–ceramics. The microstructure of the oxynitride glass of composition (in equiv.%) 28Ca:57Si:15Al:80O:20N is shown in Fig. 6(a) and crystallises to form small columnar crystals of gehlenite with lengths of 2–3 μm and diameters of <1 μm and a minor amount of quartz (black regions). Addition of 1 equiv.% F does not change the crystallisation products but the gehlenite crystals have grown as a result of fluorine addition to 5–15 μm, some with a more equiaxed morphology but the columnar structure can still be observed as shown in Fig. 6(b). The fluorine remains in the residual glass. At 3 equiv.% F, the amount of gehlenite decreases slightly but it still retains its columnar appearance with crystals >10 μm as can be seen (grey crystals) in Fig. 6(c). Quartz disappears to provide sufficient Ca and Si for crystallisation of cuspidine (very light grey crystals). The residual glassy phase (dark grey) is more obvious and it is stable enough not to crystallise readily. Finally with the addition of 5 equiv.% F, the amount of gehlenite reduces slightly to ∼80% and calcium fluoride (CaF_2) appears as the secondary fluorine-containing phase as well as cuspidine. As shown in Fig. 6(d), the gehlenite crystals (grey) have grown significantly to form large crystals with sizes in the range 20–50 μm which have impinged on their neighbouring crystals. There is a substantial amount of residual glass (dark grey matrix) with very light grey small cuspidine and calcium fluoride growths entrapped. EDX analysis confirms the types of crystalline phases in the microstructures.

The microstructures of the oxyfluoronitride glass–ceramics containing 5 equiv.% F as a function of N content are shown in Figs. 5(d), 6 and 7(d). Without nitrogen present – Fig. 5(d), the microstructure consists of a dendritic network of cuspidine crystals (very light grey) with wollastonite (grey) and anorthite (dark grey) appearing as thin platelets among the dendrites. A similar microstructure is also evident for the glass-ceramic containing 5 equiv.% N and 5 equiv.% F as shown in Fig. 7(a) with the amount of anorthite increasing slightly at the expense of cuspidine. The addition of 10 equiv.% nitrogen does not change significantly the phase assemblage or amounts of crystalline phases formed but the morphology of the thin wollastonite platelets and the dendritic cuspidine crystals change to form smaller more eqiaxed crystals as shown in Fig. 7(b). It is difficult to distinguish the anorthite from the wollastonite in this micrograph. The darkest phase is the residual glass. Further nitrogen incorporation to 15 equiv.% leads to the disappearance of wollastonite and reductions of the amounts of cuspidine and anorthite, which provides sufficient Ca, Si and Al for crystallisation of gehlenite as shown by the grey crystals in Fig. 7(c) and this is the dominant phase (60%) at high nitrogen concentrations. The lighter crystals are cuspidine and the darker grey are anorthite and residual glass is evident as the black phase in which some of the fluorine is concentrated. At 20 equiv.% N, the

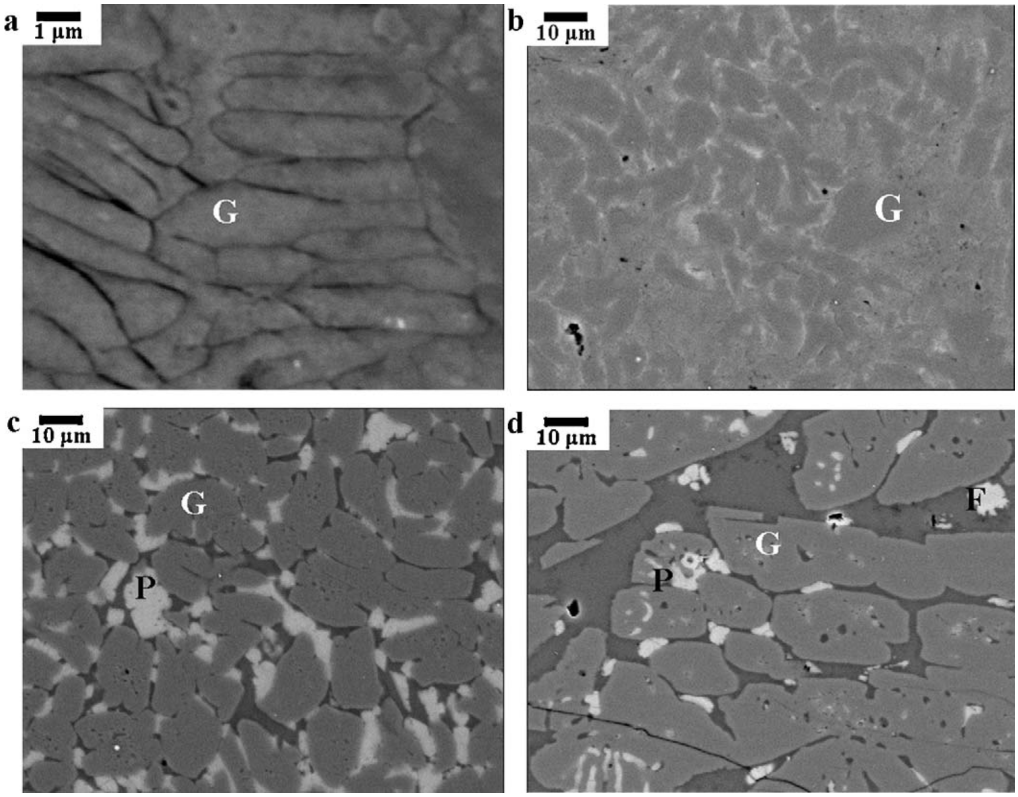

Fig. 6. Back scattered SEM micrographs of oxyfluoronitride glass–ceramics. (a) 28Ca:57Si:15Al:80O:20N equiv.%, (b) 28Ca:57Si:15Al:79O:20N:1F equiv.%, (c) 28Ca:57Si:15Al:77O:20N:3F equiv.% and (d) 28Ca:57Si:15Al:75O:20N:5F equiv.% (G, gehlenite; P, cuspidine; F, calcium fluoride).

gehlenite content increases, the amount of cuspidine decreases and anorthite does not crystallise. Calcium fluoride appears as another fluorine-containing phase. The microstructure is shown in Fig. 6(d).

In this study, the phases which crystallised, as the nitrogen content of the glasses was varied, were all known silicates or aluminosilicates suggesting that nitrogen may have substituted for oxygen in one or more of the crystalline phases or it may have remained in the residual glass. It is clear that with increasing nitrogen content in oxyfluoronitride glass–ceramics, gehlenite is stabilised instead of anorthite and wollastonite, again suggesting that gehlenite may potentially accommodate nitrogen into its crystal lattice and therefore its crystallisation would be expected from a high nitrogen-containing glass rather than anorthite or wollastonite.

Table 3 shows the Young's moduli and hardness of the oxyfluoride and oxyfluoronitride glasses and glass–ceramics as a function of fluorine or nitrogen contents. In the case of the oxide glass, the Young's modulus is 92 GPa and hardness is 6.1 GPa and these values remain constant as F content increases from 0 to 5 equiv.%. At fixed F content of 5 equiv.%, a gradual increase in both Young's modulus and hardness by ∼15–20% occurs with increasing N content. At a fixed N content of 20 equiv.%, these properties remain fairly constant with a slight decrease in microhardness observed as F content increases.

It is clear that the glass–ceramics all exhibit higher elastic moduli compared with their corresponding glasses at different fluorine or nitrogen contents. The highest value of Young's modulus at 134 GPa is observed for the glass-ceramic containing 20 equiv.% N and 1 equiv.% F and values of both elastic modulus and microhardness decrease with further increase in F content. Generally, Young's modulus of the glass–ceramics increases with N content. However, similar trends are not observed for microhardness and, depending on the fluorine or nitrogen contents, glass–ceramics exhibit lower or higher hardness values than their parent glasses and the hardness values do not show any trends as functions of F or N content. This is because of the complex nature of the microstructures produced by crystallisation.

4. Discussion

The oxide glass composition (28Ca:57Si:15Al:100O equiv.%) lies within the pseudowollastonite–gehlenite–anorthite compatibility triangle in the CaO–Al_2O_3–SiO_2 ternary phase diagram[27] and these three phases are the ones that crystallise after heat treatments of this oxide glass. Pseudo-wollastonite (β-$CaSiO_3$) with a triclinic structure is the high temperature polymorph of wollastonite (α-$CaSiO_3$) and its lattice parameters are different to those of wollastonite. The Tc for this glass was found to be 1090 °C which is close to the transformation temperature of α to β-$CaSiO_3$ under thermodynamic equilibrium conditions. Addition of 1 equiv.% fluorine decreases the Tc to 1020 °C which favours the crystallisation of α-$CaSiO_3$ instead of pseudo-wollastonite. Further fluorine increase leads to appearance of cuspidine,

Table 3
Elastic modulus and hardness of the Ca–Si–Al–O–N–F glasses and glass–ceramics as a function of nitrogen or fluorine contents.

Ca (equiv.%)	Si (equiv.%)	Al (equiv.%)	O (equiv.%)	N (equiv.%)	F (equiv.%)	Glasses		Glass–ceramics	
						E (GPa)	H (GPa)	E (GPa)	H (GPa)
28	57	15	100	0	0	92	6.1	109	5.0
			99	0	1	92	6.2	100	6.3
			97	0	3	92	6.1	104	6.5
			95	0	5	92	6.1	104	6.7
			80	20	0	107	7.5	123	6.9
			79	20	1	107	7.6	134	6.5
			77	20	3	105	7.2	127	6.1
			75	20	5	107	7.2	112	5.2
			95	0	5	92	6.1	104	6.7
			90	5	5	93	6.4	107	6.7
			85	10	5	96	6.7	115	7.1
			80	15	5	99	6.9	115	6.3
			75	20	5	107	7.2	112	5.2

containing F, in place of gehlenite. Fluorine has important effects on crystallisation of glasses to glass–ceramics as it affects the crystallisation mechanism by reducing the thermal energy barrier for crystallisation and also affects the crystalline phases formed and subsequent microstructures. A previous study[28] on the addition of fluorine to CaO–Al_2O_3–SiO_2 glasses showed that crystallisation of these glasses allows the formation of directional or columnar crystals as was observed in the current study. Based on the microstructures of the oxyfluoride glass–ceramics, it can be concluded that progressive additions of fluorine lead to significantly different morphologies and crystal sizes for cuspidine, anorthite and wollastonite phases and lead to different amounts of residual glass phase.

When N is present, however, cuspidine is a minor phase in the glass–ceramics and its content is controlled by gehlenite which is the major crystalline phase. With progressive fluorine additions, significant growth of the gehlenite crystals occurs because of the reduction of melt viscosity. The presence of gehlenite as the major crystalline phase was also confirmed by other crystallisation studies of Ca-SiAlON glasses.[7,29] Hampshire et al.[7] not only showed that gehlenite is the dominant crystalline phase following heat treatment of Ca-SiAlON glasses but also suggested that nitrogen may be soluble in the gehlenite crystal structure. Lederer et al.[30] also found that on crystallisation of Zr-doped Mg–Ca–Si–Al–O–N glasses, the main crystalline phase changes from anorthite to gehlenite with increasing nitrogen content and concluded that gehlenite should be able to accommodate more nitrogen into its structure than anorthite. It should be noted that gehlenite is stable up to 5 equiv.% F, probably due to the effect of nitrogen and it reduces only slightly as F content increases to allow the crystallisation of fluorine-containing phases.

In order to assess the potential of N to dissolve in the gehlenite structure, "pure" gehlenite of composition 28.57Ca:28.57Si:42.86Al:100O (in equiv.%) was fired under air and the XRD pattern was compared with that of "N-gehlenite" with the same cation composition and substitution of 20 equiv.% N for oxygen (28.57Ca:28.57Si:42.86Al:80O:20N equiv.%), fired under 0.1 MPa nitrogen. The results for the lattice parameters of gehlenite and gehlenite + 20 equiv.% N are shown in Table 4 and it can be seen that there is a slight difference in cell parameters with nitrogen. These differences are only marginal since the values of ionic radii of both anions (144 pm for nitrogen and 135 pm for oxygen)[31] are very close and it is also expected that there will only be a substitution of N for oxygen. In gehlenite ($Ca_2Al_2SiO_7$), if 1 oxygen atom is replaced by 1 N, then 1 Si should substitute for 1 Al to charge balance the composition so the assumed N-gehlenite composition will be $Ca_2AlSi_2O_6N$. Crystallisation of oxyfluoronitride glasses with cation composition (in equiv.%) of 28Ca:57Si:15Al ($Ca_{14}Al_5Si_{14.25}$ in at.%) tends to result in formation of gehlenite only above 10 equiv.% N. This composition has slightly less Al than in the assumed N-gehlenite formula ($Ca_2AlSi_2O_6N$) and therefore it may substitute less than 1 in 7 oxygen by nitrogen atoms and such a composition would not show a considerable difference in lattice parameters compared with ($Ca_2Al_2SiO_7$). Such a low level of N substitution in the gehlenite should lead to the formation of a nitrogen-rich residual glass phase in the glass-ceramic. Whereas the formation of gehlenite is enhanced with N addition as confirmed by other researchers,[30] it can be concluded that, when the nitrogen content increases in the parent oxyfluoronitride glass, a nitrogen rich glassy phase also forms as well as gehlenite. Previous work has shown that on crystallisation of an oxynitride glass with composition (in equiv.%) of 28Y:56Si:16Al:83O:17N at temperatures below 1200 °C,[7] no nitrogen containing phases were obtained in the glass-ceramic and the nitrogen content of the residual glass increases significantly.

Table 4
Lattice parameters of gehlenite composition and gehlenite containing 20 equiv.% N.

Composition (equiv.%)	Lattice parameters
28.57Ca:28.57Si:42.86Al:100O	$a = b = 7.688$ Å $c = 5.066$ Å $\alpha = \beta = \gamma = 90°$
28.57Ca:28.57Si:42.86Al:80O:20N	$a = b = 7.690$ Å $c = 5.055$ Å $\alpha = \beta = \gamma = 90°$

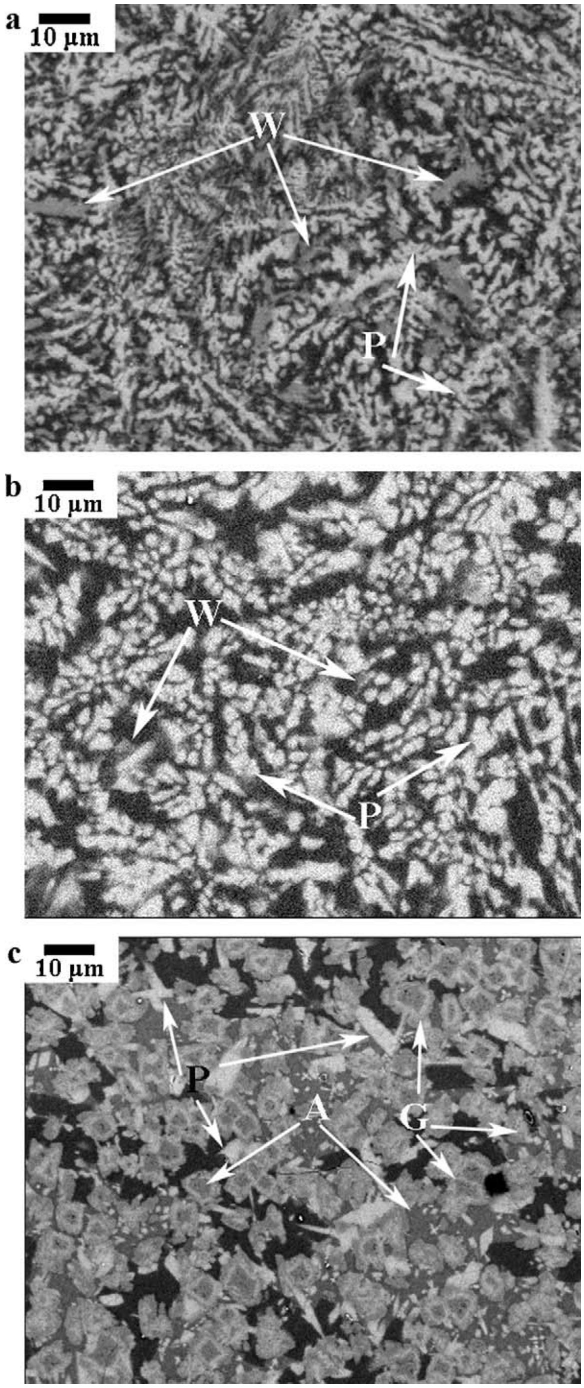

Fig. 7. Back scattered SEM micrographs of oxyfluoronitride glass–ceramics. (a) 28Ca:57Si:15Al:90O:5N:5F equiv.%, (b) 28Ca:57Si:15Al:85O:10N:5F equiv.% and (c) 28Ca:57Si:15Al:80O:15N:5F equiv.% (W, wollastonite; G, gehlenite; A, anorthite; P, cuspidine).

Fluorine seems to have negligible effects on the Young's modulus and hardness of oxyfluoride and oxyfluoronitride glasses while nitrogen results in significant increases in these properties.[15] Elastic modulus of a composite is a function of the elastic moduli of its different crystal components, their proportions and their orientations. With an increase in fluorine content in the oxyfluoride glass–ceramics, when gehlenite disappears and the proportion of cuspidine increases, there is a reduction in Young's modulus. This is due to the lower elastic modulus of cuspidine compared with other phases. Addition of fluorine changes the microstructure of oxyfluoride glass–ceramics to a dendritic network of cuspidine crystals which may be more resistant to indentation forces due to their morphology and this explains the increased microhardness of the glass–ceramics with increasing fluorine content.

In the oxyfluoronitride glass–ceramics, with an increase of fluorine, the amount of cuspidine and calcium fluoride, which have lower elastic moduli compared with gehlenite, increases. This causes a reduction in the overall elastic modulus for this series of glass–ceramics containing more than 1 equiv.% F. In addition to the formation of fluorine-containing phases, fluorine coarsens the gehlenite crystals in the microstructure of the oxyfluoronitride glass–ceramics and this is responsible for the decrease in microhardness. The incorporation of nitrogen into the oxyfluoronitride glass–ceramics causes an increase in Young's modulus due to the appearance of gehlenite.

The initial increase in the microhardness of the oxyfluoronitride glass–ceramics with N content (up to 10 equiv.% N) is due to an increase in the nitrogen content of the residual glass phase. Further nitrogen increase leads to the appearance of coarse gehlenite crystals and disappearance of dendritic cuspidine crystals which together weakens the structure leading to reduced microhardness. Hardness values depend on the proportions of the different phases in the glass-ceramic microstructure and their crystal sizes as well as their individual hardness values.[32,33] It should be noted that the trends for the effect of fluorine on microhardness of the oxyfluoride and oxyfluoronitride glass–ceramics are different. Hardness is more sensitive to changes in microstructure, phase morphology and crystal size compared with elastic modulus which is related to the amounts of constituent phases present.

5. Conclusions

The effect of nitrogen and fluorine on crystallisation of Ca–Si–Al–O–N–F glasses has been studied.

1) Addition of fluorine lowers the Tg, crystallisation and melting temperatures of oxyfluoride and oxyfluoronitride glasses and influences the crystallisation products and microstructures, including crystal size and morphology.
2) The calcium aluminosilicate oxide glass crystallised to form 50% pseudo-wollastonite ($CaSiO_3$), 37% gehlenite ($Ca_2Al_2SiO_7$) and 13% anorthite ($CaAl_2Si_2O_8$) as expected from the $CaO–Al_2O_3–SiO_2$ ternary phase diagram.
3) As fluorine content increases, gehlenite is not formed and this provides the required concentrations of Ca and Si for precipitation of cuspidine ($Ca_4Si_2O_7F_2$) with a dendritic microstructure which coarsens with increase in F content.
4) In oxynitride glasses containing 20 equiv.% N, gehlenite is the dominant crystalline phase and fluorine does not change this significantly. Above 3 equiv.% F, only minor amounts of

cuspidine and calcium fluoride (fluorine containing phases) form. The residual glass is nitrogen-rich.

5) Nitrogen enhances the formation of gehlenite suggesting that nitrogen may be accommodated in the gehlenite structure and results for crystallisation of gehlenite containing N suggest that N is soluble in the gehlenite structure to a limited extent. Nitrogen is present mainly in the residual glass after crystallisation of oxyfluoronitride glasses.
6) Combinations of both nitrogen and fluorine in oxyfluoronitride glasses allow changes in nucleation and growth of the crystalline phases which controls their morphologies in the microstructure.
7) Young's modulus of the oxide glass is 92 GPa. For both the oxyfluoride and oxyfluoronitride glasses, F content has little or no effect on elastic modulus or hardness. On the other hand, at fixed F content of 5 equiv.%, N increases Young's modulus and hardness by $\sim$15–20%.
8) The glass–ceramics all exhibit higher elastic moduli compared with their corresponding glasses at different fluorine or nitrogen contents. Highest Young's modulus is 134 GPa for the glass containing 20 equiv.% N and 1 equiv.% F. Generally, Young's modulus of the glass–ceramics increases with N content. However, similar trends are not observed for microhardness. This is because of the complex nature of the microstructures produced by crystallisation. Hardness is more sensitive to changes in microstructure, phase morphology and crystal size compared with elastic modulus which is related to the amounts of constituent phases present.

Acknowledgment

The authors wish to acknowledge Science Foundation Ireland for financial support for this work under grant no. 04/BR/C0163.

References

1. Becher P, Hampshire S, Pomeroy MJ, Hoffmann M, Lance M, Satet R. An overview of the structure and properties of silicon-based oxynitride glasses. *Int J Appl Glass Sci* 2011;**2**(1):63–83.
2. Hampshire S. Oxynitride glasses. *J Euro Ceram Soc* 2008;**28**(7):1475–83.
3. Loehman RE. Preparation and properties of yttrium–silicon–aluminum oxynitride glasses. *J Am Ceram Soc* 1979;**62**:9–10, 491–94.
4. Sakka S, Kamiya K, Yoko T. Preparation and properties of Ca–Al–Si–O–N oxynitride glasses. *J Non-Cryst Solids* 1983;**56**:147–55.
5. Jankowski P, Risbud SH. Formation and characterization of oxynitride glasses in the Si–Ca–Al–O–N and Si–Ca–Al–B–O–N systems. *J Mater Sci* 1983;**18**:2087–94.
6. Brow RK, Pantano CG. Nitrogen coordination in oxynitride glasses. *J Am Ceram Soc* 1984;**67**(4):C72–4.
7. Hampshire S, Drew RAL, Jack KH. Oxynitride glasses. *Phys Chem Glasses* 1985;**26**:182–6.
8. Rouxel T, Besson JL, Rzepka E, Goursat P. Raman spectra of SiYAlON glasses and ceramics. *J Non-Cryst Solids* 1990;**122**:298–302.
9. Sun EY, Becher PF, Hwang SL, Waters SB, Pharr GM, Tsui TY. Properties of silicon–aluminum–yttrium oxynitride glasses. *J Non-Cryst Solids* 1996;**208**:162–9.
10. Ramesh R, Nestor E, Pomeroy MJ, Hampshire S. Formation of Ln–Si–Al–O–N glasses and their properties. *J Euro Ceram Soc* 1997;**17**:1933–9.
11. Becher PF, Waters SB, Westmoreland CG, Riester L. Influence of composition on the properties of SiREAl oxynitride glasses: RE = La, Nd, Gd, Y, or Lu. *J Am Ceram Soc* 2002;**85**(4):897–902.
12. Hampshire S, Pomeroy MJ. Oxynitride glasses. *Int J Appl Ceram Technol* 2008;**5**(2):155–63.
13. Stamboulis A, Hill RG, Law RV. Characterization of the structure of calcium alumino-silicate and calcium fluoro-alumino-silicate glasses by magic angle spinning nuclear magnetic resonance (MAS-NMR). *J Non-Cryst Solids* 2004;**333**:101–7.
14. Hanifi AR, Pomeroy MJ, Hampshire S. Novel glass-formation in the Ca–Si–Al–O–N–F system. *J Am Ceram Soc* 2011;**94**(2):455–61.
15. Hanifi AR, Genson A, Pomeroy MJ, Hampshire S. Oxyfluoronitride glasses with high elastic modulus and low glass transition temperatures. *J Am Ceram Soc* 2009;**92**(5):1141–4.
16. Thomas G, Ahn C, Weiss J. Characterization and crystallization of Y–Si–Al–O–N glass. *J Am Ceram Soc* 1982;**65**(11):C185–8.
17. Dinger TR, Rai RS, Thomas G. Crystallization behavior of a glass in the Y_2O_3–SiO_2–AlN system. *J Am Ceram Soc* 1988;**71**(4):236–44.
18. Besson JL, Billieres D, Rouxel T, Goursat P, Flynn R, Hampshire S. Crystallization and properties of a Si–Y–Al–O–N glass ceramic. *J Am Ceram Soc* 1993;**76**(8):2103–5.
19. Hampshire S, Nestor E, Flynn R, Besson JL, Rouxel T, Lemercier H, et al. Yttrium oxynitride glasses: properties and potential for crystallisation to glass–ceramics. *J Euro Ceram Soc* 1994;**14**:261–73.
20. Ramesh R, Nestor E, Pomeroy MJ, Hampshire S, Liddell K, Thompson DP. Potential of NdSiAlON glasses for crystallisation to glass–ceramics. *J Non-Cryst Solids* 1996;**196**:320–5.
21. Liddell K, Thompson DP. Heat treatment of wollastonite type Y–Si–Al–O–N glasses. *J Mater Sci* 1997;**32**(4):887–92.
22. Besson JL, Lemercier H, Rouxel T, Trolliard G. Yttrium sialon glasses: nucleation and crystallization of $Y_{35}Si_{45}Al_{20}O_{83}N_{17}$. *J Non-Cryst Solids* 1996;**211**:1–2. p. 1–21.
23. Young WT, Falk LKL, Lemercier H, Peltier-Baron V, Menke Y, Hampshire S. The crystallisation of the yttrium sialon glass: $Y_{15.2}Si_{14.7}Al_{8.7}O_{54.1}N_{7.4}$. *J Non-Cryst Solids* 2000;**270**:6–19.
24. Ramesh R, Nestor E, Pomeroy MJ, Hampshire S. Classical and Differential Thermal Analysis studies of the glass-ceramic transformation in a YSiAlON glass. *J Am Ceram Soc* 1998;**81**(5):1285–97.
25. Pomeroy MJ, Nestor E, Ramesh R, Hampshire S. Properties and crystallization of rare earth SiAlON glasses containing mixed trivalent modifiers. *J Am Ceram Soc* 2005;**88**(4):875–81.
26. Rafferty A, Clifford A, Hill R, Wood D, Samuneva B, Dimitrova-Lukacs M. Influence of fluorine content in apatite mullite glass ceramics. *J Am Ceram Soc* 2000;**83**(11):2833–8.
27. Levin EM, Robbins CR, McMurdie HF. *Phase diagrams for ceramists*. Columbus, OH: American Ceramic Society; 1964. p. 220.
28. Guseva EY, Gulyukin MN. Effect of fluoride additives on glass formation in the SiO_2–CaO–Al_2O_3 system. *Inorg Mater* 2002;**38**(9):962–5.
29. Hewett CL, Cheng YB, Muddle BC. Phase relationships and related microstructural observations in the Ca–Si–Al–O–N system. *J Am Ceram Soc* 1998;**81**(7):1781–8.
30. Lederer K, Deckwerth M, Russel C. Zirconia-doped Mg–Ca–Al–Si–O–N glasses: crystallization. *J Non-Cryst Solids* 1998;**224**:109–21.
31. Shannon RD, Prewitt CT. Effective ionic radii in oxides and fluorides. *Acta Crystal* 1968;**B25**:925–47.
32. Roesky R, Varner JR. Influence of thermal history on the crystallization behaviour and hardness of a glass-ceramic. *J Am Ceram Soc* 1991;**74**(5):1129–30.
33. Unyi T, Juhász A, Tasnádi P, Lendvai J. Changes of the mechanical properties during the crystallization of bio-active glass–ceramics. *J Mater Sci* 2000;**35**:3059–68.