CRYSTALLIZATION BEHAVIOUR OF FLUORPHLOGOPITE GLASS CERAMICS

ESMAT M.A.HAMZAWY

Glass Research Department National Research Centre, 12622 Dokki, Cairo, Egypt E-mail: ehamzawy@eudoramail.com

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Transparent fluorphlogopite based glasses were prepared using talc, glass sand and phosphate raw material. The effect of TiO₂, ZrO₂, phosphate or combinations of either B₂O₃-phosphate or TiO₂-ZrO₂ on the crystallization of fluorphlogopite base glass was examined. X-ray diffraction analysis showed formation of fluorphlogopite at 765 °C in the base glass. Addition of ZrO₂ or 5 wt.% phosphate did not affect the monophase crystallization. However, when the amount of phosphate was increased to 10 wt.%, fluorapatite was crystallized together with fluorphlogopite. TiO₂ and TiO₂-ZrO₂ addition enhance the formation of fluorphlogopite as a main phase. The addition of TiO₂ alone or mixed with ZrO₂ catalyzed crystallization of enstatite and fluorphlogopite above 1000 °C. SEM analysis showed that glasses containing fluorphlogopite was modified into interlocked flakes. Vicker's hardness values of the glass-ceramics increased in presence of enstatite (7358 MPa) and decreased in the presence of fluorapatite (4905 MPa). Addition of B₂O₃ decreased the density of glass to 2.634 g/cm³ and glass-ceramic to 2.780 g/cm³. Phosphate or ZrO₂ additions showed a reverse effect (2.864 g/cm³). Thermal expansion coefficients of fluorphlogopite glass-ceramic samples in temperature range 20 - 500 °C changed from 7.8 × 10⁻⁶ °C ⁻¹ in case of the dominance of enstatite.

Keywords: Glass-ceramics, Fluorphlogopite, Eustantite, Fluorsilicate glasses

INTRODUCTION

The importance of glass-ceramics, in general, is derived from the advantages of being produced by conventional glass-forming techniques followed by controlled crystallization [1, 2]. The fluorphlogopite glass-ceramics are characterized by their unique physical properties; in particular, cleavage, flexibility and elasticity. These properties are unique among glassceramics because such glass-ceramics can easily be worked on machines [3, 4]. In addition, these materials enjoy fracture resistance, thermal shock-resistance, and have excellent dielectric properties [5]. Recently, the former properties were improved by control of either orientation [6], or the grain size and morphology [7] of the crystalline phase formed in mica glass-ceramics. These exceptional properties give such glasses preference in several fields of application [8].

The fluorphlogopite glass-ceramics can be produced from low cost abundant natural raw materials. The present investigation deals with the effect of some combinations and some additives on the type of crystalline phases developed in tetrasilicic mica glasses. The density, microhardness and thermal expansion coefficient of the obtained glass-ceramics were measured and related to the type, concentration and microstructure of the crystalline phases formed.

EXPERIMENTAL PART

The raw materials used include talc, glass sand and phosphate, which is composed mainly from fluorapatite $Ca_5(PO_4)_3F$. The chemical analyses of these raw materials are shown in table 1. Other additives, i.e. K_2CO_3 , H_2BO_3 and MgF_2 were introduced as minor components. TiO₂ or ZrO₂ and their mixtures were tested as nucleating agents for the base glass.

The principal type of glass studied was the glass, fluorphlogopite base which had the $KMg_2 Si_4O_{10}F_2$ stoichiometric formula (G₀). This glass was prepared from talc, glass sand, MgF₂ and K₂CO₃. This basic composition was modified by the addition of phosphate raw material to replace 5 or 10 wt.% of fluorphlogopite base glass. In addition, a mixture of equal amounts of phosphate material and B₂O₃ was introduced to replace 10 wt.% of the fluorphlogopite base glass. The chemical compositions of the glasses prepared are shown in table 2.

The appropriate amounts of powdered glass batch materials and chemicals were well mixed and melted in

Table 1. Chemical composition of the raw materials (wt.%).									
raw material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	P_2O_5	I.L
talc ¹	62.00	1.60	0.40	0.40	30.30	0.11	0.32	-	4.7
phosphate ²	11.19	0.66	1.83	45.43	0.20	0.10	0.86	29.44	1.66
sand ³	99.2	0.28	0.03	0.10	-	-	-	-	-

Table 1. Chemical composition of the raw materials (wt.%)

¹Hamata, Eastern Desert, EGYPT.

² Sibaya, Western Desert, EGYPT.

³ Abu Zenima, Sinai, EGYPT.

Table 2. Chemical composition of glasses prepared (wt.%).

Glass Constituents	Glass No.							
	G_0	G_1	G_2	G ₃	G_4	G ₅	G ₆	
SiO ₂	57.81	54.52	52.14	51.13	57.81	57.81	57.81	
Al ₂ O ₃	0.77	0.79	0.72	0.77	0.77	0.77	0.77	
Fe_2O_3	0.19	0.33	0.32	0.46	0.19	0.19	0.19	
CaO	0.19	3.62	3.63	7.06	0.19	0.19	0.19	
MgO	14.55	14.00	12.76	12.60	14.55	14.55	14.55	
K ₂ O	11.37	10.50	10.01	10.05	11.73	11.73	11.73	
Na ₂ O	0.16	0.22	0.19	0.25	0.16	0.16	0.16	
P_2O_5	-	2.23	2.24	4.47	-	-	-	
MgF ₂	14.95	13.81	13.16	13.21	14.95	14.95	14.95	
B_2O_3	-	-	4.83	-	-	-	-	
TiO ₂ *	-	-	-	-	2.00	-	2.00	
ZrO_2^*	-	-	-	-	-	2.00	2.00	

* Amount added to 100 wt.% of glass batch.

covered platinum crucibles for 3 hours at a temperature in the range 1350 - 1450 °C. After melting, the glass melts were cast into rods and patties, which were subsequently annealed at 500 °C for 15 min, and left to cool inside the muffle furnace which was switched off.

The differential thermal analyses (DTA) were performed using a Shimadzu, DT 30 apparatus. 70 mg of granular glass samples (0.25 - 0.60 mm) were used. The heating rate applied was 10 °C/min. The XRD spectrometer, Philips 1390, Cu-target Ni- filter, was used for the identification of crystalline phases developed after heat treatment. Microhardness was measured on polished crystalline samples using Vicker's microhardness indenter (Shimadzu, type-M, Japan). The densities of glass and glass ceramic samples were determined at room temperature by the Archimedes method using xylene. The arithmetic mean of three readings for each sample was calculated.

Representative SEM micrographs were obtained for gold coated freshly etched crystalline samples using SEM Philips XL30.

The coefficients of thermal expansion of glassceramic samples (dimension $0.3 \times 0.3 \times 1.6$ cm) were determined by Linseis dilatometer (model L76/1250) using a heating rate of 5 °C/min.

RESULTS

Crystallization of the base glass

The heat-treatment, according to the DTA results (figure 1 and table 3), brings the formation of crystalline fluorphlogopite phase alone at a low heat-treatment temperature (765 °C). The transparency of the base glasses is slightly reduced by the formation of the fluorphlogopite phase. The transparency of the glass changed to white translucent material when the glass was heat-treated at 898 °C. This effect was associated with the crystallization of enstatite phase. At still higher temperatures (1000 °C, 10 hours), a white opaque glassceramic was developed and fluorphlogopite decomposed partially to the enstatite becoming the major phase at very high temperature (1100 °C, 5 hours, table 4). The SEM micrograph of the former transparent crystallized glass shows a fine microstructure of the monocrystalline fluorphlogopite phase in minor glassy



Figure 1. DTA thermograms of some investigated glasses.

matrix (figure 4). However, the microstructure of all other glass-ceramic materials, with or without any additives, could not be viewed under the polarizing microscope magnifications.

Effect of phosphates on base glass

The XRD analysis of G_1 sample having lower phosphate content treated at 755 °C (the first exothermic temperature) shows the growth of transparent monophase of fluorphlogopite, the same as in the base glass. This phase crystallized with enstatite (G_2) or fluorapatite (G_3). The second exothermic peak reflected the crystallization of fluorapatite (G_3 , bearing higher phosphate content). However, the second and third exotherms in G_2 and G_3 showed only the formation of the fluorphlogopite, enstatite and fluorapatite phases (table 3). Treatment at higher temperature showed an increase in the crystallinity but with relative decrease in fluorinated phases contents (figure 3 and table 4).

It should be noted that the softening and exothermic peak temperatures observed for these glasses decreased with an increase in the phosphates addition (nominal fluorapatite) (figure 1). The introduction of B_2O_3 to phosphate-containing glass (G_2) lead to the development of another exothermic peak (compare G_0 , G_1 &G₂, table 3).

The SEM micrograph of the white G_3 sample heattreated at high temperature (1000 °C/10 hours) shows

glass no.	peak temp. (°C)	crystalline phases formed	transparency of glass
$\overline{G_0}$	650	amorphous*.	transparent glass**.
	765	formation of fluorphlogopite.	transparent glass with faint opacity
	898	formation of enstatite	translucent white opalescence
G_1	650	*	**
	755	formation of fluorphlogopite.	transparent glass with faint opacity
	890	co-crystallization of enstatite & fluorapatite	white translucent
G ₂	640	*	**
	775	co-crystallization of enstatite &fluorphlogopite	light white translucent opal
	835	formation of fluorapatite	white translucent opal
	950	crystallization increase of enstatite & fluorapatite	translucent dark opal
G ₃	630	*	**
2	715	co-crystallization of fluorphlogopite&fluorapatite	semi-transparent white opal
	835	crystallization increase of the former phases	opaline
G_4	680	*	**
	755	co-crystallization of fluorphlogopite & enstatite	whitish-translucent
	890	crystallization increase of enstatite	white translucent
G ₅	700	*	**
	818	formation of fluorphlogopite	transparent glass with faint opalescence
	910	crystallization of enstatite	translucent opal
	990	crystallization increase of enstatite	white translucent opal
G ₆	680	*	**
-	775	co-crystallization of fluorphlogopite & enstatite	white translucent
	890	crystallization increase of enstatite	like the above

Table 3. Results of crystallization behaviour of glass samples.



Figure 2. XRD patterns of G_0 , G_4 , G_5 & G_6 glasses heat-treated as indicated on figure. \bigcirc - fluorphlogopite, \triangle - enstatite.

interlocked flakes of fluorphlogopite with enstatite and fluorapatite (figure 5).

Nucleation in base glass

The XRD patterns of the heat-treated glasses at each endothermic and exothermic peaks or at a higher temperature, 1000 and 1100 °C showed the effect of TiO₂ (G₄) in catalyzing the fluorphlogopite and pyroxene crystallization especially at higher temperatures (figure 2, table 4). At the first exotherm of G₄ (755 °C), the incorporation of TiO₂ enhanced the crystallization of enstatite in addition to fluorphlogopite, which crystallized as monophase in the base glass at 765 °C. The temperature increase to 890 °C (G₄, the second exotherm), lead to an increase in the intensities of X-ray



Figure 3. XRD patterns of G_0 , G_1 , G_2 & G_3 glasses heat-treated at 1000 °C for 10 hours.

 \bigcirc - fluorphlogopite, \blacksquare - fluorapatite, \triangle - enstatite.



Figure 4. SEM of G_0 glass heat-treated at 650 °C for 1 hour and at 765 °C for 3 hours, show spread of fluorphlogopite microcrystalline structure in little glassy matrix.

d-lines of enstatite at the expense of the fluorphlogopite (compare crystallization of G_4 in figure 2). The later results showed the role of TiO_2 in catalyzing the

Table 4. Crystalline phases developed at higher temperatures as detected by XRD analysis.

glass	G ₁	G ₂	G ₃	G ₀	G ₄	G ₅	G ₆
heat- treatment (°C/h)				phases presen	t		
1000/10 1100/5	FP+EN+FA FP+EN+FA	EN+FP+FA EN+FP+FA	FP+FA+EN FP+EN+FA	FP+ EN EN+FP	EN+FP EN+FP	FP+EN FP+EN	EN+FP EN+FP

FP - Fluorphlogopite, FA - Fluorapatite, EN - Enstatite.



Figure 5. SEM of G_3 glass heat-treated at 1000 °C for 10 hours, shows the growth of the main fluorphlogopite interlocked flakes with fluorapatite and enstatite.

crystallization of pyroxene, which also depicted in the crystallization at higher temperatures (i.e. at 1000 and 1100 °C of G_4 and G_6 samples table 2). On the other hand, ZrO_2 enhanced the fluorphlogopite as the major phase under wide range of heat-treatment temperatures. This was shown either in crystallization of fluorphlogopite alone (in G_5 at the first exotherm i.e. 818 °C, figure 2) or its persistence as the main phase at higher temperatures (table 4). Similar effect increasing the pyroxene over the fluorphlogopite at higher temperature was also observed when TiO₂ mixed with ZrO_2 (G_6).

When looking into the DTA thermogram, the addition of TiO_2 (G₄), ZrO_2 (G₅) or their mixture TiO_2 --ZrO₂ (G₆) to the parent glass shifted the endothermic and the exothermic peaks to higher temperatures especially in case of ZrO_2 addition (figure 1).

Density

The density of the base glass varied significantly with the addition of phosphate, B₂O₃ or TiO₂, ZrO₂ and their mixture. Figure 6 shows the densities of glasses and glass-ceramics formed at given temperatures. In glass, the density increased with an increase in phosphate content. The smallest increase in density was observed for glass G₂ containing 5 wt.%. Density of the corresponding glass-ceramics, compared to that of the base glass, increases with heat-treatment at 1000 °C in a way similar to glass, with the exception of G₂ (containing 5wt.%) of the lower value. On the other hand, an increase in the heat-treatment temperature to 1100 °C decreased density relative to those of glass-ceramics obtained by heat-treatment at 1000 °C. The greatest decrease in density was observed for glass G2. The addition of nucleating agents increased the density in the following order: $TiO_2 + ZrO_2$, $(G_6) > ZrO_2$, $(G_5) > > TiO_2$, $(G_4) > G_0$. The density of the corresponding glass-ceramics also



Figure 6. Schematic representation of calculated glass and glass-ceramic densities,

a) combined with phosphate,

b) nucleated by TiO₂, ZrO_2 and TiO₂- ZrO_2 . \blacktriangle - Glass, \bullet - glass heat-treated glass at 1000 °C for 10 hours, \bigcirc - glass heat-treated glass at 1100 °C for 5 hours

increased in the same way as that of glass. Due to the partial decomposition of the fluorphlogopite to enstatite and glassy phase, the densities of the resultant glass-ceramics, in particular those containing B_2O_3 decreased at higher temperature i.e 1100 °C (figure 6*a*).

Microhardness

The Vicker's hardness values of the glass-ceramics (developed after heat-treatment at DTA temperature peaks) showed continuous decrease with increase in the phosphate addition (i.e. fluorapatite content). This value ranged from 6082 MPa (base glass) to 4905 MPa (G_3). In case of the added nucleants, the value increased up to 7358 MPa (G_6) as the pyroxene crystallization took place.

Thermal expansion

For the samples heat treated at 1100 $^{\circ}$ C, marked changes in the thermal expansion occurred depending on the type of both the major and minor crystalline phases formed. Table 5 shows that the thermal

glassno.	thermal expansion coefficient (10 ⁻⁶ C ⁻¹)		identified phases
	20-300 °C	20- 500 °C	
G0	9.2	9.1	EN+FP
G1	7.6	7.8	FP+EN+FA
G2	7.7	7.9	EN+FP+FA
G3	8.6	8.7	FP+EN+FA
G4	8.9	9.2	EN+FP
G5	8.4	8.9	FP+EN
G6	9.0	9.2	EN+FP

Table 5.. Thermal expansion coefficient of glass samples heat treated at 1100 °C for 5 hours.

expansion coefficient decreased with formation of fluorapatite (G_1 , G_2 & G_3) and increased under the dominance of the enstatite (G_0 , G_4).

DISSCUSION

The internally fluorine-nucleated fluorphlogopite component, lead to the reduction of the viscosity of the melt. The presence of fluorine ions facilitates the mobility of structural elements in glass and enhances the fluorphlogopite crystallization. Due to these combined factors, transparent glass-ceramic material of nearly single phase resulted from heat treatment at 755-818 °C. This transparency reflects the ultra-fine microstructure and the similarity of the refractive indices of the monophase fluorphlogopite and the remaining residual glass.

Literature survey proposed different concepts to explain the mechanism of fluorphlogopite glass crystallization. Daniel and Moore [8] show that crystallization of fluorphlogopite glass takes place in two stages: (i) Initial structural ordering which occur at ~600 °C. The value of the transformation temperature depends on the fluorine content. (ii) Crystal morphology of the glass-ceramic changes from 900 to 1150 °C. Chung et al [5] suggested a complex multi stage sequence for crystallization: (a) heterogeneous nucleation of BCC chondrodite (Mg₅Si₂O₈F₂)-like crystals in glass matrix, (b) re-crystallization of chondrodite to norbergite $(Mg_3F_2SiO_4)$, (c) epitaxial growth of fluorphlogopite. Others added that the thermal treatment increase fluorphlogopite content and decreases chondrodite and norbergite amount observed at temperatures above 800 °C [9, 10]. Recent work [6] by Habelitz et al. mentioned that norbergite serve as a fluorine reservoir for the fluorphlogopite formation.

The aforementioned phases chondrodite and norbergite were not detected in the present samples. These phases may be separated in the glassy state which act as nuclei for subsequent fluorphlogopite crystallization. However, the proposed nucleation mechanism mentioned before [11], which has been supported recently [12] may depict the sequence of crystallization. This means that, the introduced constituent in glass batch increase the rate of nucleation and decrease the interfacial energy between the crystals and glass. In other words, the sequence of fluorphlogopite crystallization may be expressed as: Fluophlogopite glass {heat-treatment at nucleation temperature} \rightarrow Separated nuclei of Mg and F rich phases {treatment at crystallization temperature} \rightarrow Fluorphlogopite crystals + Residual glass.

When looking for the effect of combined samples with phosphate and B_2O_3 , some previous work can depict their actions. The higher field strength of P⁵⁺ (2.1) ions compared with Si⁴⁺ (1.57) ions cause drainage of the Mg, Al, alkali cations and fluorine ions from the silicate droplet [10]. Due to this strong effect, the lower percentages of combined phosphates in base composition yield easily fluorapatite. This amount of crystallized fluorapatite increases with the addition of phosphates when it compensates usually major phase fluorphlogopite. On the other hand, B^{3+} (ionic radius = = 0.020 nm and atomic weight = 10.81) ion can be expected to enter the tetrahedral layer (substituted for Si of ionic radius = 0.041 nm and atomic weight = 28.09) in phlogopite [13]. Other results show that B_2O_3 in trisilicic mica may be replaced by ~ 10 wt.% Al₂O₃ [5]. These data can depict the distinct lower density in the present samples. Another noticed effect of boron addition is the coexistence of F-free and F-containing phases resulting from the effect of lower viscosity of glass melt and subsequent higher ions mobility during heat-treatment.

The influence of the nucleants added was studied by many authors [13 - 15]. Solubility of ZrO_2 in the glass melt reaches 4 wt.% [14]. Other authors have found that ZrO_2 addition of 8 wt.% leads to the crystallization of tetragonal ZrO_2 and fluorphlogopite and suppressed other silicate phases [15]. In agreement with these results, ZrO_2 addition investigated in this work supports the fluorphlogopite crystallization and decreases the amount of silicate phases formed. TiO₂ additions induce mica growth [15 - 17] and the higher percentages tend to form titanate phases [15]. However, the lower amount of TiO₂ in our samples (even those mixed with ZrO_2) has strong effect on the usual dominant enstatite crystallization especially at higher temperatures.

The values of thermal expansion coefficient vary considerably with both the temperature range used and the contents of developed phases. In previous glass-ceramic works, the measured thermal expansion coefficient was $6.4 - 7.1 \times 10^{-6} \,^{\circ}\text{C}^{-1}$ for fluorphlogopite [18], and was $7.4 - 11.9 \times 10^{-6} \,^{\circ}\text{C}^{-1}$ for fluorphlogopite [19], where it was $7.5 - 10.0 \times 10^{-6} \,^{\circ}\text{C}^{-1}$ for enstatite [20] (20 - 300 $\,^{\circ}\text{C}$). In the present investigation, the thermal expansion coefficient of the glass ceramics was practically influenced by the type and the concentration of combined phosphate and nucleant used which had a

significant on the resulting crystalline phases (table 5). These expansion coefficients were a composite of the percentages of low-expansion phases and the high--expansion ones (usually includes the residual glass). However, depending on the substitution of phosphates in the parent sample, the thermal expansion coefficient change from 9.1 in the base glass to $7.8 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ (20-500 °C) in glass containing lower amount of phosphate (5 wt. %). On the other side, addition of TiO_2 alone or admixed with ZrO_2 increases the thermal expansion coefficient to $9.2 \times 10^{-6} \text{ °C}^{-1}$ (20 - 500 °C). The comparison of the expansion coefficient as the function of the developed phases in fluorphlogopite glass ceramic samples shows that when enstatite becomes the major phase the value of thermal expansion coefficient increases but the presence of fluorapatite decreases this value. It must be added that the decomposition of fluorphlogopite into enstatite accompanied by residual glass rich in potassium, which lead to increase in thermal expansion too.

CONCLUSION

The study of crystallization behaviour of fluorphlogopite glasses can be summarized by followed conclusions:

- 1. Transparent glass-ceramics of single phase fluorphlogopite was prepared.
- 2. The addition of phosphates enhanced the formation of fluorapatite, in compensation of fluorphlogopite contents, which decreased at higher temperatures.
- 3. The addition of B_2O_3 decreases the viscosity of glass making possible the coexistence of the dominating enstatite and the F-containing phases at all heat-treatment regime used.
- 4. ZrO₂ additions induce fluorphlogopite crystallization as predominant phase.
- 5. The addition of TiO_2 or mixture with ZrO_2 induces the enstatite and fluorphlogopite formation, with predominance of the enstatite particularly at high temperatures.
- 6. Density trend of glasses and glass-ceramics increases in direction of TiO_2+ZrO_2 addition $>ZiO_2$ addition $>TiO_2$ addition >base glass. Glass and glass-ceramic in B_2O_3 –containing sample show lower density than other samples.
- 7. Microhardness values increase up to 7358 MPa when enstatite is dominating phase and decreases to 4905 MPa when fluorapatite phase is developing.

The thermal expansion coefficient of fluorphlogopite glass-ceramic samples increases to $9.2 \times 10^{-6} \,^{\circ}\text{C}^{-1}$ in presence of enstatite as a major phase, but decrease to $7.8 \times 10^{-6} \,^{\circ}\text{C}^{-1}$ (20 - 500 $\,^{\circ}\text{C}$) in case of crystallization the fluorapatite.

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KRYSTALIZAČNÍ CHOVÁNÍ FLUORFLOGOPITOVÉ SKLOKERAMIKY

ESMAT M.A.HAMZAWY

Glass Research Department, National Research Centre 12622 Dokki, Cairo, Egypt

Byla připravena transparentní fluorflogopitová skla s použitím mastku, sklářského písku a fosforečnanů. Dále byl sledován účinek přídavků TiO₂, ZrO₂, fosforečnanů nebo kombinací B_2O_3 -fosforečnan a TiO₂-ZrO₂ na krystalizační chování základního fluorflogopitového skla. RTG difrakční analýza prokázala tvorbu fluorflogopitu při 765 °C v základním skle. Přídavek ZrO₂ nebo 5 hmotn.% fosforečnanu neovlivnil monofázovou krystalizaci. Zvýšený přídavek 10 hmotn.% fosforečnanu však vedl ke společné krystalizaci fluorapatitu a fluorflogopitu. TiO₂ a TiO₂-ZrO₂ přídavky zvýšily tvorbu enstatitu spolu s fluorflogopitem. Ohřev skel s přídavkem ZrO₂ indukoval krystalizaci fluorflogopitu jako hlavní fáze. Přídavek samotného TiO₂ nebo ve směsi se ZrO₂ podnítil krystalizaci enstatitu a fluorflogopitu nad 1000 °C. SEM analýza ukázala, že skla obsahující fluorflogopit měla jemnozrnou strukturu při 650 až 765 °C. Při vyšší teplotě (1000 °C) se krystalická struktura fluorflogopitu změnila na formu vzájemně spojených šupinek. Hodnoty mikrotvrdosti sklokeramiky vzrostly za přítomnosti fluorapatitu (4905 MPa). Přídavek B₂O₃ snížil hustotu skla na 2,634 g cm⁻³ a sklokeramiky na 2,780 g cm⁻³. Přídavek fosforečnanů a ZrO₂ měl opačný účinek (2,864 g cm⁻³). Koeficient teplotní roztažnosti vzorků fluorflogopitové sklokeramiky dosahoval hodnot 7,8 × 10⁻⁶ °C⁻¹ za přítomnosti fluorapatitu a 9,2 × × 10⁻⁶ °C⁻¹ v případě dominujícího enstatitu.