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Manufacture, characterisation and properties of novel fluorcanasite glass–ceramics

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ABSTRACT

Objective: The aim of this study was to investigate the manufacture and characterisation of different compositions of fluorcanasite glass–ceramics with reduced fluorine content and to assess their mechanical and physical properties.

Methods: Three compositional variations (S80, S81 and S82) of a fluorcanasite glass were investigated. Differential thermal analysis (DTA) and X-ray diffraction (XRD) identified crystallisation temperatures and phases. X-ray fluorescence (XRF) determined the element composition in the glass–ceramics. Different heat treatments [2 h nucleation and either 2 or 4 h crystallisation] were used for the glasses. Scanning electron microscopy (SEM) examined the microstructure of the cerammed glass. The chemical solubility, biaxial flexural strength, fracture toughness, hardness and brittleness index of S81 and S82 fluorcanasite were investigated with lithium disilicate (e.max CAD, Ivoclar Vivadent) as a commercial comparison. Statistical analysis was performed using one-way ANOVA with Tukey's multiple comparison tests ($P < 0.05$). Weibull analysis was employed to examine the reliability of the strength data.

Results: All compositions successfully produced glasses. XRD analysis confirmed fluorcanasite formation with the S81 and S82 compositions, with the S82 (2 + 2 h) showing the most prominent crystal structure. The chemical solubility of the glass–ceramics was significantly different, varying from 2565 ± 507 μg/cm^2 for the S81 (2 + 2 h) to 722 ± 177 μg/cm^2 for the S82 (2 + 2 h) to 37.4 ± 25.2 μg/cm^2 for the lithium disilicate. BFS values were highest for the S82 (2 + 2 h) composition (250 ± 26 MPa) and lithium disilicate (266 ± 37 MPa) glass–ceramics. The fracture toughness was higher for the S82 compositions, with the S82 (2 + 2 h) attaining the highest value of 4.2 ± 0.3 MPa m$^{1/2}$($P = 0.01$). The S82 (2 + 2 h) fluorcanasite glass–ceramic had the lowest brittleness index.

Conclusion: The S82 (2 + 2 h) fluorcanasite glass–ceramic has acceptable chemical solubility, high biaxial flexural strength, fracture toughness and hardness.

Clinical significance: A novel glass–ceramic has been developed with potential as a restorative material. The S82 (2 + 2 h) has mechanical and physical properties that would allow the glass–ceramic to be used as a machinable core material for veneered resin-bonded ceramic restorations.

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1. Introduction

All-ceramic restorations are becoming increasingly popular for use as dental restorations due to their biocompatibility, high compressive strength, low thermal conductivity, abrasion resistance and natural appearance compared to metal–ceramics. However, the possible applications for glass–ceramic restorations are limited due to their brittle nature, sensitivity to flaws and defects, low tensile strength and fracture toughness.[1,2] For use as a restorative material, glass–ceramics have to demonstrate durability in the oral environment, have excellent aesthetics and exhibit high strength and wear resistance. The strength of the restoration is also considerably enhanced if it can be resin bonded to the underlying tooth structure.[3,4]At present the only glass–ceramic materials that approaches these requirements are lithium disilicate and some leucite glass–ceramics.

Chain silicates, or inosilicates, are polymeric crystals in which single or multiple chains of silica tetrahedra form the structural backbone. In the late 1970s, Beall demonstrated that glass–ceramics based on modified chain silicate compositions (enstatite, potassium fluorrichterite and canasite) have a particularly high fracture toughness (3–5 MPa $m^{1/2}$) and bending strength (200–300 MPa).[5] Fluorcanasite, a machinable synthetic double chain silicate, has high flexural strength and fracture toughness and is a potential material for all-ceramic restorations. Anusavice and Zhang[6,7] have reported different fluorcanasite compositions with fracture toughness values from 2.7 to 5.0 MPa $m^{1/2}$. High biaxial flexural strength of 261 $\pm$ 21.1 MPa to 280 $\pm$ 34.3 MPa has also been reported Johnson et al.[8,9] Consequently, fluorcanasite could fulfil the demand for a tougher, tooth-coloured biocompatible dental material if it were not for the fact that these materials have high chemical solubility.

In previous studies, fluorcanasite glasses derived from the stoichiometric formulation of Beall,[5] $60SiO_2$–$10Na_2O$–$5K_2O$–15CaO–$10CaF_2$, have been investigated and various modifications to the composition have been undertaken in an attempt to produce a chemically durable fluorcanasite composition with satisfactory mechanical properties.[8–11] Stokes et al.[10] found that increasing the CaF_2 content of the fluorcanasite glass improved the fracture toughness of the material but at the expense of the chemical durability. Decreasing the CaF_2 content reduced the chemical solubility but resulted in a mechanically weaker material. CaF_2 is critical to fluorcanasite formation as it is required within the fluorcanasite structure as well as acting as a nucleating agent. A minimum amount of CaF_2 is required to crystallise fluorcanasite, otherwise frankamenite will form as the major crystalline phase instead.[12] The phase evolution in canasite-based compositions is complex and small modifications in composition radically change the crystallised product and fundamentally alter the mechanism of nucleation.[13] Increasing the silica content in the base glass may achieve a high strength, high durability formulation and the addition of zirconia may supplement the nucleation of CaF_2.[5,14] However, despite extensive research it is still not known whether a relative increase in silica content can achieve the low solubility without a reduction in toughness needed for clinical applications in dentistry. The aim of this study was therefore to investigate the manufacture, characterisation and properties of different compositions of fluorcanasite with high silica, reduced CaF_2 content and zirconia addition.

2. Materials and methods

2.1. Glass formulation

Three glass compositions were prepared using K_2CO_3, Na_2CO_3, Ca_2CO_3, SiO_2, CaF_2 and ZrO_2 reagent grade raw materials to produce approximately 200 g of glass (Table 1). The batches were melted in a tapered zirconia grain-stabilised platinum crucible at 1350 °C in a silicon carbide element electric furnace. Varying melt durations were used in the manufacture of the fluorcanasite glasses (Table 2). The first hour of the melts was static to allow the glass to become fluid and the initial batch reactions to occur. Following this, the melts were stirred for varying durations using a platinum paddle rotating at 60 rpm. Subsequently the melt was poured into a preheated steel mould to produce a block with dimensions of 4 cm $\times$ 10 cm $\times$ 1.5 cm. The glasses were then annealed at varying temperatures from 450 °C to 490 °C for 1 h with a cooling rate of 1 °C per min in a muffle furnace (Lenton Thermal Design, Derbyshire, UK).

2.2. Phase analysis

Differential thermal analysis (Diamond TG/DAT, Perkin Elmer, MA, USA) was used to determine glass transition (T_g) and crystallisation temperatures (T_c) for all compositions studies by heating glass powder from room temperature to 1000 °C at a heating rate of 5 °C/min in platinum crucibles.

To determine the concentrations of elements present in the glasses, X-ray fluorescence analysis was undertaken. The

Table 1 – Glass compositions (as batched) in molar percent.

Composition	K_2O	CaO	Na_2O	SiO_2	CaF_2	ZrO_2
S80	5.35	11.46	6.11	64.82	11.46	0.80
S81	5.60	12.00	6.40	64.0	11.20	0.80
S82	5.65	12.10	6.00	65.0	10.0	0.81

Table 2 – Melting schedules employed for the fluorcanasite glass.

Glass	Static (h)	Stir (h)	Static remelt (h)	Total (h)
S80	1	1	N/A	2
S80	1	1.5	N/A	2.5
S80	1	2	N/A	3
S80	1	0.5	1	2.5
S80	1	1	1	3
S81	1	1	N/A	2
S82	1	1	N/A	2