# The crystallisation of glasses from the ternary $CaF_2$-$CaAl_2Si_2O_8$-$P_2O_5$ system

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A study of glasses from the ternary system $CaF_2$-$CaAl_2Si_2O_8$-$P_2O_5$ has been carried out. It has been shown that glasses with low phosphorus contents and high fluorite contents crystallise to fluorite. Fluorine reduces the glass transition temperature and is also required for the formation of fluorapatite (FAP). In the absence of fluorine in the glass no apatite phase is formed. Bulk nucleation of FAP is favoured for glasses with Ca:P ratios close to the apatite stoichiometry of 1.67 and with low crosslink densities. Thermal gravimetric analysis showed significant weight losses attributable to the formation of volatile silicon tetrafluoride to occur on crystallisation of the aluminium containing phases, anorthite and mullite, which supports the view that silicon tetrafluoride formation is hindered by fluorine bonding to the aluminium atoms of the glass network. Anorthite crystallisation always occurred by a surface nucleation mechanism and appeared to be favoured by the higher silicon to aluminium ratio in these glasses compared to previously studied glass compositions. © *2001 Kluwer Academic Publishers*

## 1. Introduction

Apatite based materials are attractive for dental and medical applications. Hydroxyapatite (HA) is the subject of extensive research, since it is chemically very similar to the mineral phase of bone and tooth [1]. However HA and to a lesser extent its fluorine analogue, fluorapatite are prone to degradation at the high temperatures achieved during sintering and plasma spraying. Sintering is not an attractive commercial route for the production of biomedical prostheses, which nearly always have a complex shape.

A glass-ceramics processing route is an attractive method. It enables the component to be formed at high temperature in the glassy state, for example by lost wax die casting, and then converted to the ceramic by a controlled heat treatment. Such a production route offers the advantage of being able to form complex shapes, with near net shape and without the need for expensive machining with diamond tipped tools.

A number of apatite based glass-ceramics have been developed based on the $SiO_2$-$P_2O_5$-$CaO$-$MgO$ system [2, 3], but these materials can not be successfully cast and are generally produced by a sintering route, followed by expensive machining to shape. The most extensively studied system is the Apatite-Wollastonite (AW) system developed by Kokubo *et al.* [2] for medical applications as a bone substitute and by Hobo *et al.* [3] as a dental ceramic.

Recently fluoro-alumino-silicate known as "Ionomer" glasses used for the production of Glass Ionomer(pol-

yalkenoate) cements have been developed as an apatite-mullite (AM) glass-ceramic [4–7]. These new glass-ceramics can be lost wax cast to shape using currently available dental alloy casting equipment. The generally high fluorine content of these glasses results in low liquidus temperatures that facilitate casting. Furthermore the fluorine content of the glass generally facilitates amorphous phase separation, leading to bulk crystal nucleation. Bulk crystal nucleation is a prerequisite for a successful castable glass-ceramic. The castable AW glass-ceramics developed by Hobo *et al.* [3] suffered from uncontrolled surface nucleation and the subsequent inability to control the microstructure and resulting properties. These new apatite-mullite glass-ceramics have a microstructure based on interlocking needle like apatite crystals (Fig. 1) with a high length to diameter aspect ratio [3–7] that give rise to high strength and fracture toughness [6, 7]. Recently Frank *et al.* [8, 9] have developed Leucite-Apatite glass-ceramics with expansion coefficients matched to high gold content alloys, where improvements in strength result from the elongated apatite crystals. The intended application of these glass-ceramics is as pressable dental crowns, inlays, bridges as an alternative dental porcelains.

Ionomer glasses generally lose silicon tetrafluoride ($SiF_4$) on melting. Up to 80% of the fluorine present in the starting batch can be lost as $SiF_4$ during melting [10]. Hill and coworkers found that $SiF_4$ formation can be prevented by incorporating a basic oxide in the melt [11–13] and ensuring that there was a least one non

*Figure 1* Micrograph showing elongated fluorapatite crystals.

bridging oxygen per silicon and sufficient aluminium to bind the fluorine present. Using this approach loss of $SiF_4$ can be prevented.

However AM glass compositions developed to date have been shown to exhibit weight loss upon crystallisation [14], this weight loss is attributed to the volatilisation of silicon tetrafluoride, $SiF_4$ and will be detrimental to controlling the developing glass-ceramic microstructure. On crystallisation of FAP and mullite the rules for preventing $SiF_4$ formation in the residual glass phase are broken and $SiF_4$ is lost from the surface of the sample. The commercially available tetrasilicic mica glass-ceramic Dicor[TM] also undergoes loss of $SiF_4$ during the ceramming cycle [15, 16] leading to the formation of protoenstatite ($MgO \cdot SiO_2$) at the surface, rather than the tetrasilicic fluormica. Dicor[TM] contains no aluminium and the loss of $SiF_4$ is therefore very marked.

A number of the Ionomer glass compositions studied to date crystallise to fluorite and anorthite [14]. The crystallisation of a fluorine rich phase, such as fluorite ($CaF_2$) is advantageous given that the incorporation of fluorine into a crystal phase will deplete the fluorine content of the residual glass and will prevent the volatilisation of fluorine as $SiF_4$. Studies on one of these glass compositions [11–13], showed it to bulk nucleate and crystallise readily to fluorite. These results are not surprising, since the components of the fluorite crystalline phase, calcium and fluorine, are both network modifiers.

One of the objectives of the present study was to try and develop fluorite-fluorapatite glass-ceramics that do not lose silicon tetrafluoride during the ceramming cycle. A second objective was to investigate compositions based on a ternary system, rather than based on stoichiometric compositions of the type $PSiO_2QAl_2O_31.5P_2O_5(5-X)CaOXCaF_2$ that have been studied previously.

The Anorthite-Fluorite-Phosphorus Pentoxide system was chosen for study because it contained a previously studied [11–13] glass based on $2SiO_2Al_2O_3CaOCaF_2$ and offered the potential to form glasses across a wide compositional range. The development of a ternary system had added incentives in terms of structural understanding of the glasses, completing a structured study of the glass-ceramics and the potential to allow for the definition of a suitable glass forming region and its boundaries.

## 2. Experimental
### 2.1. Glass design
The previously studied glass $2SiO_2Al_2O_3CaOCaF_2$ which exhibited bulk nucleation of fluorite and anorthite, which contained no phosphate was the basis of the glass compositions designed. It was considered possible that such a glass composition could be modified to crystallise to; fluorite, fluorapatite and mullite or anorthite. New compositions were considered and developed as a ternary system based on the crystalline

phases; fluorite ($CaF_2$), phosphorus pentoxide ($P_2O_5$) and anorthite ($2SiO_2Al_2O_3CaO$).

Initial compositions were designed and chosen using the criteria of a Ca/P ratio equal to 1.67, and crosslink densities (CLD) greater than 1 and less than 1.3. Crosslink densities were calculated using the method outlined by Ray [17]. Other criteria included ensuring the presence of at least one non-bridging oxygen per silicon, maintaining $Al^{3+}$ in a four fold co-ordination state by providing sufficient charge balancing cations and ensuring the fluorine content was less than the aluminium content in order to minimise $SiF_4$ volatilisation during melting. These criteria are based on the fact that an $Si^{4+}$ cation will have a higher affinity for a non-bridging oxygen or $O^{2-}$ anion than for a non-bridging fluorine or $F^-$ anion and that an $Al^{3+}$ ion will bond the $F^-$ anion so hindering the formation of Si-F bonds in the glass network. The model of the glass structure is supported by MAS-NMR studies [18, 19] and by a trimethylsilylation analysis [20] of the previously studied $2SiO_2Al_2O_3CaOCaF_2$ glass which demonstrated the absence of Si-F bonds. The selection of Ca/P ratio of 1.67 originated from earlier studies of Ca/P ratio which reveal that a ratio approximating to 1.67 ensured low crystallisation temperatures for fluorapatite ($Ca_5(PO_4)_3F$) as well as bulk nucleation [21].

## 2.2. Glass synthesis
Glasses of defined chemical composition were synthesised for this study. The glasses were produced by melting the silica, alumina, phosphorus pentoxide, calcium carbonate, calcium fluoride and sodium carbonate in mullite crucibles at temperatures beween 1300 and 1550°C for two hours. The glass compositions, code letters and melt temperatures are given in Table I. The resulting melts were rapidly shock quenched into water to prevent phase separation and crystallisation. The glass frit produced was ground and sieved to give particles <45 $\mu$m, which were used in the subsequent analysis.

TABLE I Glass compositions studied

| Glass Code | $CaSi_2Al_2O_8$ | $CaF_2$ | $P_2O_5$ | CLD | Ca:P | Firing Temperature °C |
|---|---|---|---|---|---|---|
| A1 | 0.70 | 0.30 | 0.00 | 1.57 | - | 1420 |
| A2 | 0.60 | 0.40 | 0.00 | 1.33 | - | 1380 |
| A3 | 0.50 | 0.50 | 0.00 | 1.00 | - | 1350 |
| B1 | 0.62 | 0.26 | 0.12 | 1.53 | 3.67 | 1460 |
| B2 | 0.53 | 0.35 | 0.12 | ? | 3.67 | 1440 |
| B3 | 0.44 | 0.44 | 0.12 | 1.00 | 3.67 | 1400 |
| C1 | 0.57 | 0.25 | 0.18 | 1.48 | 2.28 | 1440 |
| C2 | 0.49 | 0.33 | 0.18 | 1.28 | 2.28 | 1420 |
| C3 | 0.41 | 0.41 | 0.18 | 1.00 | 2.28 | 1380 |
| D1 | 0.77 | 0.00 | 0.23 | 1.87 | 1.67 | 1380 |
| D2 | 0.54 | 0.23 | 0.23 | 1.47 | 1.67 | 1410 |
| D3 | 0.47 | 0.30 | 0.23 | 1.46 | 1.67 | 1410 |
| D4 | 0.46 | 0.31 | 0.23 | 1.26 | 1.67 | 1450 |
| D5 | 0.40 | 0.37 | 0.23 | 1.03 | 1.67 | 1410 |
| D6 | 0.39 | 0.38 | 0.23 | 1.02 | 1.67 | 1410 |
| E1 | 0.50 | 0.21 | 0.29 | 1.45 | 1.22 | 1430 |
| E2 | 0.43 | 0.28 | 0.29 | 1.26 | 1.22 | 1440 |
| E3 | 0.36 | 0.35 | 0.29 | 1.02 | 1.22 | 1440 |

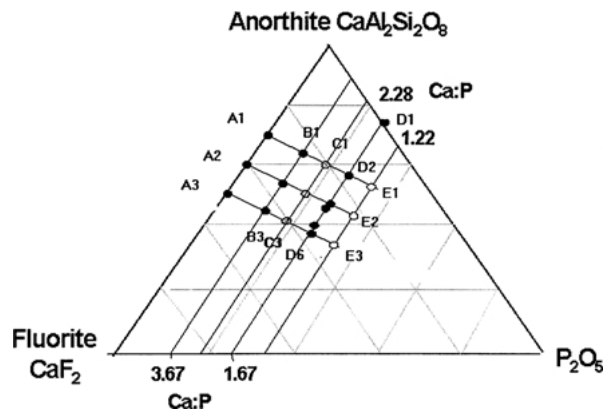Ca* = network disrupting calcium cations



*Figure 2* Ternary diagram for the Anorthite-Fluorite-Phosphorus Pentoxide system showing the glass compositions produced.

The composition of the glasses produced were based on previous studies [11–14] and chosen to prevent silicon tetrafluoride formation and loss during melting. The glass compositions produced are shown on the ternary diagram in Fig. 2.

## 2.3. Glass characterisation
### 2.3.1. Differential scanning calorimetry (DSC)
The glasses produced were characterised by differential scanning calorimetry using a Stanton Redcroft DSC 1500 (Rheometric Scientific, Epsom, UK). The crucibles used were matched pairs made of platinum-rhodium alloy. Alumina was used as the reference material. Runs were performed in dry nitrogen at a heating rate of 10°C min$^{-1}$ unless otherwise stated. The tendency of the glasses to undergo surface nucleation was assessed by performing DSC runs using two glass particle sizes; frit particles of 1–2 mm and fine <45 $\mu$m powder.

### 2.3.2. Combined differential thermal analysis/thermal gravimetric analysis (DTA/TGA)
Combined DTA/TGA was used to study weight changes accompanying crystallisation processes. A Stanton Redcroft DTA/TGA 1600 (Rheometric Scientific, Epsom, UK) was used with a flowing dry nitrogen atmosphere and a heating rate of 10°C min$^{-1}$.

## 2.4. X-ray powder diffraction
X-ray powder diffraction analysis was completed on heat treated glass samples for qualitative purposes. Samples were heat treated in the DSC at 10°C min$^{-1}$ to the peak crystallisation temperatures observed (Tp1 and Tp2) and to a temperature half way between the peak crystallisation temperatures ((Tp1 + Tp2)/2). A Phillips powder diffractometer (Phillips Xpert diffractometer, Phillips Eindhoven, NL) was employed using Cu K$_\alpha$ X-rays. Every glass composition was heat treated using the tube furnace of the DSC to replicate the DSC analysis using an identical heating rate with samples taken at the individual peak crystallisation temperatures (Tp)s for each glass.

TABLE II Ternary glass compositions and thermal analysis for <45 $\mu$m and frit particle sizes

| Glass Code Ca/P = O | Tg (°C) | <45 $\mu$m Tp1 (°C) | <45 $\mu$m Tp2 (°C) | <45 $\mu$m Tp3 (°C) | Frit Tp1 (°C) | Frit Tp2 (°C) | Frit Tp3 (°C) |
|---|---|---|---|---|---|---|---|
| A1 | 698 | - - - - | 887 | - - - - | 920 | - - - - | - - - - |
| A2 | 667 | - - - - | 884 | - - - - | 926 | - - - - | - - - - |
| A3 | 636 | 722 | 907 | - - - - | 724 | 972 | - - - - |
| Ca/P 3.66 | | | | | | | |
| B1 | 683 | 804 | 904 | - - - - | 800 | 1010 | - - - - |
| B2 | 667 | 734 | 882 | 955 | 825 | 969 | 1128 |
| B3 | 628 | 706 | 764 | 831 | 706 | 768 | 878 |
| Ca/P 2.3 | | | | | | | |
| C1 | 662 | 791 | 970 | - - - - | 791 | 1049 | - - - - |
| C2 | 625 | 745 | 923 | - - - - | 743 | 918 | 1260 |
| C3 | 610 | 745 | 855 | - - - - | 744 | 844 | 1228 |
| Ca/P 1.67 | | | | | | | |
| D1 | 800 | 1103 | - - - - | - - - - | - - - - | - - - - | - - - - |
| D2 | 653 | 830 | 1049 | - - - - | - - - - | - - - - | - - - - |
| D3 | 620 | 755 | 937 | | 756 | 904 | |
| D4 | 618 | 756 | 941 | 1064 | 756 | 908 | 1052 |
| D5 | 606 | 743 | 876 | 895 | 743 | 879 | 898 |
| D6 | 580 | 742 | 872 | | 742 | 859 | |
| Ca/P 1.02 | | | | | | | |
| E1 | 669 | 878 | 1098 | | 899 | - | - - - - |
| E2 | 648 | 752 | 839 | 1222 | 754 | 1205 | - - - - |
| E3 | 608 | 690 | 787 | 1034 | 689 | 1014 | - - - - |

TABLE III Principal crystalline phases present at various temperatures F = Fluorite, FAP = Fluorapatite, A = Anorthite and M = Mullite, None = no Tp3

| Glass Code | Tp1 | (Tp1 + Tp2)/2 | Tp2 | Tp3 |
|---|---|---|---|---|
| A1 | F | F | F + A | None |
| A2 | F | F | F + A | None |
| A3 | F | F | F + A | None |
| B1 | | | FAP | FAP + A + M |
| B2 | F | F + FAP | F + FAP | F + FAP + A |
| B3 | F | F | F + FAP | F + FAP + A + M |
| C1 | | FAP | FAP + A + M | None |
| C2 | | FAP | FAP + A + M | None |
| C3 | | FAP | FAP + A + M | None |
| D1 | | A | | None |
| D2 | | FAP | FAP + A + M | None |
| D3 | | FAP | FAP + A + M | None |
| D4 | | FAP | FAP + A + M | None |
| D5 | | FAP | FAP + A + M | None |
| D6 | | FAP | FAP + A + M | None |
| E1 | | FAP | FAP + A + M | None |
| E2 | | FAP | FAP + A + M | None |
| E3 | | FAP | FAP + A + M | None |



*Figure 3* Glass transition temperature plotted against crosslink density for all the glasses studied.

## 3. Results and discussion

The results for the glass transition temperatures (Tg), and peak crystallisation temperatures (Tp)s are given in Table II for fine (<45 $\mu$m) glass powder and for frit particles (>1 mm) respectively. Table III summarises the crystalline phases found for each glass composition after heat treatment.

The glass transition temperature reduces with increasing fluorite content for each of the five series of glasses. The data is plotted in Fig. 3 against the calculated crosslink density of the glass. Both fluorite and fluorine have previously been shown to reduce glass transition temperatures in fluoro-alumino-silicate glasses [13, 14] and in fluoro-alumino-silicate
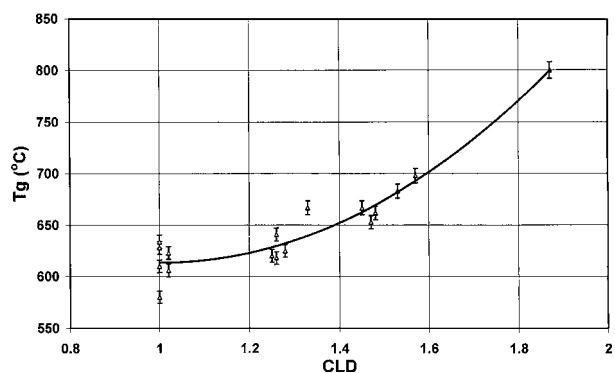
glasses that crystallise to canasite [22] and to potassium fluorphologopite [23]. The dominant effect with fluorite is due to the fluorine rather than the calcium and it is thought fluorine replaces bridging oxygens in the glass structure by non-bridging fluorines. Fluorine therefore serves to disrupt the glass network. Increasing the phosphate content generally reduces the glass transition temperature slightly, which is consistent with the weaker phosphorus-oxygen bond strength relative to the silicon-oxygen and aluminium-oxygen bond strengths and also the lower glass transition temperatures found for phosphate glasses [17].

The A3 glass having the composition $2SiO_2Al_2O_3CaOCaF_2$ exhibited bulk nucleation of the first crystalline phase to form as demonstrated by the fact that the first peak crystallisation temperature (Tp1) was independant of glass particle size and X-ray powder diffraction showed it to correspond to the crystallisation of fluorite in agreement with previous studies [11–13]. Bulk crystal nucleation has been shown to occur as a result of prior amorphous phase separation of the glass [4–6].

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In contrast the second peak crystallisation process was particle size dependant indicating a surface nucleation mechanism. The second crystallisation process was shown to correspond to anorthite in agreement with the studies of Hill and Wood [11–13]. However in the previous studies anorthite bulk nucleated. Given the glasses of the previous studies were synthesised using the same reagents, but of different purity to the present compositions the surface nucleation of anorthite is some what surprising. Unfortunately Wood and Hill [11–13] did not make any other glass compositions on this tie line, but did remake several batches of this glass all of which bulk nucleated to anorthite. While an explanation for this ambiguity is not easy to resolve it is probably an indication of the sensitivity of the nucleating behaviour of glasses to very small changes in composition.

Glasses A1 and A2 also lie on the $CaF_2$-$CaAl_2Si_2O_8$ join and contain no phosphate. All the glasses on this join crystallised to fluorite and anorthite, with bulk nucleation of fluorite and surface nucleation of anorthite. The surface nucleation of the anorthite phase is again surprising given that the residual glass composition after the complete crystallisation of fluorite is that of stoichiometric anorthite. Zanotto *et al.* [24] predicted that glasses having compositions close to the crystalline phase will bulk nucleate given that minimal structural rearrangement will be required for nucleation, however this theory is not reflected in these results. Wu *et al.* [25] studying an apatite-anorthite glass ceramic also found anorthite to surface nucleate strongly.

Combined differential thermal analysis/thermal gravimetric analysis of the A3 glass (Fig. 4) exhibited a 0.06% weight loss up to a temperature of 1200°C. The DTA analysis exhibits an endothermic event occurring at 1140°C which corresponds to the onset of the weight loss. The endothermic event may be attributed to the melting of a crystalline phase or the liquidus temperature of the residual glass, either event will result in altering the glass composition and the likely breaking of the rules of the structural model developed to rationalise $SiF_4$ loss from fluoro-alumino-silicate melts. The weight loss was much less than that found previously for the equivalent glass studied by Hill *et al.* [11–13] which was about 0.9%, the reduced weight loss is thought to reflect the fact that a dry nitrogen atmosphere was used in the present analysis compared to air, which will contain some water and therefore fluo-
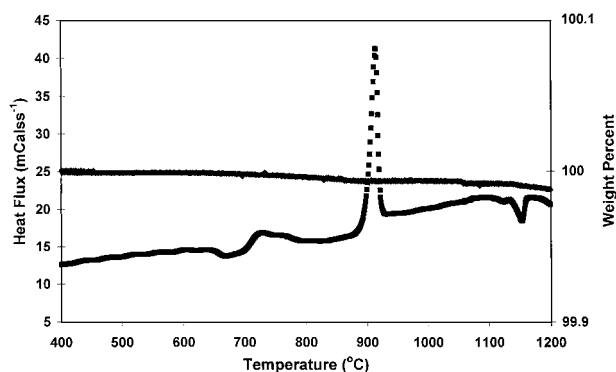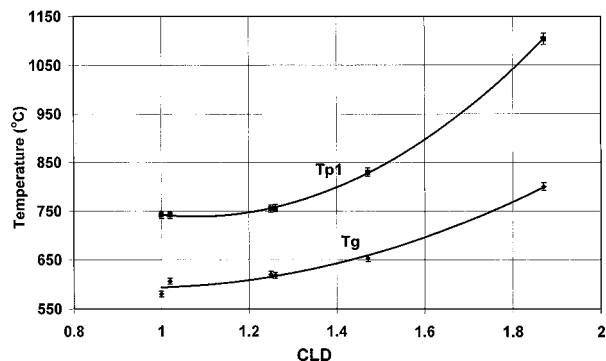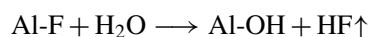


*Figure 5* Glass transition temperature and first peak crystallisation plotted against crosslink density for glasses with a Ca:P ratio of 1.67.

rine in the glass studied previously may react to form hydrofluoric acid according to the following equation:

$$Al\text{-}F + H_2O \longrightarrow Al\text{-}OH + HF\uparrow$$

The hydroxyl group formed will react with a further fluorine in the glass to form another hydrofluoric acid molecule and form a bridging oxygen bond.

The smallest addition of phosphorus pentoxide corresponds to the tie lie with a Ca/P ratio equal to 3.67, this line includes the B3 glass and two other glasses (B2 and B1) with decreased fluorite content (see Fig. 5). The first peak crystallisation temperarature for the B3 and B2 glasses corresponds to the crystallisation of fluorite and the second to fluorapatite, Unlike B3 and B2, B1 does not show the exotherm corresponding to crystallisation of fluorite on its DSC traces, but X-ray powder diffraction of heat treated samples showed evidence of small quantities of fluorite relative to the fluorapatite line intensities, Decreasing the fluorite content favours the crystallisation of fluorapatite at the expense of fluorite. Phosphate content was increased further producing glasses on tie lines with Ca/P ratios equal to 2.28, 1.67 and 1.02. All the glass compositions on these tie lines crystallised to fluorapatite and mullite without any evidence of fluorite. If the glasses are considered not in terms of increasing phosphate content but of varying F and A1 content then we see that the decrease in fluorine and increase in the intermediate oxide content, alumina, results in increasing crosslink density which is reflected in the increase in glass transition temperature.

The first peak crystallisation temperatures (Tp1), which generally corresponded to fluorapatite were always independent of particle size, indicating bulk nucleation of fluorapatite. Bulk nucleation has been shown to occur following prior amorphous phase separation in related glass compositions [4, 5]. The peak crystallisation temperature corresponding to apatite formation decreases with increasing fluorite content or decreasing crosslink density for all the series of glasses studied. Heat treatments up to Tp1 (or Tp2 where fluorite was present) frequently did not show the presence of apatite by X-ray powder diffraction. However at temperatures above Tp1 but below Tp2 apatite was present. It is thought that very small less than 0.5 $\mu$m apatite crystals are formed that give rise to pronounced line broadening. Frank *et al.* [9] observed a similar phenomenon in



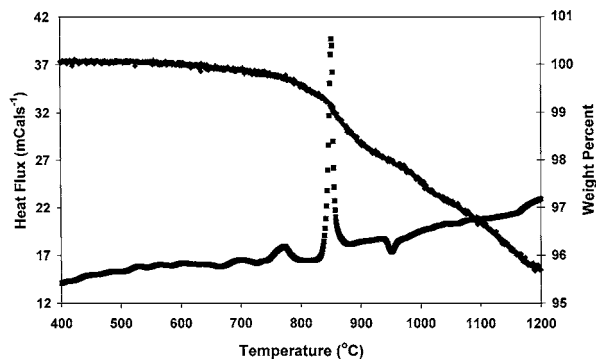*Figure 4* DTA/TGA results for the A3 glass showing negligible weight loss.

*Figure 6* DTA/TGA results for the B3 glass showing significant weight loss corresponding to the second peak crystallisation temperature.

Leucite-Apatite glass-ceramics. It is thought that amorphous phase separation leads to nucleation of a large number of small apatite crystals, however subsequent crystal growth is suppressed by the fine scale of the APS step.

The second peak crystallisation temperature unusually decreases with increasing particle size for the higher Ca:P series and at higher fluorite contents. Such a phenomena is unusual. Increasing the particle size would be expected to result in the peak crystallisation temperature occurring at higher temperatures if surface induced crystallisation was occurring and at the same temperature if bulk nucleation was occurring. The only explanation for this phenomena is that the glass composition must change during the DSC run. This is supported by the combined DTA/TGA data, which shows negligible weight loss for frit particles and up to 4% weight loss for $<45\,\mu m$ particles. Previous studies [21] have shown that the weight loss found for closely related glass compositions depends on fluorine content, particle size and the crystalline phases that form. A typical example of a DTA/TGA trace is shown in Fig. 6 for the B3 glass composition with a Ca/P ratio of 3.67. Weight losses are negligible for frit samples and increase with the surface to volume ratio of the particles analysed. It is likely that loss of $SiF_4$ from the surface of $<45\,\mu m$ glass particles, prior to the second peak crystallisation temperature changes the glass composition. Loss of $SiF_4$ is likely to be more pronounced in the higher fluorine content glasses. The weight loss generally occurs in two steps. The first loss accompanies the apatite crystallisation peak and probably arises as a result of a reduction in non-bridging oxygen content, accompanying the removal of $Ca^{2+}$ and $PO_4^{3-}$ ions from the glass into the crystalline apatite phase or calcium phosphate rich droplet phase. This first loss is small. A second much larger weight loss accompanies the second crystallisation peak corresponding to the crystallisation of anorthite and mullite. The glasses are deficient in aluminium with respect to mullite ($2SiO_2 \cdot 3Al_2O_3$) and stoichiometric with regard to anorthite ($CaAl_2Si_2O_8$) and so crystallisation of these two species will result in the formation of a silicon fluorine rich residual glass phase which will favour $SiF_4$ loss.

Anorthite which has a high tendency to surface nucleate is readily formed in almost all compositions.

Mullite, an alternative aluminosilicate species, is also evident, but sometimes in small quantities. The temperature ranges for mullite and anorthite crystallisation overlap making analysis difficult. There was generally more anorthite present in $<45\,\mu m$ samples than frit samples suggesting that anorthite is favoured by the increased surface area for nucleation and also by volatilisation of $SiF_4$ from the surface of the glass particles. Formation of mullite was surprising given that these glasses have the anorthite stoichiometry in terms of an Al:Si ratio of one. The formation of mullite following crystallisation of fluorapatite in previously studied glass compositions [4–6] is thought to be brought about by two factors;

(i) An aluminium to silicon ratio greater than 1:1 where phosphorus is required to prevent the formation of Al-O-Al bonds, which according to Lowenstein's aluminium avoidance principle [26] would cause some of the aluminium atoms present to take up a higher coordination state than four, thereby destabilising the glass and favouring the crystallisation of mullite, a phase in which aluminium is in both four and six coordination states.

(ii) The requirement of $AlO_4$ tetrahedra for a charge balancing cation either in the form of network dwelling $Ca^{2+}$ ions or adjacent $PO_4$ tetrahedra.

In the case of the present glasses (i) does not apply, but mullite still forms because some of the calcium from the original anorthite is used in addition to the calcium from fluorite to form fluorapatite, thus there is insufficient charge balancing species to keep aluminium in a four coordinate tetrahedral state.

The D1 glass composition lies on the anorthite - phosphorus pentoxide join having a Ca/P ratio of 1.67 and zero fluorine content. This glass showed complete surface nucleation to the single crystalline phase anorthite. The absence of apatite in this glass composition despite having a Ca/P ratio of 1.67 agrees with previous studies [4–6, 14, 21] that demonstrated fluorine to be critical to the formation of the apatite phase. The present study provides further evidence of the dependence of apatite formation on the presence of fluorine and supports the view that the apatite phase formed is a fluorapatite. Hartmann and Jana [27] also found evidence for crystallisation of fluorapatite in Ionomer glass compositions from MAS-NMR studies.

## 4. Conclusions
An extensive area of glass formation was found in the $CaF_2$-$CaAl_2Si_2O_8$-$P_2O_5$ ternary. The fluorine content of the glasses was found to reduce the glass transition temperatures and peak crystallisation temperatures. In the absence of fluorine, no apatite phase was formed, which supports the view that the apatite formed in this system is a fluorapatie. Anorthite was found to crystallise in all the compositions studied and to surface nucleate. Fluorite was found to crystallise from the glass for compositions rich in fluorite and of low phosphate content.

Thermal gravimetric analysis showed significant weight loss corresponding to the crystallisation of aluminium containing crystalline phases and was only very

slightly reduced by the prior formation of crystalline fluorite.

The surface nucleation of anorthite is likely to be detrimental to the control of the glass-ceramic microstructure and compositions from this ternary system are therefore unlikely to have commercial application.

## Acknowledgements

## References

1. R. D. RAWLINGS, *Clinical Materials* **14** (1993) 155.
2. T. KOKUBO, S. ITO and S. SAKKA, *J. Mater. Sci.* **21** (1986) 535.
3. S. HOBO and T. IWATA, *Quintessence Int.* **16** (1985) 207.
4. R. G. HILL, M. PATEL and D. J. WOOD, *Bioceramics* **4** (1991) 79.
5. R. HILL and D. J. WOOD, *Mater. Sci., Mater. In Med.* **6** (1995) 311.
6. A. CLIFFORD and R. HILL, *J. Non Cryst. Solids* **196** (1996) 346.
7. M. DIMITROVA-LUKACS and L. GILLEMOT, in Proceedings of the Third Euroceramics, Vol. 3, edited by P. Duran and J. F. Fernandez (Faenza Editrice Iberica S. L., Spain, 1993), p. 179.
8. W. HOELAND, V. RHEINBERGER, M. FRANK and M. SCHWEIGER, *Bioceramics* **8** (1995) 299.
9. M. FRANK, M. SCHWEIGER, V. RHEINBERGER and W. HOELAND, US Patent no. 5,698,019 (1997).
10. H. W. KING, E. A. PAYZANT, D. W. JONES and A. S. RIZKALLA, *J. Can. Ceram Soc.* **62** (1993) 248.
11. D. WOOD and R. HILL, *Biomaterials* **12** (1991) 164.
12. R. G. HILL, C. GOAT and D. WOOD, *J. Amer. Ceram. Soc.* **75** (1992) 778.
13. D. WOOD and R. G. HILL, *Clinical Materials* **7** (1991) 301.
14. A. CLIFFORD, PhD thesis, University of Limerick, 1997.
15. S. D. CAMPBELL and J. R. KELLY, *Int. J. Prosthodont.* **2** (1989) 459.
16. D. J. WOOD, N. L. BUBB, A. CLIFFORD, R. G. HILL and J. C. KNOWLES, *J. Mater. Sci. Lett.* **18** (1999) 1001.
17. N. H. RAY, "Inorganic Polymers" (London, Academic Press, 1978).
18. S. C. KOHN, R. DUPREE, M. G. MORTUZA and C. M. B. HENDERSON, *American Mineralogist* **76** (1991) 309.
19. N. B. MOHIALDAN, MSc thesis, University of Greenwich, 1996.
20. R. HILL, D. WOOD and M. THOMAS, *J. Mater. Sci.* **34** (1999) 1767.
21. A. CLIFFORD, A. RAFFERTY, P. MOONEY, R. G. HILL, D. WOOD, B. SAMUNEVA and M. DIMITROVA-LUKACS, *J. Amer. Ceram. Soc.*, accepted.
22. S. LIKITVANICHKAL and W. C. LA COURSE, *J. Mater. Sci.* **30** (1995) 6151.
23. Brite EuRam Report, Novel machinable mica based glass-ceramics (NOVMAC), University of Limerick, June 1998.
24. E. ZANNOTTO and E. MULLER, "Phy. of Non. Cry. Solids, Soc. Glass Tech." (Taylor and Francis, London, 1992).
25. S. WU, C. L. WANG and M. HON, *J. Ceram. Soc. Japan* **103**(2) (1995) 99.
26. W. LOWENSTEIN, *Am. Mineral.* **39** (1954) 92.
27. P. HARTMANN, C. JANA and M. BRAUN, *Glass Tech. Berlin Glass Sci. and Technol.* **69** (1996) 25.