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Fluorphlopgopite ceramic via sintering of glass using inexpensive natural raw materials

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Abstract

Fluorphlopgopite ceramic was prepared from kaolin, feldspar and steatite with the addition of pure chemicals Na_2CO_3, $AlOOH{\cdot}H_2O$ and MgF_2. Glass-ceramics containing the crystal phase fluorphlogopite were prepared using two different routes. The first route was to melt a glass and to crystallize fluorphlogopite by subsequent annealing at temperatures in the range from 900 to 1050 °C kept for 2 h. Here, fluorphlogopite and cordierite were formed. In the other route a sintering procedure was applied using the pre-mentioned materials and sintering temperatures in the range from 900 to 1200 °C kept for 2 h. Here, fluorphlogopite [$(Na,K)Mg_3(AlSi_3O_{10})F_2$], spinel and norbergite were precipitated. The unit cell parameters of the formed fluorphlogopite phase are larger than those according to JCPDS data. This is caused by a partial replacement of Mg by Ca or Ba from the raw materials. The microstructure of sintered samples show interlocked fluorphlogopite rods and small spinel crystals. The samples prepared by thermal annealing of the glass showed curved fluorphlogopite and additionally tiny cordierite crystals.

Keywords: D. Spinel; D. Cordierite; D. Glass-ceramics; Fluormica

1. Introduction

Glass-ceramics are polycrystalline materials prepared by glass crystallization containing crystalline and glassy phase. They have become established in a wide range of technical and technological applications [1]. Glass-ceramic processes involve the controlled devitrification of a glass to provide a homogeneous microcrystalline structure. To achieve this, it is usually necessary to introduce a nucleating agent, such as TiO_2, ZrO_2 or metal fluorides, in the glass that will provide the formation of nuclei for subsequent crystal growth and affect the structural reorganization in the glass in such a manner that a large volume concentration of crystals grow in the glass [1,2]. Mica-containing glass-ceramics have attracted much attention because of their unique properties [3].

Mica containing glass-ceramics are used as high-quality electrical insulators and show high resistance to thermal shock and exhibit good machinability [4–6]. The latter is due to the cleavage of fluorphlogopite crystals. Fluorphlogopite ($KMg_3(Si_3Al)O_{10}(OH)_2$, K-fluorine micas), contain potassium ion incorporated in the interlayer, they show excellent thermal and chemical stability because and are the most stable in the mica group. Therefore, several works have been conducted in the last years to establish the crystallization kinetics [7–9], to obtain oriented mica glass-ceramics by extrusion [10] and to enhance the mechanical properties of mica glasses and glass-ceramics [11,12]. Recent work in fluorphlogopite glass-ceramic indicated that specimens prepared using sintering method had better machinability and mechanical properties due to higher volume of mica percent and finer crystallite size [13].

Raw materials such as kaolin $Al_2(Si_2O_5)(OH)_4$, talc $Mg_3(OH)_2Si_4O_{10}$, steatite $3Mg_{0.4}SiO_2{\cdot}H_2O$ and feldspars $K_{0.5}Na_{0.5}AlSi_3O_8$ may be used in preparation fluorphlogopite ceramic or glass-ceramics [14–16]. In this paper, the preparation of fluorphlogopite of trisilicic composition (K, Na) $Mg_3(Si_3Al)O_{10}(OH)_2$ with ~4.5% F_2 using two different routes is reported: a melt quenching route and a sintering method. The samples are studied by differential thermal analysis, X-ray diffraction and scanning electron microscopy.

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2. Experimental and procedures

The natural raw materials kaolin, feldspar, steatite and quartz were collected from Germany; furthermore, some pure grade chemicals Na_2CO_3, $AlOOH \cdot H_2O$ and MgF_2 were added as initial compounds to prepare fluormica or fluorophlogopite parent glass. The chemical compositions of the used kaolin, feldspar and steatite are summarized in Table 1.

Two processes were used for the preparation of phlogopite, $(Na,K)Mg_3(AlSi_3O_{10})F_2$, containing glass-ceramics. In the first, a glass was melted and subsequently crystallized by thermal annealing. The other route was to mix the raw materials and to sinter them. The procedures are illustrated in the flow chart shown in Fig. 1.

The starting materials shown in Table 2 were mixed together and milled in a zirconia mill for 2 h. Then the powders were sieved to grain sizes smaller than 75 μm. For the sintering route, disc samples were prepared by pressing at 100 MPa. The pressed discs were sintered at temperatures in the range from 900 to 1200 °C in an electric furnace using a heating rate of 10 K/min. The soaking time applied was 2 h, then the samples were cooled down.

For glass preparation, the carefully mixed batch components shown in Table 2 was first melted in a covered alumina crucible at 1500 °C for 1 h then crushed and re-melted in a covered platinum crucible at 155 °C kept for 1 h. Finally, the homogenized glass melt was casted between copper plates. The casted glass samples were then transferred to a muffle furnace preheated to a temperature 20 K higher than the expected glass transition temperature. In order to minimize strains, this temperature was kept for 10 min; then the furnace was switched off allowing the sample to cool down to room temperature.

This glass was crushed, powdered and finally sieved to a grain size fraction of 45–75 μm. The thermal behavior was characterized using differential thermal analysis (DTA-50; Shimadzu, Japan) with a heating rate of 10 K/min.

For the identification of the crystalline phases resulting from thermal treatment, a Siemens X-ray diffractometer (D-5000) with CuKα-radiation was used.

The microstructure and the chemical composition of the resulting materials were examined by scanning electron microscopy with attached energy dispersive X-ray analysis (SEM/EDAX, JSM.7001 F, Japan). The sample was polished, etched for 1 min with 1% HF solution and coated with carbon.

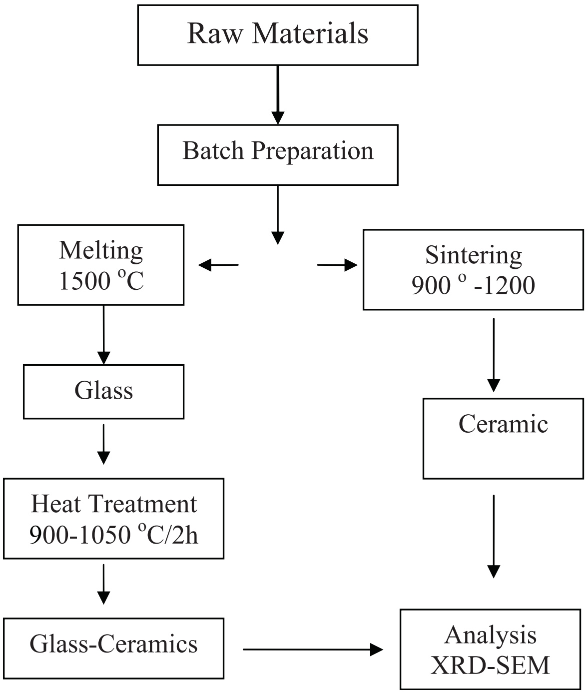


Fig. 1. Flow chart shows the methods followed for preparation of fluorphlogopite.

3. Results and discussion

3.1. Differential thermal analysis of the glass and the sample prepared from the raw materials

Fig. 2 shows DTA-profiles of samples prepared by the two preparation routes. For the specimen prepared form the natural raw materials (see graph a), a slight endothermic effect is observed in the temperature range from 400 to 650 °C. It is due to the evaporation of water, mainly from the kaolin and of CO_2 from the soda. An exothermic peak was detected at the temperatures of 1000 and 1150 °C most probably due to crystallization. At higher temperatures, again an endothermic signal is observed. For the glassy powder (see graph b), an exothermic peak appears at 990 °C followed by abrupt drop caused by partial melting of the specimen.

3.2. Identification of crystalline phases

The shape of the sintered samples prepared by the ceramic route, show changes in the visual shape with the temperature supplied during heat treatment (see Table 3). After sintering at

Table 1
Chemical compositions of the used natural raw materials.

Raw materials	Chemical Composition (wt.%)									
	SiO_2	Al_2O_3	MgO	K_2O	Na_2O	Fe_2O_3	CaO	BaO	TiO_2	P_2O_5
Kaolin	53.35	45.10	0.40	0.53	0.00	0.34	0.29	0.00	0.00	0.00
Feldspar	66.03	17.87	0.02	14.70	0.80	0.04	0.04	0.36	0.04	0.09
Steatite	56.76	6.80	32.72	0.31	0.14	0.49	1.00	1.41	0.29	0.09

Table 2
Constituent of the batch composition from raw materials and some required added chemical.

Ingredients	Required batch components (wt.%)	Feldspar (g)	Kaolin (g)	Steatite (g)	Total comp. (g)	Added* chemicals (g)
SiO_2	45.5	19.2	12.0	14.3	45.5	0.0
Al_2O_3	30.5	5.4	10.2	0.0	15.6	14.9[a]
MgO	7.2	0.0	0.0	7.2	7.2	0.0
K_2O	5.0	5.0	0.0	0.0	5.0	0.0
Na_2O	4.5	0.0	0.0	0.0	0.0	4.5[b]
MgF_2	7.3	0.0	0.0	0.0	0.0	7.3
Total	100.0	29.6	22.2	21.5	73.3	26.7

[a] $AlOOH{\cdot}H_2O$.
[b] Na_2CO_3.

1000 °C/2 h, the samples are slightly deformed at the edges of the disc.

The XRD-patterns of the samples sintered at temperatures in the range from 900 to 1200 °C are shown in Fig. 3. After sintering at a temperature of 900 °C kept for 2 h, the only crystalline phase detected is mica. With increasing the sintering temperature, spinel ($MgAl_2O_4$, JPCDS: 86-2258) and norbergite ($Mg_3F_2SiO_4$, JCPDS:71-2401) are formed. Besides, a broad hump is observed in the XRD-patterns at 2θ-values in the range from 15 to 35° which is a hint of the occurrence of large quantities of glassy phase (see Fig. 3).

Norbergite appears as traces even after sintering at 1100 °C/2 h, while spinel as well as fluorphlogopite becomes the major phase after sintering at higher temperatures (compare X-ray diffraction patterns in Fig. 3).

For the prepared fluorphlogopite glass samples, the crystalline phases developed through thermal annealing at temperatures in the range from 900 to 1050 °C/2 h range are shown in Fig. 4. Only fluorphlogopite ($(Na,K)Mg_3(AlSi_3O_{10})$, ICPDS: 16-0352) and cordierite $(Mg, Fe)_2Al_3Si_5AlO_{18}$ (JCPDS: 83-1385) are identified in the X-ray diffraction patterns (see Fig. 4). From the X-ray diffraction patterns, it can be seen that the increase in the concentrations of these two phases took place with increasing the temperature (up to 1050 °C/2 h). Hence, the quantity of the glassy phase decreases at higher temperatures due to a continuous crystallization process (see Fig. 4).

The crystallization process of mica (fluorphlogopite) depends on the initial composition of the glass. The sequence of fluorphlogopite crystallization in glass-ceramic was expressed by Cheng et al. [7] as follows: (i) heterogeneous nucleation of chondrodite-like ($Mg_5Si_2O_8F_2$) crystals in the

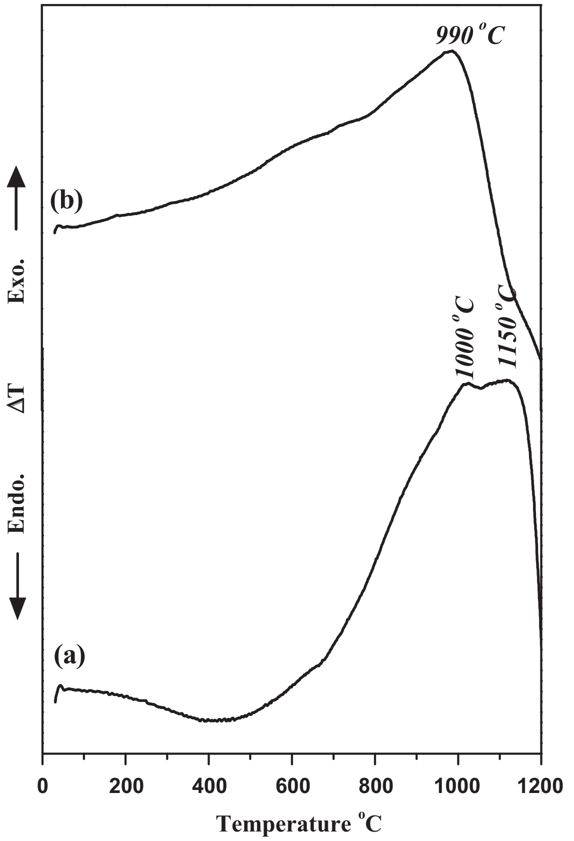


Fig. 2. DTA profiles of the well mixed samples: (a) presintered powder, (b) glass powder.

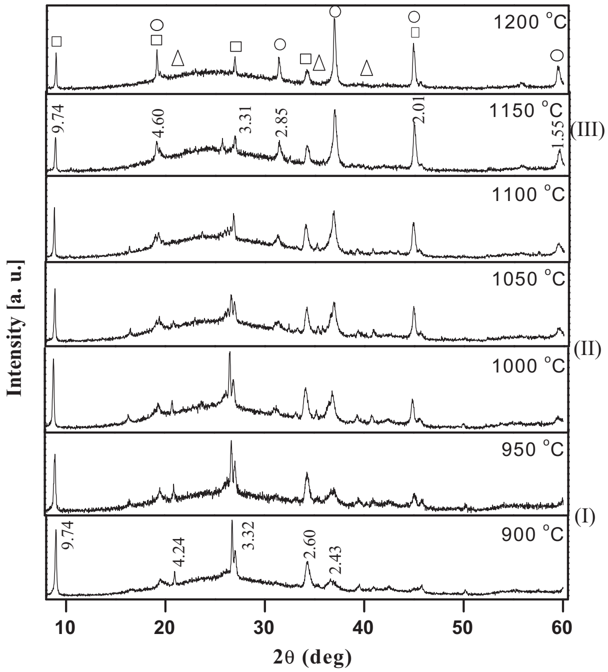
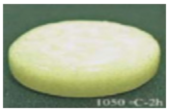
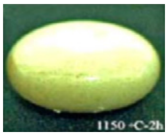
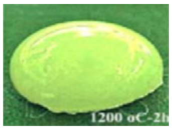


Fig. 3. X-ray diffraction patterns of samples sintered at temperatures in the range from 900 to 1200 °C, (□) mica, (○) spinel and (△) norbergite.

Table 3
Crystalline phases developed in sintered samples during sequential heat-treatment.

Heat-treatment (°C)	Crystalline Phases	Sample morphology
900	Fluorphlogopite, spinel, norbergite (traces)	
950	Fluorphlogopite, spinel (little), norbergite (traces)	
1000	Fluorphlogopite, spinel (little), norbergite (traces)	
1050	Fluorphlogopite, spinel, norbergite (traces)	
1100	Fluorphlogopite, spinel, norbergite (traces)	
1150	Spinel, fluorphlogopite	
1200	Spinel, fluorphlogopite	

glass matrix, (ii) re-crystallization of chondrodite to norbergite ($Mg_3F_2SiO_4$) and (iii) finally the epitaxial growth of fluorphlogopite. The aforementioned results in the fluorphlogopite glass-ceramics showed that in some cases norbergite or chondrodite are not observed. Within $MgO–SiO_2–Al_2O_3–K_2O–F–B_2O_3$ glass-ceramics, MgF_2 phase was detected as the only phase in glasses with low B_2O_3 concentrations [17], in glasses with higher B_2O_3 concentration, however, fluorphlogopite was formed as the major phase in all applied heat-treatment schedules, however, forsterite (Mg_2SiO_4, JCPDS: yzyzyz) was also developed at >900 °C [17]. In other reports, glasses with high fluorine concentrations were crystallized. This resulted in the formation of norbergite, which, with increasing temperature, does not transform into phlogopite [18]. Hamzawy [15] suggested that both intermediate phases, i.e. chondrodite and norbergite, may separately be formed in the glassy state. Subsequently fluorphlogopite is nucleated which possibly grows epitaxially on these phases. In the present work, although norbergite appeared in sintered ceramic samples it is not detected in the sintered glass-ceramics.

3.3. Unit cell parameters of fluorphlogopite

The unit cell parameters determined for the crystallized fluorphlogopite, either formed during sintering or thermal annealing are shown in Table 4.

The cell parameters a and c-axis of the formed fluorphlogopite [$(Na,K)Mg_3(AlSi_3O_{10})$] in both the sintered sample as well as in the annealed glass are larger than those according to the standard sample (ICPDS 16-0352). This might be due to the partial replacement of Mg^{2+} by Ca^{2+} or Ba^{2+}. Calcium and barium are present in the raw materials kaolinite and steatite, respectively. The increase in the lattice parameters should then be due to the larger ionic radii of Ca (0.99 Å) and Ba (1.35 Å) in comparison to that of Mg (0.72 Å). The length of the

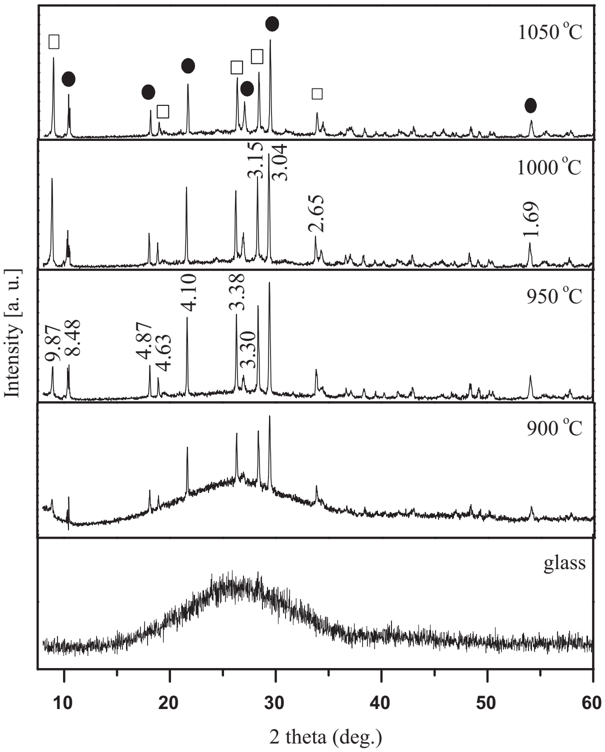


Fig. 4. X-ray diffraction patterns of glass-ceramic samples (□) fluorphlogopite and (●) cordierite.

Table 4
Lattice parameters of fluorphlogopite calculated from the XRD-patterns for of samples and samples prepared by thermal annealing at 1000 °C for 2 h.

Sample	Lattice constants (Å)		Unit cell volume (Å^3)
	a = *b*	*c*	
Mica(JCPDS) No.(16-0352)	5.30700	29.98000	731.24
For sintered sample 1000 °C/2 h	5.36221 ± 0.00019	30.3839 ± 0.0035	756.59 ± 0.27
For annealed glass 1000 °C/2 h	5.33151 ± 0.00088	29.8662 ± 0.0084	735. 21 ± 0.32

crystallographic *a* and the *c*-axes of the sintered samples are larger than those observed in the samples prepared by annealing of the glass.

3.4. Scanning electron microscopy

The microstructures of the sintered samples and the annealed glasses are shown in Fig. 5.

In the samples sintered at 900 °C/2 h, numerous crystals of ellipsoidal shape are seen. The size of the crystals is in the range from 1 to 2 μm. Besides, high volume concentrations of glassy phase occur. Increasing the sintering temperature to 1000 °C/2 h leads to an increase in the concentration of the crystalline phase and to a decrease of the concentration of the glassy phase (compare samples a and b in Fig. 5). These crystals are supposedly consisting of phlogopite, which is in agreement with

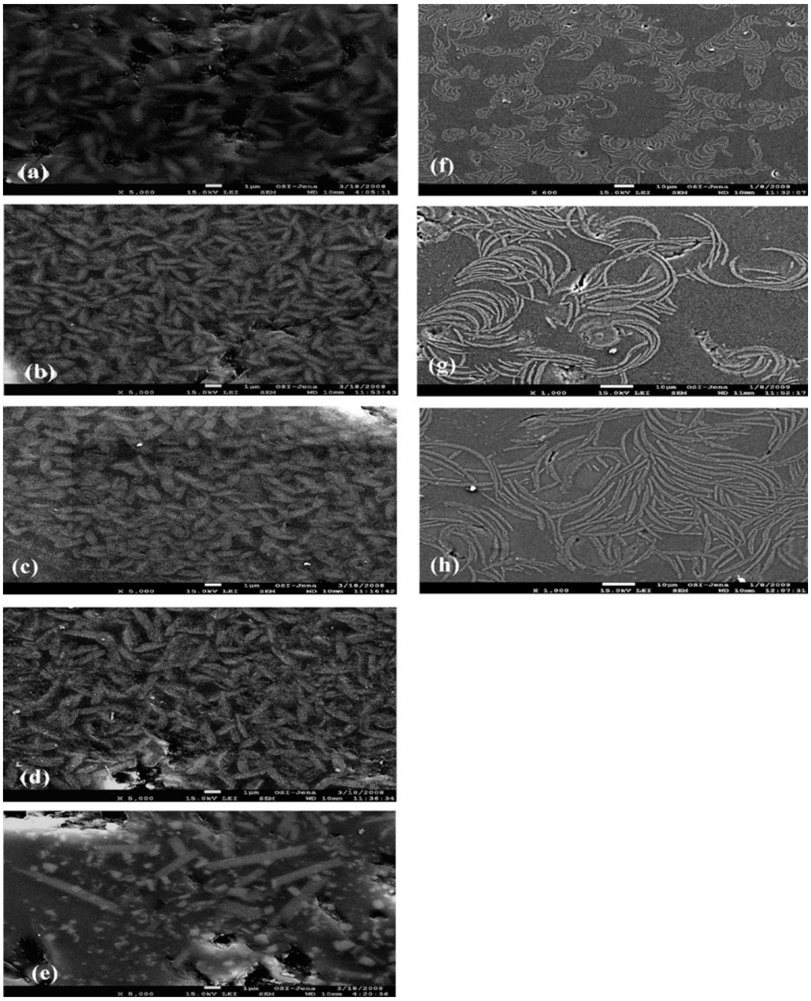


Fig. 5. SEM micrographs of sintered samples (a) 900, (b) 1000, (c) 1050, (d) 1100, (e) 1200 °C and glass ceramic samples annealed at (f) 900, (g) 1000 and (h) 1050 °C.

the corresponding XRD-patterns. An increase in temperature to 1050 °C, 1100 °C and 1150 °C leads to approximately the same microstructure; the concentration of the crystalline phase does not notably change, however, the size of the crystals slightly increases. Sintering at 1200 °C/2 h, leads to an increase in the concentration of the glassy phase and to the formation of much longer crystals which possess a length of approximately 5 μm. These crystals are supposed to consist of phlogopite. Additionally, tiny crystals with sizes in the range of 0.5–1 μm are observed. The latter crystals are supposed to consist of spinel (see sample e in Fig. 5).

In comparison to the sintered samples, the thermally annealed glass samples show very different microstructures. The samples were annealed at temperatures of 900 °C, 1000 °C and 1050 °C, and all show curved crystals [5], which possess the typical morphologies of curved phlogopite. In the samples crystallized at 900 °C/2 h, the crystals have lengths of around 10–20 μm (see Fig. 5f). In samples annealed at 1000 °C/2 h and 1050 °C/2 h, the lengths of the crystals are 20–30 μm and 25–40 μm, respectively (see Fig. 5g and h), however, additionally tiny crystals supposedly consisting of cordierite are spread in glassy matrix.

Generally, in sintered ceramic sample, crystalline fluorphlogopite occurs in ellipsoidal morphology whose sizes increase with increasing annealing temperature. Additionally much smaller spinel crystals are observed. By contrast in the thermally annealed glasses, curved fluorphlogopite occurs which mean sizes also increase with increasing temperature. Additionally tiny cordierite crystals are observed which are embedded into the in glassy matrix.

4. Conclusion

Fluorphlogopite ceramic and glass-ceramics were prepared using natural raw materials. Fluorphlogopite, norbergite and spinel were developed in samples prepared by ceramic route while fluorpholgopite and cordierite were only grown in the thermally annealed glass specimens. The increase in volume of unit cell parameters of fluorphlogopite, compared with both the sintered ceramic and glass-ceramic sample formed at 1000 °C may be due to the partial replacement of Mg by or Ca, Ba from the raw materials. The fluorphlogopite crystals, in sintered ceramic samples, occur in ellipsoidal morphology; the size of the crystals increase with increasing sintering temperature. On the other hand, in thermally annealed glass samples, curved fluorphlogopite occurs which mean sizes also increase with increasing annealing temperature. Cordierite was also detected as tiny nano crystals through the curved fluorphlogopite in glassy matrix. It must be mentioned that, the ceramic method was better than melt quench route because a more homogenous and fine grain microstructure was obtained. Furthermore, it is less energy consumptive.

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