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Effect of fluorine content on the crystallization and flexural strength of fluoro-mica glass ceramics

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Abstract

Two glasses with different contents of fluorine were fabricated. A single phase, $KMg_{3.25}Si_{3.625}O_{10}F_2$, precipitated in both of the glass samples after heat treatment. Both the crystallization activation energy (En) and the frequency factor (v) increased with increasing fluorine content. This means that the fluorine content has a dual effect on the crystallization of fluorosilicic mica glass; the effect on the frequency factor is predominant. The flexural strength of the as-cerammed glass ceramic containing more fluorine is larger than that containing less fluorine when heated to the same temperature.

Keywords: Fluorine; Crystallization; Flexural strength; Fluoro mica glass ceramic

1. Introduction

Fluoromica glass ceramics are widely used in the dental field because of their high esthetics, excellent machinability, and good mechanical properties [1–3]. The main crystalline phase in fluoromica glass ceramics is either fluorophlogopite or fluorosilicic mica [1–4].

The properties of glass ceramics strongly depend on the crystallinity and crystal morphology [5,6]. Fluorine plays an important role in the crystallization and crystalline phases of fluoric glass ceramics [5–7]. It has previously been shown that a high fluorine content is important in ionomer glasses for promoting bulk nucleation of the principal phase, fluorapatite [8]. Likitvanichkul et al. reported that nucleus formation was difficult with the depletion of fluorine, while a new phase would precipitate with a surplus of fluorine in canasite glass ceramics [9–11]. Grossman reported that enstatite developed at ≈980 °C in the crystallization of a tetrasilicic mica glass ceramic with a gross composition of approximately $K_2Mg_5Si_8O_{20.5}F_{3.0}$, i.e., ≈25 mol% deficient in fluorine [1]. In this paper, the effect of fluorine content on the crystallization and flexural strength of fluorosilicic mica glass ceramics was investigated.

2. Experimental

The nominal composition of F12 glass in mole percent was SiO_2 45–60%, MgO 12–18%, MgF_2 8–16%, K_2O 12–20% and ZrO_2 0–5%. Compared with F12 glass, an additional 3 mol% MgF_2 is added in F15 glass while holding the magnesium content constant by changing the ratio of MgF_2:MgO. All the raw materials were of reagent grade, from Sinopharm Chemical Reagent Beijing Co., Ltd. Batches were first melted for 2 h in alumina crucibles in an electric furnace (RHF, Carbolite, Parsons Lane, Hope, Hope Valley, S33 6RB, England) at 1500 °C, and then quenched in deionized water to form a frit. To obtain homogeneous glass, the frit was ground, well mixed and remelted for 30 min at 1450 °C. The melt was partly cast into graphite molds to form glass blocks and partly quenched in deionized water to form the frit. The frit was ground and screened with a 100-mesh sieve to perform the differential thermal analysis (DTA) runs. The non-isothermal crystallization behaviors of the glass samples were determined by DTA (DTA/TGA, STA409,

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Netzsch Gerätebau GmbH, Selb, Germany) using fine powder weighing 50 ± 2 mg in air at a heating rate of 5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min. The reference material was alumina. Transition temperature (*Tg*) was evaluated using the tangent intersection method.

Crystalline phases developed during the heat treatment were determined by X-ray diffraction (XRD) using a diffractometer (Rigaku, Japan) employing Co*K*α. The fractured surfaces of the as-cerammed glass ceramic blocks were etched in 20% HF solution for 15 s, sputtered with gold, and observed under a scanning electron microscope (SEM) using a VEGA II LMH (TESCAN, Czech). The strength of the as-cerammed samples was evaluated by three-point bending tests in an MTS tensile machine (SANS CMT4304). The crosshead speed was 0.5 mm/min. The sample size for the bending test was 2 mm × 3 mm × 24 mm, with the upper surface ground with 1200 SiC paper, and the lower surface polished with 1 μm diamond paste. The specimens' edges were chamfered to minimize local stress concentration during mechanical testing. The maximum load was 98 N.

3. Results and discussion

3.1. Kinetics of crystallization

Typical DTA curves of the two glasses at a heating rate of 10 K/min are shown in Fig. 1. The single exothermic peak indicates that only one crystalline phase is formed during the DTA run. This is confirmed by the XRD patterns of samples heated at 1060 °C for 6 h, illustrated in Fig. 2. According to the JCPDS No. 26-1321 card, the crystalline phase formed is $KMg_{3.25}Si_{3.625}O_{10}F_2$.

According to Fig. 1, the glass *Tg* shifts to a low temperature as the fluorine content increases. This confirms the results of previous investigations [12–14]. *Tg* is related to the viscosity of the glass and determined by the structure of glass. The incorporation of F^- in the glass network results in the substitution of one Si–O–Si bond by two Si–F bonds. The glass network is broken at the Si–F bonds [14]. Therefore, the higher the F^- content , the larger the number of Si–F bonds are generated, and the lower the viscosity and *Tg* .

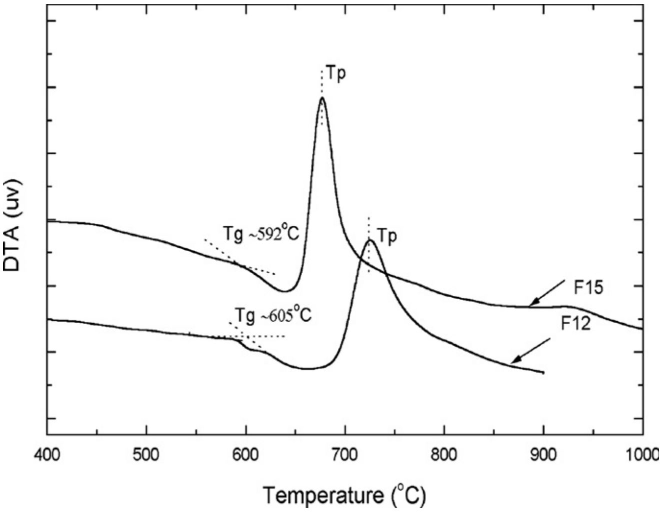

Fig. 1. Typical DTA curves of the glass samples for a heating rate of 10 K/min.

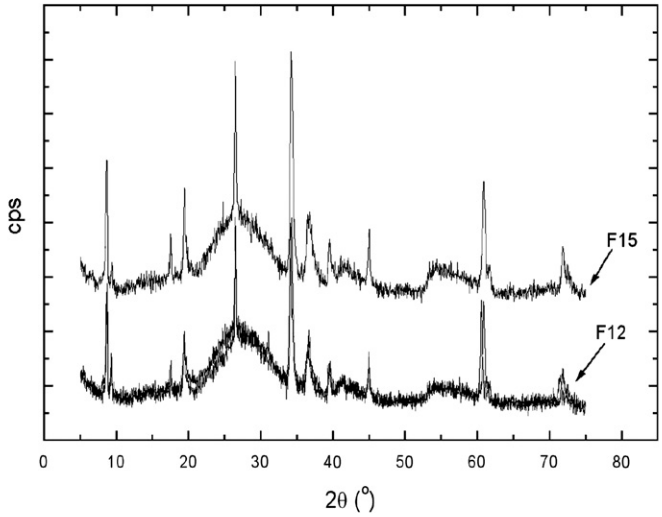

Fig. 2. XRD patterns of the glass blocks after crystallization at 1060 °C for 6 h.

In general, the frequency factor *v* and the effective overall activation energy *E* are used to describe the kinetics of the chemical reaction. In terms of the crystallization of the glass, researchers [12–14] derived the following expression based on the Johnson–Mehl–Avrami (JMA) equation to calculate *E* and *v*:

$$\ln\frac{Tp^2}{\alpha} = \frac{E}{RTp} + \ln\frac{E}{R} - \ln v. \tag{1}$$

where *R* is the gas constant, *Tp* is the crystallization peak maximum temperature in a DTA curve, and α is the heating rate of DTA. Values of *E* and ν can be derived from the plot of $\ln(Tp^2/\alpha)$ vs. $1/Tp$. The results of our experiments and the maximum temperatures, *Tp*, are summarized in Table 1.

As listed in Table 1, compared with F12 glass, both the frequency factor (*v*) and the activation energy of crystal growth (*En*) of F15 glass are greater. According to the derivative equation (Eq. (2)) of the effective overall reaction rate (κ), which is usually assigned an Arrhenius type temperature dependence [12], a high *v* and a low *E* give a high κ. This means that the fluorine content has a dual effect on the crystallization of this glass system.

$$k = v\ \exp\left(-E/RT\right). \tag{2}$$

To clarify the dual effect of the fluorine content on the crystallization of fluoromica glass, the effective overall reaction rates κ of both the glass samples in the range 650–800 °C (because crystallization occurs in this range) are illustrated in Fig. 3. At any given *T*, the figure indicates that the F15 glass has a higher value of κ. This means that the

Table 1
Characteristics of the glass samples.

	Tp [°C]				E [kJ mol^{-1}]	v [min^{-1}]
	$\alpha=5$ [°C/min]	$\alpha=10$ [°C/min]	$\alpha=15$ [°C/min]	$\alpha=20$ [°C/min]		
F12	706	725	740	751	240	1.1×10^{12}
F15	661	677	689	699	260	6.8×10^{13}

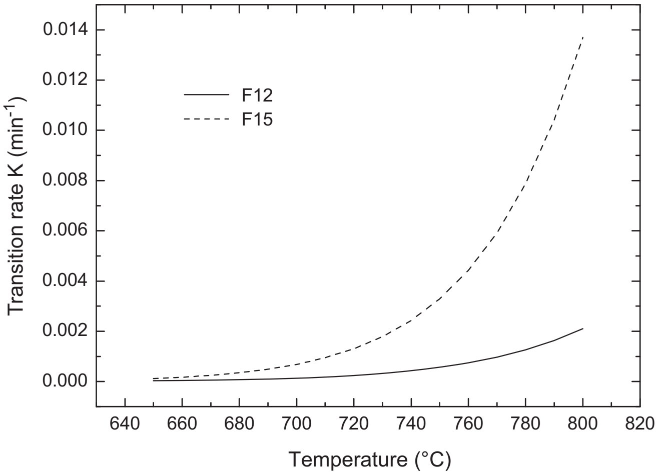

Fig. 3. Transition rate κ vs. temperature T.

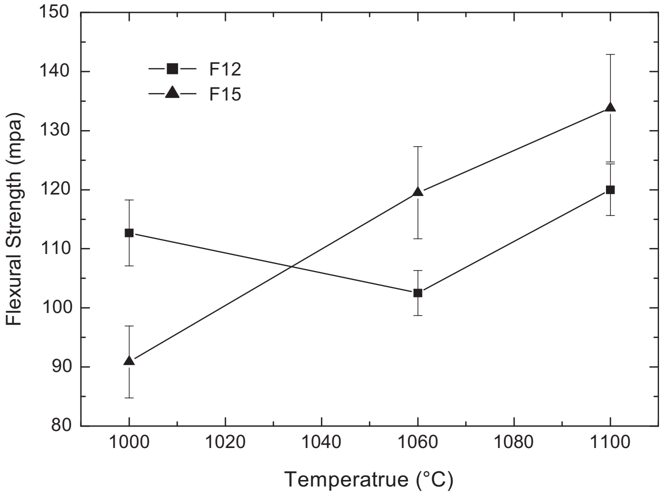

Fig. 4. Flexural strength vs. temperature for a soaking time of 6 h.

effect of fluorine on the frequency factor v is stronger than the effect on the activation energy of crystal growth. It can be concluded that fluorine improves the crystallization in this glass system.

3.2. Flexural strength.

It is shown in Fig. 4 that the strength of F15 glass ceramics is larger than that of F12 glass ceramics when held at the same temperature for the same amount of time at temperatures other than 1000 °C. This is because the crystalline volume content of F15 is larger than that of F12. Fluorine acts as a nucleation agent in this glass system. When the glass samples were subjected to heat treatment, more nuclei formed in the F15 glass. During the subsequent heat treatment, more, smaller crystals developed in the F15 glass because the crystal growth of fluorosilicic mica involves a dissolution and reprecipitation mechanism.

(Fig. 4) also shows the flexural strength of as-cerammed F12 and F15 glass ceramics heat-treated at different temperatures for a soaking time of 6 h. With the increase of the holding temperature, the flexural strength of the F15 glass ceramics increased. This is consistent with Grossman's experiments [1]. He proposed that the large-aspect-ratio crystals were more effective in limiting the effective flaw size within the material, resulting in an increase in the strength. As shown in Fig. 5, the aspect ratio of mica crystals in both F12 and F15 glass ceramics increased with increases in the holding temperature. Whether the variation of the crystal size was directly related with the increased mechanical character of the glass ceramics or not and its underlining mechanism still remains unknown. Further work should be performed to explain why the strength of F12 glass ceramics heat-treated at 1000 °C is much higher than the strength of F12 glass ceramics heated at 1060 °C. Generally, larger crystal sizes lead to a reduced machinability in the dental CAD/CAM machines. But we also noticed that a direct result of the increase in the crystal size was the mutually overlapping microstructure of mica crystals, which enabled local cracks produced by processing to deflect and branch, so the increase of the crystal size does not necessarily exert negative effect on the machinability of glass ceramic. Therefore, further challenging work is still needed to improve the strength of the glass ceramics while keeping excellent machinability.

Fracture toughness is one of the important properties of the fluorosilicic mica glass, which is related to the structure of the glass. Peitl et al. [15] pointed out that the increase in strength was not related to fracture processes that occurred within the precipitates. The present results manifested the effect of fluorine content on the crystallization and flexural strength of fluorosilicic mica glass ceramics. In the future, work should be done to study the relationship of fracture toughness and aspect ratio/sizes of crystals.

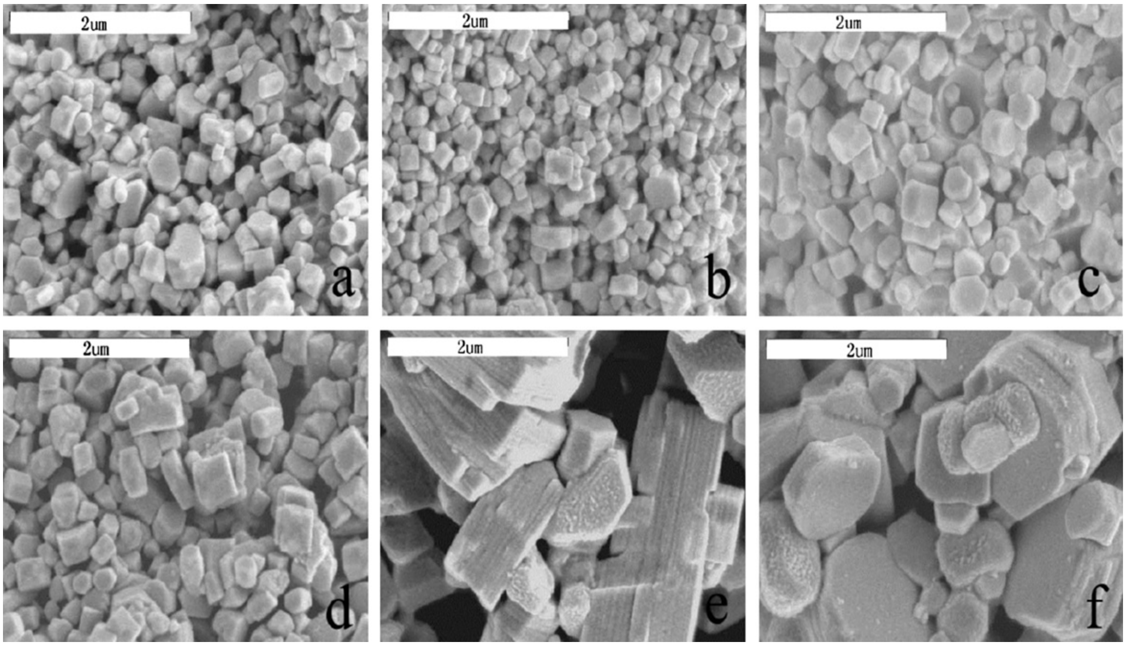

Fig. 5. SEM photos of as-cerammed F12 and F15 glass ceramics: (a) F12, $T=1000$ °C; (b) F15, $T=1000$ °C; (c) F12, $T=1060$ °C; (d) F15, $T=1060$ °C; (e) F12, $T=1100$ °C; and (f) F15, $T=1100$ °C.

4. Conclusions

The effect of fluorine content on the crystallization of fluorine-containing mica was investigated. Only $KMg_{3.25}Si_{3.625}O_{10}F_2$ precipitated in both glass samples. The fluorine addition not only improves the activation energy of the crystal growth but also increases the frequency factor by lowering the viscosity of the glass. The latter effect is predominant.

The fluorine addition also has an effect on the microstructure and mechanical strength. A higher fluorine content leads to more, smaller crystals in and higher flexural strengths of the as-cerammed glass ceramics.

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