JOURNAL OF MATERIALS SCIENCE **37** (2002) 1789–1792

Effect of fluorine content on the crystallization of fluorsilicic mica glass

JIEMO TIAN, XIAOGANG CAO*, YONG ZHANG, CHEN WANG
Beijing Fine Ceramic Laboratory, State Key Laboratory of New Ceramics and Fine Processing. Institute of Nuclear Energy Technology, Tsinghua University, Beijing 100084, People's Republic of China
E-mail: caoxg97@mails.tsinghua.edu.cn

The effect of fluorine content on the crystallization of fluorsilicic mica glass was investigated by differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscope (SEM). A single phase, $KMg_{3.25}Si_{3.625}O_{10}F_2$, precipitates in all the glasses. Both the crystallization activation energy (E_n) and the frequency factor (ν) increase with the increase of the fluorine content. This means that the fluorine content has dual effects on the crystallization of fluorsilicic mica glass, while the effect on the frequency factor is predominant. © *2002 Kluwer Academic Publishers*

1. Introduction

Fluormica glass-ceramics are widely used in dental field because of their high esthetics, excellent biocompatibility, and good mechanical properties and machinability [1–3]. The main crystalline phase in fluormica glass-ceramics is either fluorophlogopite or fluorosilicic mica [1–4]. Dicor® is the most notable commercialized fluorosilicic mica glass-ceramics [3–5].

The properties of glass-ceramics depend highly on the crystallinity and crystal morphology [6]. Fluorine plays an important role on the crystallization and crystalline phase of fluoric glass-ceramics. It has previously been shown that a high fluorine content is important in ionomer glasses in promoting bulk nucleation of the principal phase, fluorapatite [5]. Likitvanichkul and Lacourse [7] reported that the nucleus formation is difficult with the depletion of fluorine, while a new phase would precipitate with the surplus of fluorine, in canasite glass-ceramics. Shell and Ivey [8] verified that a fluorine deficiency caused fluormica compounds to decompose to forsterite and norbergite. Grossman [1] has reported that enstatite develops at ≈980°C in the crystallization of a tetrasilicic mica glass-ceramic with gross composition near $K_2Mg_5Si_8O_{20.5}F_{3.0}$, i.e., ≈25 mol% deficient in fluorine. Daniels and Moore [2] found that fluorine content profoundly influenced the temperature position of the exotherm in DTA run of tetrasilicic glass.

In this paper, the effect of fluorine content on the crystallization of fluorsilicic mica glass-ceramics was investigated.

2. Theoretical background

The isothermal devitrification kinetics of glass is described by the Johnson-Mehl-Avrami (JMA) equation [9, 10]

$$\chi = 1 - \exp\left[-(kt)^n\right] \qquad (1)$$

where χ is the volume fraction crystallized at a given temperature during time t; n is the dimensionless Avrami exponent, which is dependent on the crystallization mechanism; and κ is the effective overall reaction rate, which is usually assigned an Arrhenian temperature dependence

$$k = \nu \exp(-E/RT) \qquad (2)$$

where ν is the frequency factor of the overall process, R is the gas constant, T is the absolute temperature, and E is the effective overall activation energy.

According to the JMA equation, Bansal [11] and Hu [12] derived the same expression to describe the non-isothermal crystallization kinetics of glass, respectively

$$\ln \frac{T_p^2}{\alpha} = \frac{E}{RT_p} + \ln \frac{E}{R} - \ln \nu \qquad (3)$$

where T_p is the crystallization peak maximum temperature in a DTA curve, α is the heating rate of DTA. Values of E and ν can be derived from the plot of $\ln(T_p^2/\alpha)$ versus $1/T_p$. Matusita [13] proposed that the heat released from nucleation process was negligible during DTA run. This implies that the E calculated from Equation 3 can be thought as the activation energy of crystal growth, E_n.

3. Experimental procedures

Three glasses based on Dicor® were prepared from reagent grade MgF_2, MgO, ZrO_2, K_2CO_3 and SiO_2. The compositions of the batches are listed in Table I. The fluorine content varied while holding the magnesium content constant by the change of the ratio of $MgF_2 : MgO$. Batches were firstly melted for 2 h in alumina crucibles in an electric furnace at 1500°C, and then quenched

---

*Author to whom all correspondence should be addressed.

TABLE I Nominal composition of the glasses in mol%

Composition no.	SiO_2	MgO	MgF_2	K_2O	ZrO_2
F12	58.8	16.2	11.4	11.2	2.4
F15	58.8	13.4	14.2	11.2	2.4
F18	58.8	10.5	17.1	11.2	2.4

in deionized water to form frit. In order to obtain homogeneous glass, the frit was ground, well mixed and remelted for 30 min at 1450°C. The melt was partly cast into a graphite mould to form glass blocks, and partly quenched in deionized water to from frit. The frit was ground and screened with a 100-mesh sieve to undertake differential thermal analysis (DTA) run.

The non-isothermal crystallization of the glasses were determined by DTA, using fine powder weighing 50 ± 2 g in air, at a heating rate of 5 k/min, 10 k/min, 15 k/min and 20 k/min, respectively. The reference material is alumina. T_g is evaluated using the tangent intersection method.

To identify the crystalline phases precipitated during the heat treatment, X-Ray (Cu K_α) powder diffraction (XRD) was employed. Fractured surfaces of the glass-ceramics blocks heat-treated were etched in 20% HF solution for 15 s, sputtered with gold, and observed under scanning electron microscope (SEM).

4. Results

After being cooled down, the F12 and F15 glass blocks are clear, while the F18 glass has a foggy appearance.

Typical DTA curves of the three glasses at a heating rate of 10 k/min are shown in Fig. 1. One exotherm peak indicates that only one crystalline phase is formed during the DTA run. This is confirmed by the XRD patterns of samples heated at 1075°C for 6 h, illustrated in Fig. 2. Accroding to JCPDS No.26-1321 card, the crystalline phase formed is $KMg_{3.25}Si_{3.625}O_{10}F_2$ fluormica.

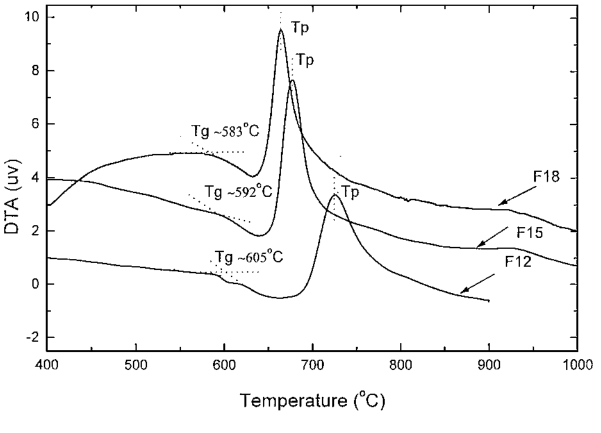


Figure 1 Typical DTA curves of the glasses at a heating rate of 10 K/min.

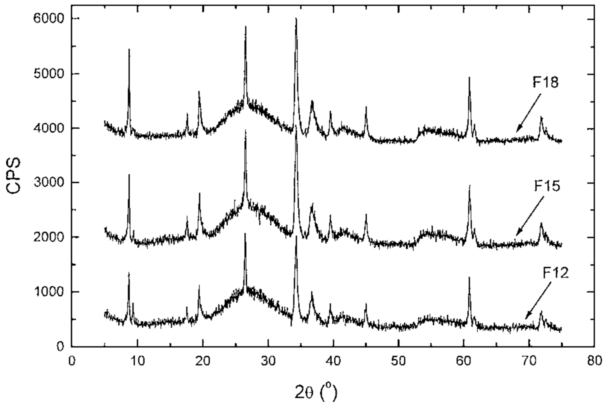


Figure 2 XRD patterns of the glass blocks after crystallization at 1075°C for 4 h.

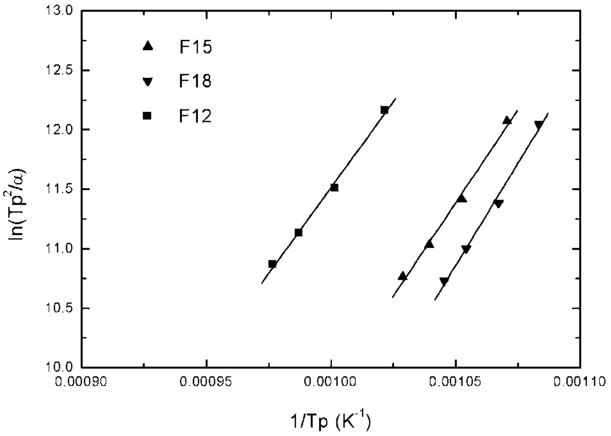


Figure 3 Plots of $\ln(T_p^2/\alpha)$ vs $1/T_p$ of the glasses.

The maximum exotherm temperature, T_ps, are summarized in Table II. The plots of $\ln(T_p^2/\alpha)$ versus $1/T_p$ of the glasses are presented in Fig. 3. Values of activation energy E and frequency factor ν determined by linear fitting of the experimental data are also listed in Table II. Based on the E_s and νs, κ dependence of T are derived for each glass

$$k_1(T) = 1.1 \times 10^{12} \times \exp(-240 \times 1000/RT) \quad (4)$$

$$k_2(T) = 6.8 \times 10^{13} \times \exp(-260 \times 1000/RT) \quad (5)$$

$$k_3(T) = 3.3 \times 10^{15} \times \exp(-286 \times 1000/RT) \quad (6)$$

Where Equation 4–6 are corresponding to F12, F15 and F18 glasses, respectively.

TABLE II Characteristics of the glasses

	T_p/°C					
	$\alpha = 5$ k/min	$\alpha = 10$ k/min	$\alpha = 15$ k/min	$\alpha = 20$ k/min	E/KJ · mol^{-1}	ν/min^{-1}
[a]Dicor®	–	744	–	766	203	2.8×10^{11}
F12	706	725	740	751	240	1.1×10^{12}
F15	661	677	689	699	260	6.8×10^{13}
F18	650	664	676	684	286	3.3×10^{15}

[a]The data in this line were quoted from the no.5 paper listed in the references.

5. Discussion

5.1. The glass transition temperature (T_g)

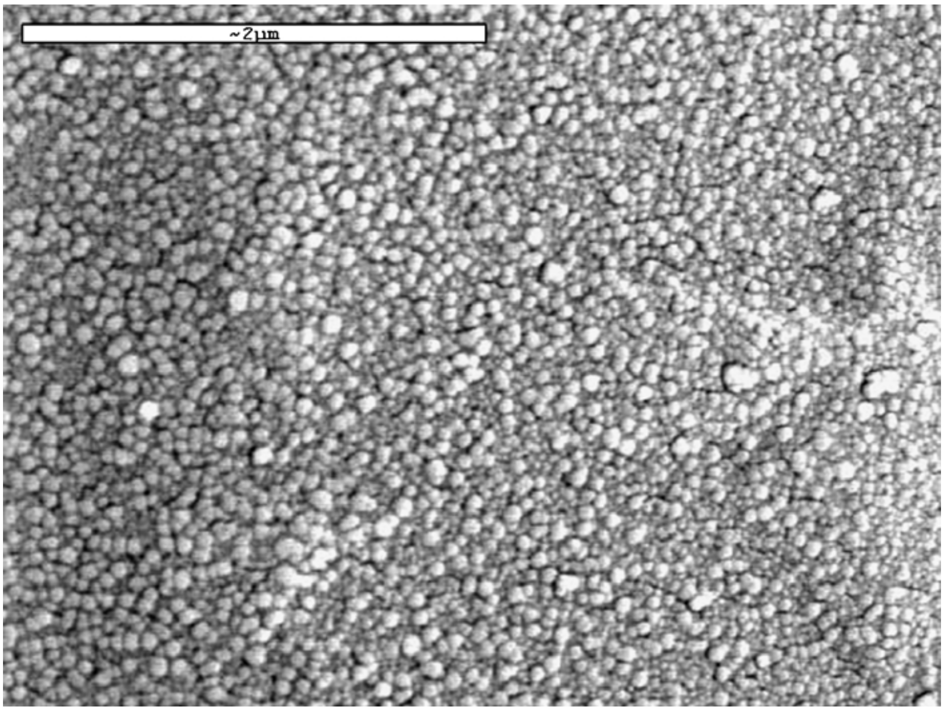
According to Fig. 1, the glass transition temperature (T_g) shifts to low temperature as the fluorine content increases. This conforms to previous investigations [2, 7, 14]. T_g is related to the viscosity of the glass and determined by the structure of glass. The incorporation of F^- in the glass network results in the substitution of one Si—O—Si bond by two Si—F bonds. The glass network is broken at Si—F bonds [2, 14, 15]. Therefore, the higher the F^- content is, the more Si—F bonds are generated, the lower the viscosity and T_g are.

5.2. The kinetic parameters of crystallization

As listed in Table II, with the increase of the fluorine content, the maximum exotherm peak temperature (T_p) at each heating rate decreases, while both the frequency factor (ν) and the activation energy of crystal growth (E_n) increase. These results are well consistent with the Bapna and Muller's results on Dicor® [5], also listed in Table II. According to their report, all the maximum exotherm peak temperatures of Dicor® glass at each heating rate were biggest among all the four glasses listed in Table II, while both the activation energy and the frequency factor of the Dicor® glass were the smallest. According to Equation 2, a low value of E_n and a high value of ν give a high transition rate (K). This means that the fluorine content has a dual effect on the crystallization of this glass system [16].

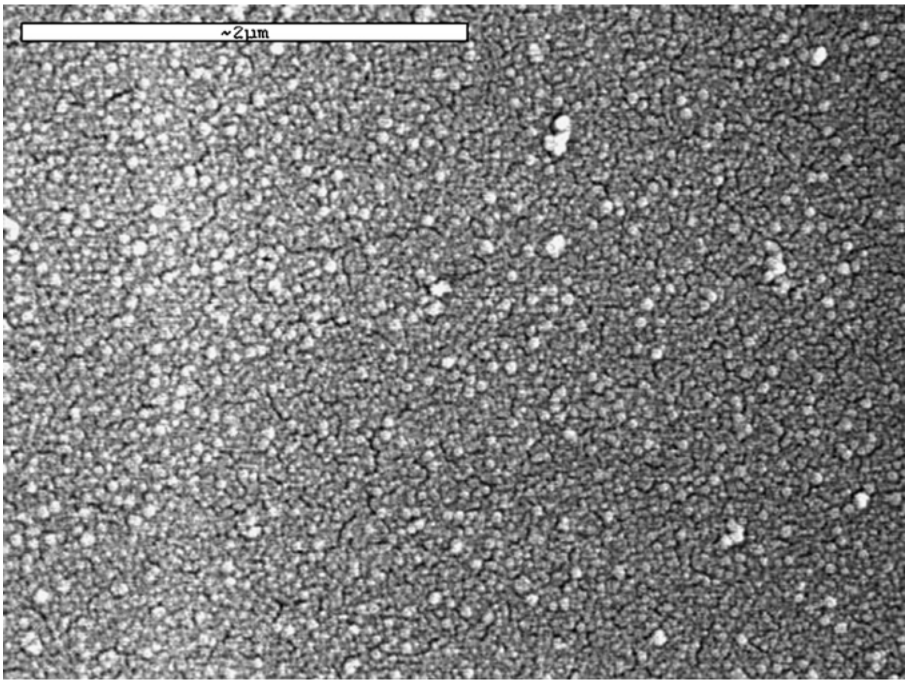
The fluorosilicic mica crystal growth is of a dissolution and reprecipitation mechanism and controlled by diffusion. The fluorine and magnesium ions diffuse from the glassy matrix to the crystals, while the potassium and silicon ions diffuse towards the glassy matrix [2, 17, 18]. The analyses of T_g above showed that the glass viscosity decreased with the increase of the fluorine content, as favored the diffusion of ions. So, the frequency factor ν increased. Here, the activation energy of crystal growth (E_n) can be thought as the sum of the diffusion potential barrier during the glass matrix (q_1) and between the crystal/glass interface (q_2). As illustrated in Fig. 4, more and smaller nuclei formed in the glass of higher fluorine content. This phenomenon is consistent with Likitvanichkul's investigation [7]. Based on the classical nucleation theory [19], which proposed that the nucleus/liquid interfacial energy is approximately inversely proportional to the nucleus radius, it is concluded that the crystal/glass interfacial energy enhanced with the increase of fluorine content in this glass system. Therefore, the increase of fluorine content not only decreases the glass matrix viscosity, which favors the diffusion and makes q_1 decrease; but also enhances the irregular degree of the crystal/glass interfacial structure, which hinders the diffusion and make q_2 increase. It is obvious that the latter is predominant.

In order to make clear the dual effect of fluorine content on the crystallization of fluormica glass. Based on the Equations 4–6, the values of κ of all the glasses as a function of the temperature, T, in the range 650°C–800°C because crystallization occurs in this range, are illustrated in Fig. 5. At any given T, it shows that the glass containing more fluorine has a higher value of κ. This means that the effect of fluorine on the frequency factor ν is in the highest flight, compared with that on the activation energy of crystal growth. It can be concluded that fluorine does good to the crystallization in this glass system.



(a)

Figure 4 SEM of the glasses holding at 650°C for 1 h . (a) F12; (b) F15. (*Continued*).



(b)

Figure 4 (*Continued*).

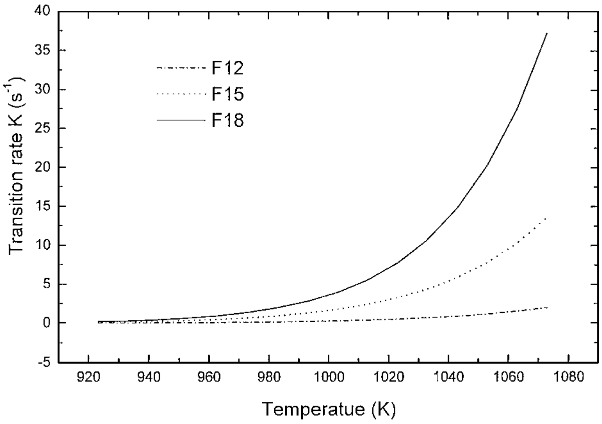


Figure 5 Transition rate κ vs the temperature T.

6. Conclusion

Based on the modified JMA equation, the effect of fluorine content on the crystallization of fluorine mica was investigated. Only $KMg_{3.25}Si_{3.625}O_{10}F_2$ crystallizes in all glasses. The fluorine addition not only improves the activation energy of crystal growth by enhancing the degree of irregularity of the interface between glass and crystal, but also increases the frequency factor by lowering the viscosity of glass, while the latter is predominant.

References

1. D. G. GROSSMAN, *J. Amer. Ceram.Soc.* **55** (1972) 446.
2. W. H. DANIELS and R. E. MOORE, *ibid.* **58** (1975) 217.
3. J. M. TZENG, J. G. DUH, K. H. CHUNG and C. C. CHAN, *J. Mater. Sci.* **28** (1993) 6127.
4. J. R. KELLY, I. NISHIMURA and S. D. CAMPBELL, *J. Prosthetic. Dentistry.* **75** (1996) 18.
5. M. S. BAPNA and H. J. MUELLER, *Biomaterials.* **17** (1996) 2045.
6. P. W. McMILLAN, in "Glass Ceramics" (Academic Press, London, 1979).
7. S. LIKITVANICHKUL and W. C. LACOURSE, *J. Mater. Sci.* **30** (1995) 6151.
8. H. R. SHELL and K. H. IVEY, *U. S. Bur. Mines. Vull.* **647** (1969) 291.
9. M. AVRAMI, *J. Chem. Phys.* **7** (1939) 1103.
10. W. A. JOHNSON and K. F. MEHL, *Trans. Am. Inst. Electr. Eng.* **135** (1939) 416.
11. N. P. BANSAL and R. H. DOREMUS, *J. Thermal. Anal.* **29** (1984) 115.
12. L. HU and Z. JIANG, *Chinese J. Ceram. Soc.* **22** (1994) 419.
13. K. MATUSITA, in "Science of Non-crystalline Glass" (Chinese Architecture Industry Press, Beijing, 1986) p. 286.
14. K. G. CHENG, J. WAN and K. M. LIANG, *Mater. Sci. Eng.* A **271** (1999) 167.
15. S. G. GRIFFIN and R. G. HILL, *Biomaterials.* **21** (2000) 693.
16. K. G. CHENG, *J. Non-Crystal. Solids* **238** (1998) 152.
17. I. L. DENRY *et al.*, *Mater. Res. Bull.* **34** (1999) 1615.
18. M. S. BAPNA, H. J. MUELLER and S. D. CAMPBELL, *Thermochimica Acta* **275** (1996) 289.
19. V. M. FOKIN and E. D. ZANOTTO, *J. Non-Crystal. Solids* **265** (2000) 105.

Received 19 April 2001
and accepted 9 January 2002