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# Fluorophlogopite porcelain based on talc–feldspar mixture

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**Abstract**

Talc–feldspar mixture was utilized for the processing of dense mica containing porcelain through controlled crystallization for dental use. Uniform microstructure with fine equigranular fluorophlogopite grains was developed at 950°C. Fluorophlogopite grains, 0.2 μm in size, are well distributed in the glassy phase. The thermal expansion coefficient was measured to be $107\times10^{-7}/°C$ (20–780°C). The first crystallization was found to be at 645°C,while the crystallization of fluorophlogopite existed at 910°C. On firing at 1050°C, a small amount of forsterite was detected associated with mica grain growth. The formation of forsterite was related to the decomposition of fluorophlogopite. Two fluorophlogopite crystal habits were detected via SEM. EDAX showed that the two crystal forms have the same composition at 950 and 1000°C. The amount of $Al_2O_3$ increases with the amount of MgO and $SiO_2$ at 1050°C. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

*Keywords:* Fluorophlogopite; $MgF_2$ mineralizer; Controlled crystallization; Uniform microstructure

## 1. Introduction

Research on the synthesis of mica started early in the current century [1]. Various synthetic micas were prepared in a trial for searching those crystallized easily and having the best microstructure [2]. The respective machinability and unique properties of synthetic micas are related to their microstructure [3].

Micas are a group of sheet silicate minerals strong, flexible and cleavable in nature. The structure of mica is composed of a octahedral layer sandwiched between two tetrahedral layers pointing toward each other. The octahedral layer consists of closely packed oxygen, hydroxyl and/or fluorine in which cations of radii from 0.5 to 0.8 Å are present. The tetrahedral layer consists of silicon-oxygen tetrahedrons linked together in a hexagonal network. The three layer composite sheet has a net negative charge. The excess charge is balanced by the uptake of cations between the composite sheets in 12 fold coordination. The interlayer cations are weakly bonded giving rise to a perfect set of cleavage [4,5].

The structural transformations of mica are followed by a change in the chemical and thermal properties. Also the isomorphous substitution has been extended to include the different cations in the structure [15]. The isomorphous substitutions include the tetrahedral layer where silicon is found in the structure. The substitution follows the solid solution chemistry of mica expressed as $K_{1-x}\ Mg_{3-y}Al_y((Al,B)_{1-z}Si_{3+z}O_{10+w})F_{2-w}$ assuming the sum of (O + F) anions = 12.

Various types of micas were synthesized, but fluorophlogopite is studied on emphasis [1,5,6–8]. Fluoride mineralizers are the keys for fluorophlogopite crystallization. Magnesium fluoride is the widely used mineralizer for its less volatility and high melting temperature (1263°C) [8]. Liquid–liquid phase separation is the most important phenomena for the initiation of the internal nucleation and crystallization of mica. Detailed studies of phase–phase separation and crystallization concerning the mechanisms and related conditions were further reported [9–12]. The crystallization of mica proceeds in several steps before the crystallization of fluorophlogopite [5,13]. Fluorophlogopite crystallizes in a range of temperatures affording a chance for reaching controlled crystallization. Typical nucleation and crystallization of fluorophlogopite exists between 600–800°C and 850–1050°C, respectively [14].

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The present paper deals with the processing of fluorophlogopite containing porcelain. The work searches for a microstructure with fine, equigranular and uniform size distribution of randomly oriented mica grains within the glassy matrix. The phase composition and microstructural variables of porcelain were emphasized. The grain size and crystallinity were assessed.

## 2. Experimental work

### 2.1. Frit preparation

Egyptian talc and feldspar raw materials with the chemical compositions displayed in Table 1 were used to prepare fluorophlogopite mica porcelain. Two batches were prepared based on the talc:feldspar mixture. Talc:feldspar ratio was taken equivalent to 1:3 in mix 1. 10% of both $MgF_2$ (Fluka) and $B_2O_3$ were added to 80% of mix 1 to form mix 2. Boron oxide was added in the form of chemical reagent boric acid (Fluka). The chemical composition of the two mixes was shown in Table 2.

Batches were milled and wet mixed in a ball mill for 1 h. The milled powders were dried at 120°C for 24 h. The materials were uniaxially pressed into 100 g cubes under a force of 50 kN. The pressed cubes were calcined at 1000°C for 1 h. The calcined materials were fused in platinium dishes using a fast firing furnace. The temperatures for complete fusion of mixes 1 and 2 were 1390 and 1180°C, respectively. The fused specimens were poured in a stream of cold water to be fritted. The resulted frits were milled in a ball mill for 4 h to pass 75 μm sieve.

### 2.2. Characterization

Samples of the milled powders were thermally analyzed via DTA apparatus type Perkin Elmer up to 1000°C with a heating rate 10°C/min. Frit powders were uniaxially pressed into 1 cm diameter specimens and 0.4 cm in height under a force of 10 kN. The specimens were heat treated between 700 and 1100°C/2 h following the results of DTA analysis. The phase composition of specimens heat treated at 950,1000 and 1050°C/2 h were followed by XRD analysis. XRD analysis was carried out using apparatus type Philips pH 9920/05 with Cu-target and Ni-filter.

Samples of mix 2 chosen according to phase composition and thermal analysis were polished. Polishing is accomplished by different grades of abrasives followed by 1.0 μm diamond paste. The polished specimens were washed by water and acetone in an ultrasonic bath. The polished samples were chemically etched using a mixture containing 1% EDTA and 5% NaOH for 30 s. The microstructure of the etched samples was analyzed via SEM Type Philips XL-30 with accelerating voltage 30 kV attached with EDAX unit. The coefficient of thermal expansion was determined for a sample of mix 2 calcined at 700°C/2 h and fired at 950°C/2 h using Shimadzu Dilatometer.

Table 1
Chemical composition of raw materials

| Oxide% | $SiO_2$ | $Al_2O_3$ | MgO | $K_2O$ | $Na_2O$ | CaO | $Fe_2O_3$ | L.O.I |
|---|---|---|---|---|---|---|---|---|
| Talc | 62.00 | 1.60 | 30.30 | 0.11 | 0.32 |  | 0.40 | 4.70 |
| Feldspar | 64.03 | 18.40 |  | 11.70 | 1.60 | 2.70 | 0.49 | 1.00 |

Table 2
Chemical composition of the different mixes

| Oxide% | $SiO_2$ | $Al_2O_3$ | MgO | $K_2O$ | $MgF_2$ | $Na_2O$ | CaO | $B_2O_3$ |
|---|---|---|---|---|---|---|---|---|
| Mix 1 | 65.21 | 14.58 | 07.79 | 09.03 |  | 01.31 | 02.08 |  |
| Mix 2 | 52.17 | 11.66 | 06.23 | 07.23 | 10.00 | 01.05 | 01.66 | 10.00 |

## 3. Results and discussion

The results of thermal analysis acts as a guide for controlling the nucleation and crystallization of fluorophlogopite from the prepared frit. DTA results of the prepared frits are shown in Table 3 and Fig. 1. In mix 1, the exothermic reaction at 1030°C is related to orthoenstatite to protoenstatite transformation [16,17].

In mix 2, the endothermic reaction at 540°C indicates the temperature at which F-anions move into ordered positions to act as a nucleation agent for the formation of octahedra. These octahedra form the central position of the synthetic mica unit cell as noted by Daniels et al. [13]. The temperature of early crystallization is 645°C. The small exothermic reaction at 750°C is related to the crystallization of norbergite ($Mg_2SiO_4.MgF_2$). On the other hand, the exothermic reaction at 910°C indicates the crystallization of fluorophlogopite.

The phase analysis of mix 1 showed the formation of forsterite in addition to enstatite as displayed in Fig. 2. No mica fluorophlogopite was detected in the absence of magnesium fluoride mineralizer. The formation of enstatite is not due to the dissociation of talc as recorded by Goeuriost et al. [18], where the fusion temperature 1390°C is too high. Eitel et al. [8] reported the formation of forsterite and leucite through the reaction of MgO and feldspar. Leucite is a feldspatoid mineral that forms

Table 3
The temperatures of peaks detected by DTA analysis

| Peak | Endo | Exo | Exo | Exo |
|---|---|---|---|---|
| Mix 1 |  |  |  | 1030°C |
| Mix 2 | 540°C | 645°C | 750°C | 910°C |

as a result of silica deficiency. In the present case, enstatite was formed through the reaction between talc and feldspar, where excess silica was introduced on the addition of talc.

In mix 2, the presence of fluorine plays a vital role in the crystallization of mica fluorophlogopite. The course of chemical reaction was completely changed on the addition of $MgF_2$ to talc and feldspar mixture. Fluorophlogopite forms instead of the two phase mixture; foresterite and enstatite. Fluorophlogopite was detected with complete XRD pattern at 950°C as shown in Fig. 3. Small amount of forsterite was found to be formed at 1050°C. The presence of mineralizer did not prevent forsterite formation. The forsterite was formed as a result of the partial decomposition of fluorophlogopite. The decomposition is related to fluorine volatilization as recorded by Grossmann [3]. The amount of fluorine not only affects the temperature of crystallization, but also phase transformation and fluorophlogopite decomposition.

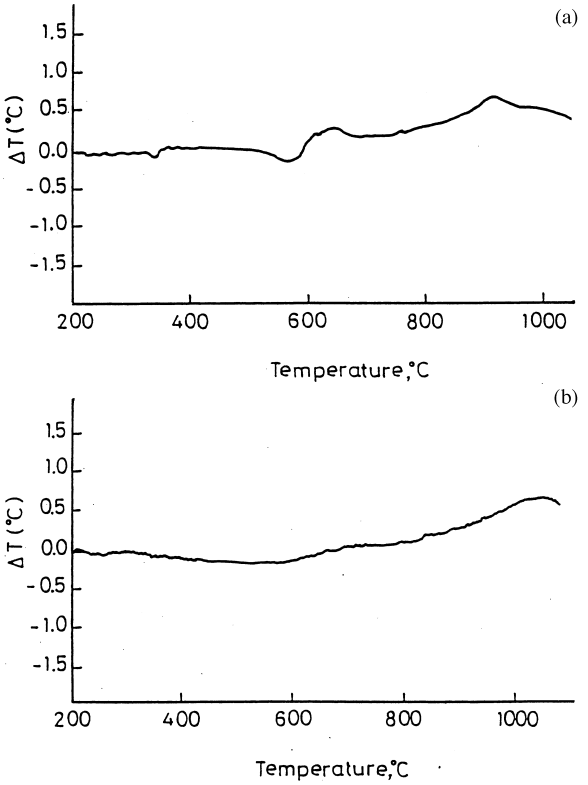


Fig.1. DTA of different frits. A. Frit of mix 2; B. Frit of mix 1.

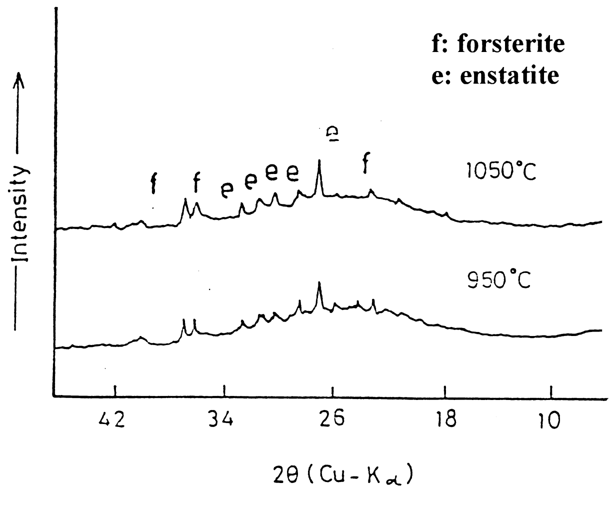


Fig.2. XRD of mix 1 fired at different temperatures.

Another phenomenon exists in mix 2 fired at 1050°C. The intensities of different fluorophlogopite XRD peaks are slightly different from that recorded in the XRD card. The peaks with hkl (003) and (001) corresponding to 65 and 100%, respectively, in the card displayed different intensities. The difference is possibly due to a kind of preferred orientation of the prismatic mica grains.

It is well known that the microstructure is critically affected by the composition of the parent frit and the heat treatment. In mix 2, the addition of $MgF_2$ and $B_2O_3$ to talc–feldspar mixture results in a melting at 1180°C. The crystallization of fluorophlogopite was

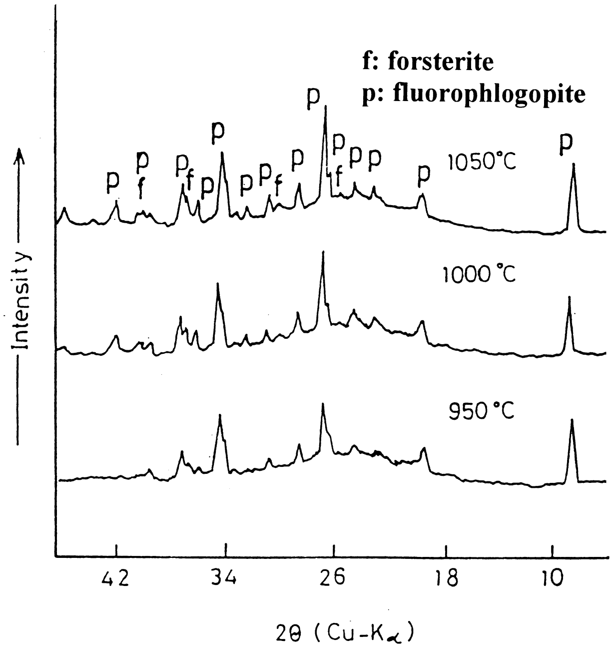


Fig.3. XRD of mix 2 fired at different temperatures.

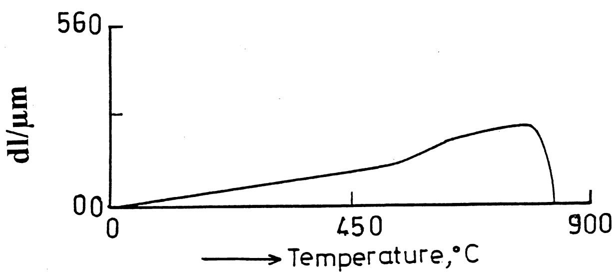
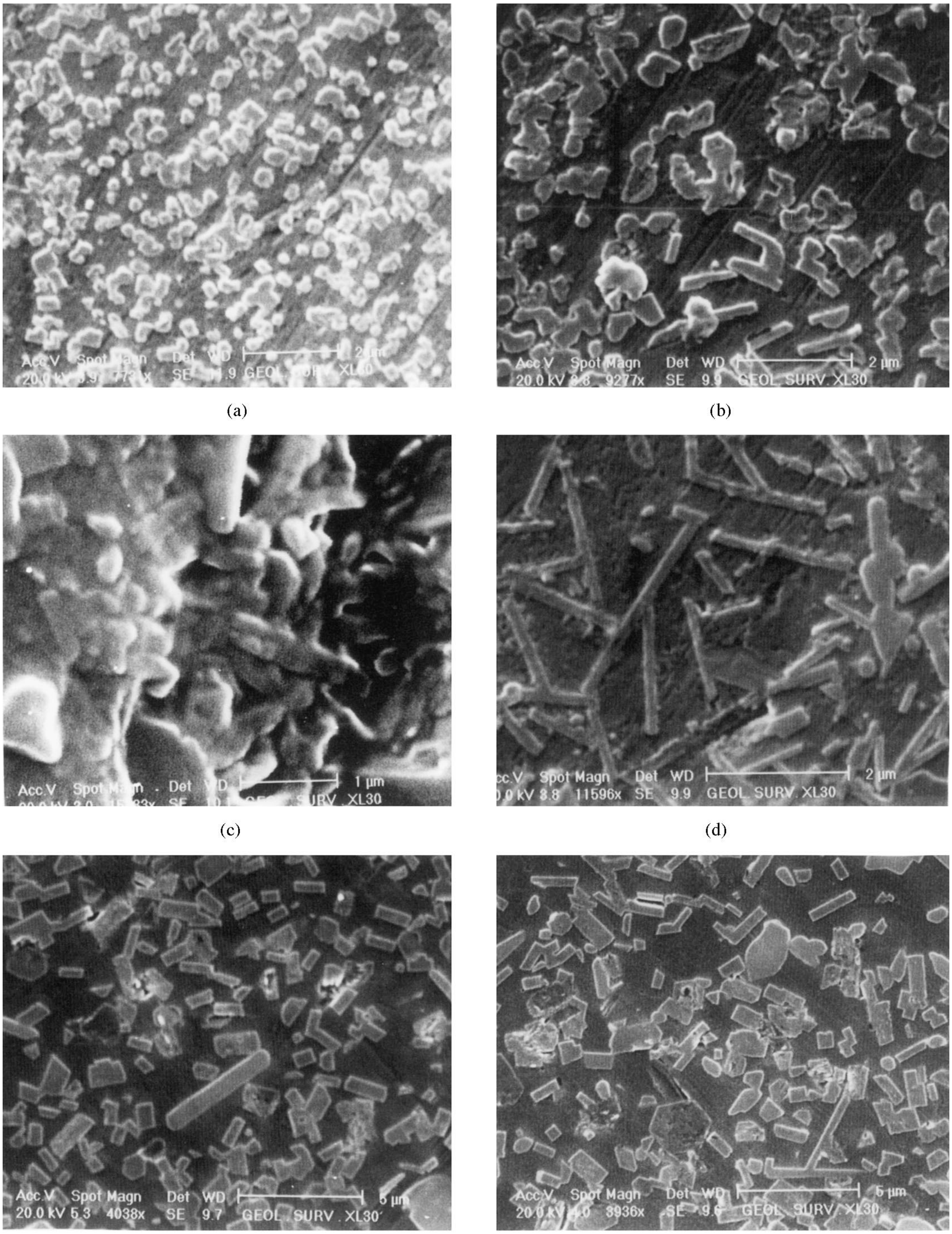


Fig.4. Thermal expansion of mix 2 fired at 700 and 950°C/2 h.

carried out at the lowest possible temperature. The crystallization follows the thermal analysis results to avoid fluorine volatilization and weight loss as well as to control grain growth. The microstructure of mix 2 fired at 950°C/2 h displayed two-grain habits; flaky and prismatic in shape, Fig. 5B. The flaky grains are equal in size, while prismatic grains are variable in size. They are distributed in the glassy phase with different orientations. The size of grains ranges from less than 0.5–1 µm in length for prisms and less than 0.3 µm in size for flaky grains. Prismatic grains are not well developed.

On raising the temperature up to 1000°C, fluorophlogopite crystals grow to some extent in spite of the narrow size distribution as shown in Fig. 5D. Some



(a) (b)

(c) (d)

(e) (f)

Fig. 5. SEM of mix 2 fired at different temperatures. A. Sample fired at 700 and 950°C/2 h (firing rate 5°C/min). B. Sample fired at 950°C/2 h. C,D. Sample fired at 1000°C/2 h. E,F. Sample fired at 1050°C/2 h.

prismatic grains are locally well developed to reach 2 μm in length and 0.1 μm in width. The two crystal habits are also present as shown in Fig. 5C,D. EDAX of the two grain habits in Fig. 6A displayed the main constituting elements in the composition of mix 2. The flaky shape grains and the prismatic grains have the same composition in different locations at 950 and 1000°C. On firing at 1050°C/2 h, fluorophlogopite grains reaches 4 μm in length as shown in Fig. 5E,F. EDAX of prisms showed the increase of $Al_2O_3$ on the extent of MgO and silica as displayed in Fig. 6B.

The results of thermal expansion in Fig. 4 displayed that the rate of expansion changes at different temperatures. Linear thermal expansion exists up to 540°C corresponding to the temperature at which fluorine ions start to be ordered to act as a nucleation agent for the formation of octahedra. The rate of expansion increases gradually up to 645°C corresponding to the temperature of first crystallization. The thermal expansion is linear between 645 and 780°C. Shrinkage starts at temperature $>780$°C due to the beginning of vitrification. The coefficient of thermal expansion was measured to be $107\times10^{-7}$/°C at within the temperature range from 20 to 780°C.

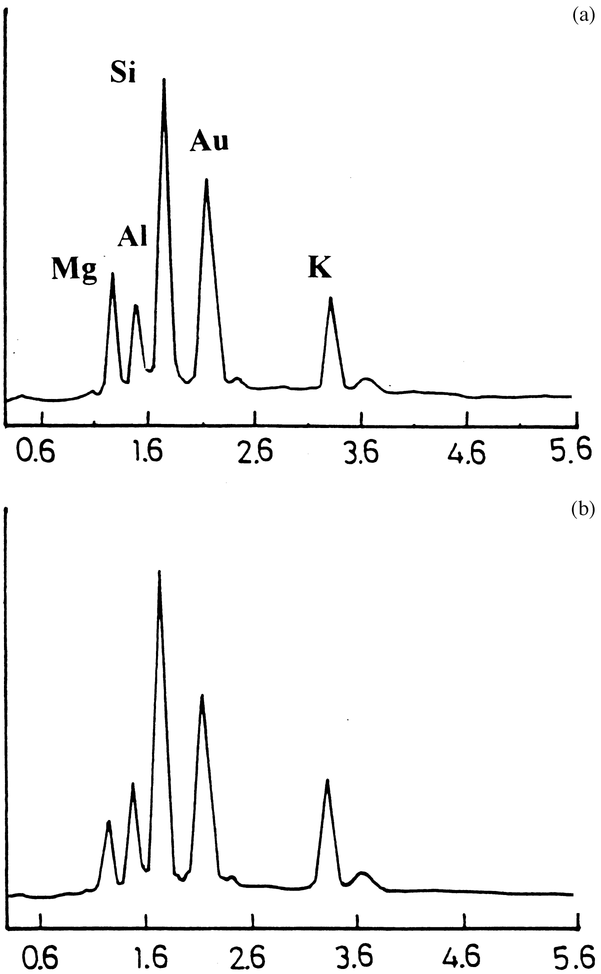


Fig. 6. EDAX of mix 2 fired at different temperatures. A. Sample fired at 1000°C. B. Sample fired at 1050°C.

Uniform microstructure with fine, equigranular and well distributed fluorophlogopite grains in the glassy matrix was formed at 950°C as shown in Fig. 5A. The morphological and microstructural properties of fluorophlogopite mica were controlled via adjusting the rate of firing to 5°C/min and the heat treatment at 700°C/2 h before crystallization. The formation of fluorophlogopite is preceded by the formation of norbergite as indicated by the results of DTA at 750°C. Norbergite phase was nucleated through quenching of the silicate melt where the possibility for nucleus formation increased rapidly with supercooling as shown by Noda [1] The nucleation process is also enhanced by the thermal treatment at 700°C/2 h in addition to the low rate of firing.

Chen et al.[14] studied the crystallization of fluorophlogopite in the composition range of $SiO_2=48–53$, $B_2O_3=6–10$, $Al_2O_3=$ 5–11, $MgO=10–13$, $MgF_2=8–10$ and $K_2O=5–8$. A similar range was studied by Höland et al. [19]. The exothermic reaction indicating the start of crystallization of fluorophlogopite exists at 860°C. They recorded that perfect mica crystals were formed between 850 and 930°C/3 h in the base composition. In the present study, mix 2 was found to be in the composition range of the base glass studied by Chen et al. [14]. The crystallization of perfect fluorophlogopite was found to be at 910°C as detected by DTA and confirmed by XRD and SEM at 950°C/2 h.

## 4. Conclusion

Uniform microstructure with fine grains 0.1 μm in size was developed at 950°C under controlled conditions. The first crystallization was detected at 645°C by DTA. Fluorophlogopite crystallization exists at 910°C as displayed by exothermic reaction. Fluorophlogopite mica was slightly decomposed at 1050°C giving forsterite as detected by XRD. SEM analysis shows the formation of two fluorophlogopite habits flaky and prismatic forms. EDAX showed that the two crystal habits have the same chemical composition at 1000°C. At 1050°C, the amount of alumina increases with the extent of magnesia and silica. The phase mixture of forsterite and enstatite was developed in talc–feldspar mixture in the absence of $MgF_2$ mineralizer. The course of the reaction was changed completely toward the formation of fluorophlogopite instead of the two phase mixture with the addition of $MgF_2$. Fluorophlogopite crystallizes at a temperature as low as possible to avoid abnormal growth. The nucleation process was found to be enhanced strongly by quenching the melt in a cold stream of water.

## References

[1] T. Noda, Synthetic mica research in Japan, J. Am. Ceram. Soc. 38 (4) (1955) 147–152.

[2] J.E. Comeforo, R.A. Hatch, R.A. Humphrey, W. Eitel, Synthetic mica investigations: I. A hot-pressed machinable ceramic dielectric, J. Am. Ceram. Soc. 36 (9) (1953) 286–294.

[3] D.G. Grossmann, Machinable glass ceramics based on tetrasilicic mica, J. Am. Ceram. Soc. 55 (9) (1972) 446–449.

[4] L. Pauling, Structure of micas and related minerals, Nat. Akad. Soc. Proc 16 (2) (1930) 123–129.

[5] S.N. Hoda, G.H. Beal, Alkaline earth mica glass-ceramics, in: Advances in Ceramics, Vol. 4: Nucleation and Crystallization in Glasses, American Ceramic Society, 1982, pp. 287–299.

[6] M. Hirao, Phosphate-bonded synthetic mica ceramics, Ceram. Bull. 55 (9) (1976) 788–891.

[7] P.A. Tick, Zirconium-alkali flourophosphate glasses, Physics and Chemistry of Glasses 23 (5) (1982) 73–76.

[8] W. Eitel, R.A. Hatch, M. Denny, Synthetic mica investigations: II. Role of fluorides in mica batch reactions, J. Am. Ceram. Soc. 36 (10) (1953) 341–348.

[9] J.F. MacDowell, G.H. Beall, Immisibility and crystallization in $Al_2O_3$–$SiO_2$ glasses, J. Am. Ceram. Soc. 52 (1) (1969) 17–25.

[10] P.E. Doherty, D.W. Lee, R.S. Avis, Direct observation of the crystallization of $Li_2O$–$Al_2O_3$–$SiO_2$ glasses containing $TiO_2$, J. Am. Ceram. Soc. 50 (2) (1967) 77–81.

[11] D.A. Duke, J.F. MacDowell, B.R. Karstetter, Crystallization and chemical strengthening of nephelene glass-ceramics, J. Am. Ceram. Soc. 50 (2) (1967) 67–74.

[12] M.H. Lewis, J.M. Johansen, P.S. Bell, Crystallization mechanisms in glass-ceramics, J. Am. Ceram. Soc. 62 (5–6) (1979) 278–288.

[13] W.H. Daniels, R.L. Moore, Crystallization of a tetrasilicic flouromica glass, J. Am. Ceram. Soc. 58 (5–6) (1975) 217–221.

[14] X. Chen, L. Hench, D. Greenspan, J. Zhong, X. Zhang, Investigation on phase separation, nucleation and crystallization in bioactive glass-ceramics containing fluorophlogopite and fluoroapatite, Ceram. Int. 24 (5) (1998) 401–410.

[15] E.A. Schatz, Isomorphous substitution for silicon in fluorophlogopite, J. Am. Ceram. Soc. 46 (2) (1963) 71–73.

[16] J.V. Sarver, F.A. Hummel, Stability relations of magnesium metasilicate polymorphs, J. Am. Ceram. Soc. 55 (4) (1962) 152–157.

[17] W.E. Lee, A.H. Heuer, On the polymorphism of enstatite, J. Am. Ceram. Soc. 70 (5) (1987) 349–360.

[18] D. Goeuriot, J. Dubois, D. Merle, F. Thevenot, P. Exbrayat, Enstatite based ceramics for machinable prosthesis applications, J. Eur. Ceram. Soc. 18 (14) (1998) 2045–2056.

[19] W. Höland, W. Vogel, K. Naumann, J. Jummel, Interface reactions between machinable bioactive glass-ceramics and bone, J. Biomed. Mat. Res. 19 (1985) 303–312.