

Development of mica glass-ceramic glazes

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Abstract

The effect of iron content on crystallization of a mica glaze as coating for fast firing stoneware substrates has been investigated. Measurements by differential thermal analysis (DTA) combined with X-ray diffraction (XRD) and scanning electron microscopy (SEM) have shown the development of preferential crystal orientation in the mica glass-ceramic glaze. By comparison with amorphous and partly crystalline glazes, an enhancement of the mechanical properties of coatings with aligned and interlocked crystals of mica has been observed.

1. Introduction

Glass-ceramics, which are polycrystalline materials comprised of crystalline and glassy phases, have become established in a wide range of technical and technological applications.¹ The glass-ceramic process involves the controlled devitrification of a glass to provide a homogeneous microcrystalline structure. To achieving this, it has usually been necessary to include a nucleating agent, such as TiO_2 or Fe_2O_3 , in the glass that will provide the nuclei for subsequent crystal growth or influence the structural reorganization in the glass in such a manner that many crystals grow in the glass.^{1,2}

Since their development in the 1950s, mica-containing glass-ceramics have attracted much attention because of their unique properties.³ Mica glass-ceramics, in particular of the phlogopite system, are high-quality electrical insulators and show high resistance to thermal shock and machinability, due to the layered atomic structure of the sheet silicates which causes a basal cleavage along the (001) planes of the plate-shaped mica crystals.⁴⁻⁶ In this sense, several works have been conducted in the last years to establish the crystallization kinetics,⁷ to obtain oriented mica glass-ceramics by extrusion^{8,9} and to enhance the mechanical properties of

mica glasses and glass-ceramics.^{10,11} However, to our knowledge, no previous work has been published regarding the development of mica glass-ceramic glazes.

Glazed ceramic tile is the most common building material for floor and wall covering in Mediterranean countries. Glazed tile is produced from frits, which are mixed with water and organic additives to yield glaze slips. These slips are applied to the surface of green tile, and after a drying step, they are subjected to a single-or double-firing process. There are a wide variety of frits, which have different characteristics such as fusibility, viscosity, gloss, and opacity.

The main objective of the present study is to develop a mica glass-ceramic glaze from a high fusibility commercial frit, which originally shows an amorphous character. For this purpose, an iron-containing glassy frit will be used as a precursor of crystallization.

2. Experimental Procedure

The compositions of the frits used for this study are given in Table I. Frit HIGHF is a high fusibility glassy frit (supplied by Fritta S.L., Castellón, Spain), whereas frit IGF is an iron glassy frit obtained from an iron-rich waste originated by a Spanish granite plant. The granite waste, which was supplied as a dried mud coming from the sawing processing of granite blocks, was melted in air at 1450°C for 1 h in silica–alumina crucibles. The fluid melt was quenched by pouring into water to obtain a glassy frit. No visible corrosion or chemical attack of the silica–alumina crucible by the melt was observed. Chemical compositions of frits were measured by wet chemistry using inductively coupled plasma emission spectroscopy (ICP).

Both HIGHF and IGF frits were crushed and sieved to <65 µm particle size. Different frit mixtures were prepared from HIGHF and granite frits as explained later.

All frit mixtures were mixed with water and organic additives (TPF and DMC) to obtain a slip, which was poured onto 80 mm x 80 mm fired ceramic tile to produce a coating with thickness of ~500 µm. The coated tile was dried in air for 24 h and heat-treated at 1120°C for 15 min with heating and cooling rates of 50°C/min.

Table I. Chemical composition (by ICP methods) of HIGHF and IGF frits

| | HIGHF frit | IGF frit |
|--------------------------------|------------|----------|
| SiO ₂ | 48.00 | 55.24 |
| Al ₂ O ₃ | 4.00 | 12.42 |
| Fe ₂ O ₃ | --- | 17.79 |
| CaO | 0.56 | 5.89 |
| MgO | --- | 1.83 |
| MnO | --- | 0.16 |
| BaO | 0.08 | 0.06 |
| ZnO | 10.07 | 0.11 |
| Na ₂ O | 13.40 | 2.64 |
| K ₂ O | 0.18 | 3.34 |
| TiO ₂ | 0.06 | 0.35 |
| P ₂ O ₅ | --- | 0.16 |
| B ₂ O ₅ | 13.65 | --- |
| F ⁻ | 10.00 | --- |

The glassy nature of HIGHF and IGF frits as well as the evolution of crystalline phases developed in glaze tile after heat treatment were determined by X-ray diffraction (Philips X'PERT MPD diffractometer) with CuK α radiation. Scanning electron microscopy (SEM) on the surface of both as-produced and etched samples (2% HF for 1 min) was used to examine the microstructure of the glass-ceramic glazes. SEM observation (Philips microscope) was conducted at an acceleration voltage of 20 kV and energy dispersive X-ray (EDX) analysis with a solid-state detector (Be window).

To study the microhardness, Vickers indentations (Matsuzawa MHT2 microhardness device) on the surface of the glazes were performed applying a load of 1 kg. Each hardness value obtained was averaged from 10 indentations. The fracture toughness was calculated following the equation of Evans and Charles¹²:

$$K_{IC} = 0.16H_v a^{1/2} (a/c)^{-3/2} \quad (1)$$

where H_v is the Vickers microhardness, a is the half-diagonal of the indentation, and c is the half-distance between the opposite crack tips.

2. Results and Discussion

Table I shows the chemical analysis by ICP of HIGHF and IGF frits. In this table, Fe_2O_3 represents the total amount of $FeO + Fe_2O_3$ in the IGF frit. The major components in the HIGHF frit are SiO_2, B_2O_3, Na_2O , and ZnO , whereas the IGF frit is mainly composed of SiO_2, Fe_2O_3 , and Al_2O_3 .

Table II gives the different mixtures prepared from diopside and granite frits. The iron content of those mixtures is also shown in Table II. As noted, the Fe_2O_3 content ranges from 0 wt% in mixture A, which is composed of only the HIGHF frit, to near 16% for mixture F, which is prepared mainly from the IGF frit (90 wt%).

Table II. Original frits mixtures prepared from HIGHF and IGF frits

| Frit mixture | HIGHF frit (wt. %) | IGF frit (wt. %) | Fe_2O_3 content (wt. %) |
|---------------------|-------------------------------|-----------------------------|---|
| A | 100 | 0 | 0,00 |
| B | 90 | 10 | 1,78 |
| C | 70 | 30 | 5,34 |
| D | 50 | 50 | 8,89 |
| E | 30 | 70 | 12,45 |
| F | 10 | 90 | 16,01 |

The frit mixtures were applied over ceramic tile substrates as explained earlier. After cooling at room temperature, glaze tile showed a homogeneous and glossy surface. Glaze defects as bubbles or crazing were not detectable.

Figure 1 shows the X-ray spectra collected on the surface of glaze tile. The XRD pattern of sample A (Fig. 1(A)), which is prepared without addition of granite frit, shows that the HIGHF frit gives rise to an amorphous glaze. Nevertheless, the DTA curve recorded from a powder sample of the HIGHF frit (Fig. 2) shows its ability to crystallize, with two exothermic peaks at 720° and $950^\circ C$, respectively. This curve is similar to typical DTA curves of mica glasses

reported in the literature,^{13,14} in which XRD was used to determine that the exothermic peak at the lower temperature (720°C in the HIGHF frit) corresponds to the crystallization of norbergite (Mg₃SiO₄F₂) whereas the second DTA peak (950°C in the HIGHF frit) is due to fluorophlogopite (KMg₃AlSi₃O₁₀F₂) precipitation. This means that although the HIGHF frit is adequate to lead a mica glass-ceramic glaze, the fast cooling rate (50°C/min) does not allow crystal growth during the manufacturing process, because an iron-containing frit has been used as a precursor of crystallization to give rise to a glass-ceramic glaze without additional change in the process conditions.

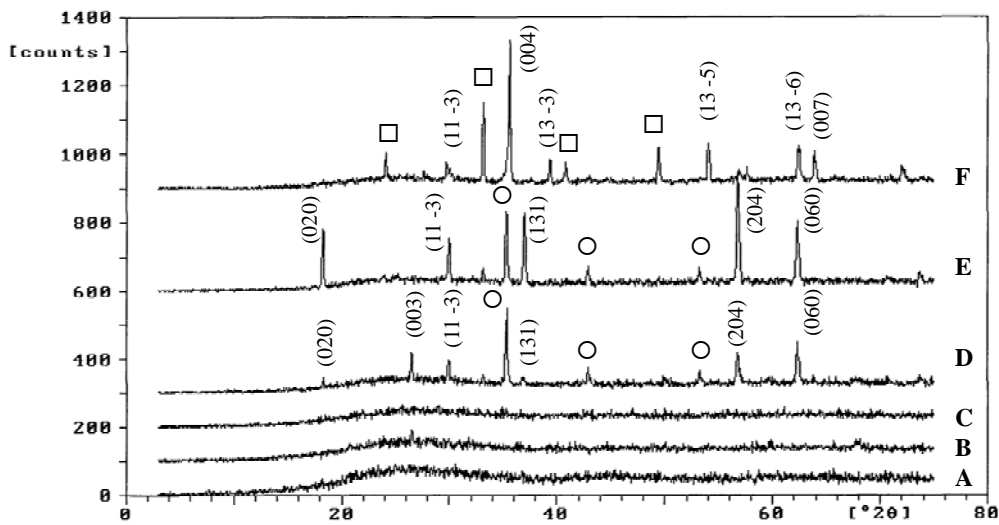


Fig. 1. X-ray spectra collected on the surface of glaze tiles (○ = franklinite (ZnFe₂O₄); □ = hematite (Fe₂O₃); (hkl) = biotite reflections).

The XRD pattern of glazes B and C (Figs. 1(B,C)), which are prepared with additions of 10% and 30% of the IGF frit, respectively, shows a diffractogram without crystallization peaks. However, the background in glazes B and C is lower than in glaze A, indicating either that glazes B and C are still amorphous, a structural change in the glass structure has taken place, or both glazes are partially crystallized with a percentage of crystalline phase lower than the detection limit of the XRD system (2% of crystalline phase). SEM confirmed the last supposition. Figure 3 shows the microstructure of glaze C prepared with addition of 30% of the IGF frit. The sample is mainly amorphous, but small crystalline regions are homogeneously dispersed on the glaze surface (Fig. 3(a)). These crystalline regions, which show irregular shape and size, comprise by small crystals whose average size is 0.5 μm (Fig. 3(b)). Table III collects the EDX analyses conducted on glaze C. As noted, small crystals show greater Fe₂O₃ and ZnO content when compared with the average composition; thus this crystalline phase could be

identified as the zinc ferrite denominated franklinite (ZnFe_2O_4). EDX analysis also shows high SiO_2 and Al_2O_3 contents; this is a consequence of the small size of franklinite crystals, which is down to the analytical resolution of the SEM/EDX system ($1\ \mu\text{m}$).

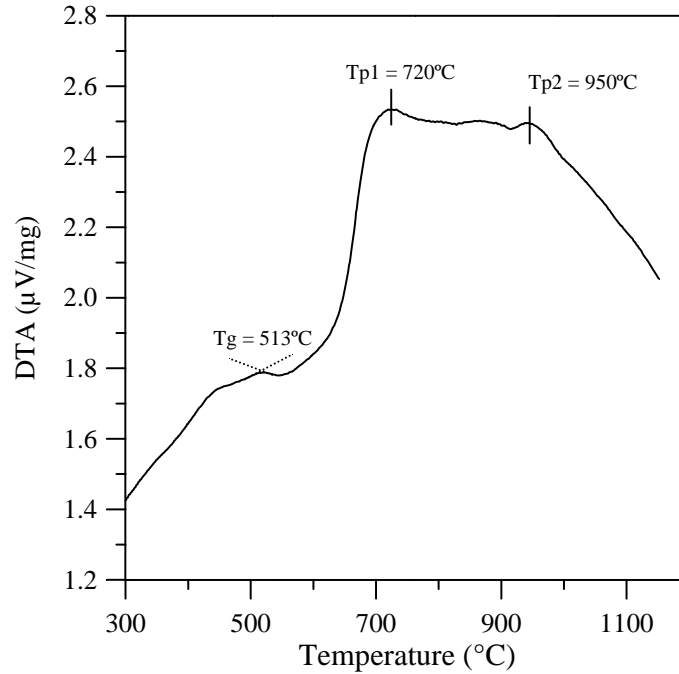


Fig. 2. DTA curve recorded from a powder sample of HIGHF frit.

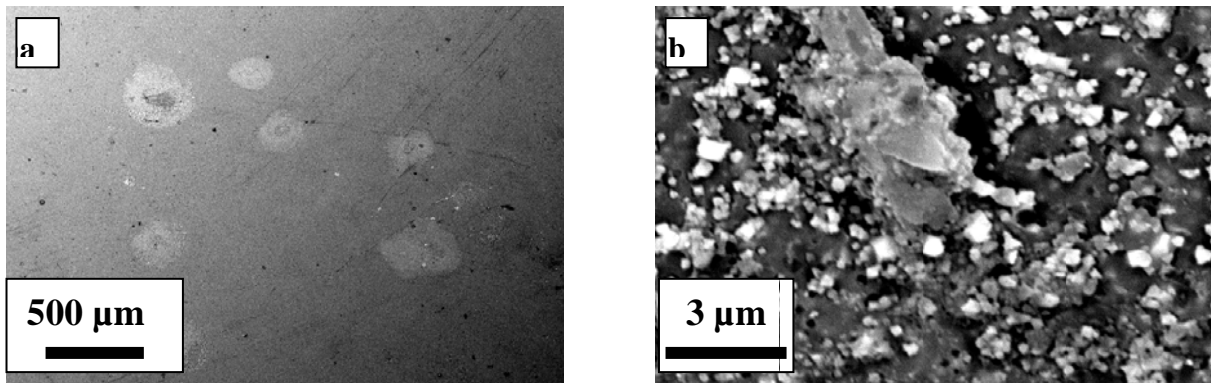


Fig. 3. SEM micrographs on the surface of glass-ceramic glaze C prepared with addition of 30% of the IGF frit: (a) general view of the surface and (b) crystals of franklinite (ZnFe_2O_4).

Franklinite crystallization begins to be detected by XRD in the diffractogram recorded on the surface of glaze D (Fig. 1(D)), which has been prepared with addition of 50% of the IGF frit. SEM observations on this glaze are presented in Fig. 4. The surface of the glaze shows a high degree of crystallinity (Fig. 4(a)) and a new phase, comprising crystals with hexagonal and rectangular habit, starts to crystallize together with franklinite phase (Figs. 4(b,c)). EDX

analyses have shown that there are not significant differences in the chemical compositions of both types of crystals; thus, hexagonal and rectangular crystals correspond only to a crystalline phase belonging to the mica group. The general formula to describe the chemical compositions of micas is $X_2Y_{4-6}Z_8O_{20}(OH,F)_4$ where X is K, Na, or Ca, Y is mainly Al, Mg, or Fe, and Z is mainly Si or Al but perhaps also Fe^{3+} and Ti. The micas can be subdivided into di-octahedral and tri-octahedral classes in which the number of Y ions is 4 and 6, respectively. The cell parameters of micas are influenced by the various ionic substitutions; thus, di-octahedral and tri-octahedral micas can in general be distinguished by the position of the 060 reflection in the XRD pattern. For the former $d_{060} \sim 1.50 \text{ \AA}$ and for the latter $d_{060} \sim 1.53\text{--}1.55 \text{ \AA}$.¹⁵ This reflection appears at 1.527 \AA in glaze D (Fig. 1(D)); therefore, mica crystals observed belong to the tri-octahedral class. The common micas in this class are phlogopite, biotite, zinnwaldite, and lepidolite. The two latter are characterized by the presence of Li as a constituent in category Y; hence, mica crystals precipitated in glaze D are phlogopite or biotite.

Table III. Chemical composition of C glaze and crystalline phase as analyzed by EDX spectrometry.

| | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | ZnO | Na ₂ O | K ₂ O | F ⁻ |
|-----------------------|------------------|--------------------------------|--------------------------------|------|------|------|-------------------|------------------|----------------|
| Average | 58.00 | 10.44 | 8.67 | 3.35 | 1.89 | 3.30 | 2.28 | 5.64 | 6.43 |
| Small crystals | 42.34 | 10.43 | 28.84 | 2.00 | 2.43 | 8.64 | 2.15 | 3.17 | --- |

Phlogopite and biotite are members of a continuous chemical and structural series whose compositions fall within the field outlined by four end members—phlogopite, annite, eastonite, and siderophyllite as can be seen in Fig. 5. The term biotite denotes an iron-rich mica which is arbitrarily differentiated from phlogopite by the Mg:Fe ratio. Therefore, Mg:Fe > 2:1 in phlogopite, whereas Mg:Fe < 2:1 in biotite. Table IV collects the average chemical composition of the mica crystals in glaze D. As noted, Mg:Fe < 2:1, and hence mica phase should be identified as biotite, $K(Mg,Fe^{2+})_3(Al,Fe^{3+})_3O_{10}(OH,F)_2$.

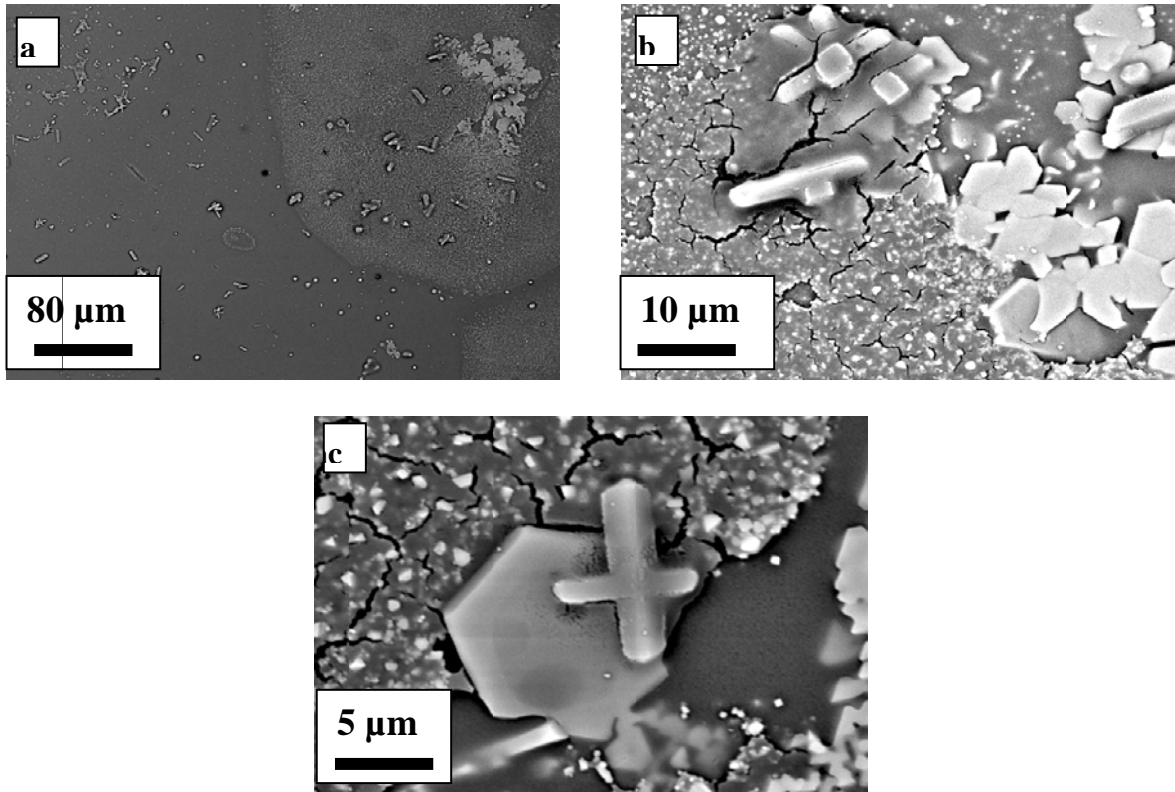


Fig. 4. SEM micrographs on the surface of D glass-ceramic glaze prepared with addition of a 50% of IGF frit.

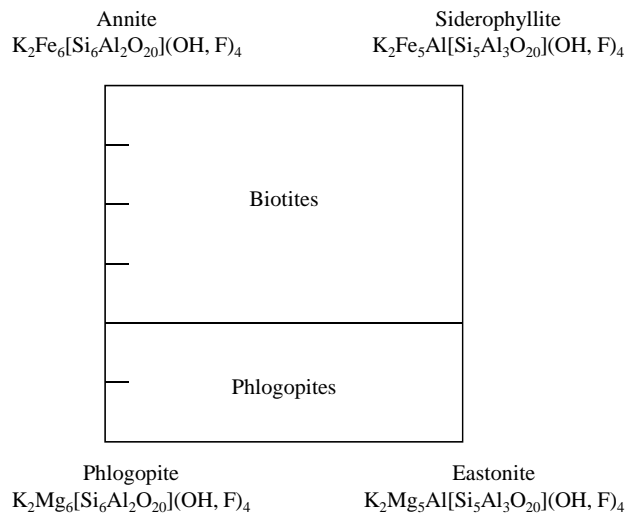


Fig. 5. Phlogopite-biotite compositional fields; the division between them is arbitrarily chosen to be where Mg : Fe = 2 : 1 (reference 15)

Table IV. Average chemical composition of mica crystals as analyzed by EDX spectrometry.

| SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | ZnO | K ₂ O | F ⁻ |
|------------------|--------------------------------|--------------------------------|------|------|------|------------------|----------------|
| 42.32 | 10.95 | 32.21 | 2.78 | 2.06 | 1.96 | 4.97 | 2.76 |

As for hexagonal and tabular habits found in SEM observations (Figs. 4(b,c)), they are owing to the spatial orientation of biotite crystals with respect to glaze surface, as shown in Fig. 6, so that hexagonal habit corresponds to crystals with the (001) basal plane parallel to the glaze surface while biotite crystals with the (001) plane perpendicular to the glaze surface show rectangular habit.

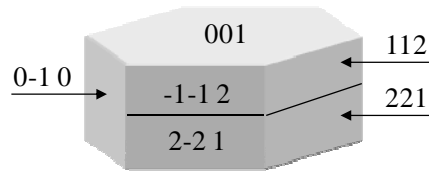


Fig. 6. Schematic representation of the different planes in a biotite crystal.

The effect of iron ions on the crystallization of biotite phase can be established by comparing the XRD patterns of glazes D, E, and F (Figs. 1(D–F)), with 8.89%, 12.45%, and 16.01%, respectively, of iron content expressed as Fe₂O₃. In the XRD pattern of glaze D several reflection peaks from different mica planes are observed. With increasing iron content up to 12.45% (glaze E) the crystallization of biotite also increases and whereas the (003) reflection peak disappears an increasing of the other reflections, specially the (020), (131), and (204) planes, is observed. Finally, an increase in the content up to 16.01% (glaze F) leads to a spatial orientation of biotite crystals with respect to the glaze surface and the XRD pattern exhibits predominantly reflections from (001) planes. Peaks referring to (131) planes, which are perpendicular or nearly perpendicular to the (001) plane, are also detected. On the other hand, hematite crystallizes instead of franklinite in glaze F. This change in the oxidation state of iron ions with the iron content has been previously detected by the authors in former investigations on the effect of iron oxide content in the crystallization of glass-ceramic glazes.¹⁶ Figure 7 shows biotite crystals and hematite regions observed by SEM on the surface of glaze F. As noted, hematite crystallizes as globular crystals whose average size is 0.15 μm.

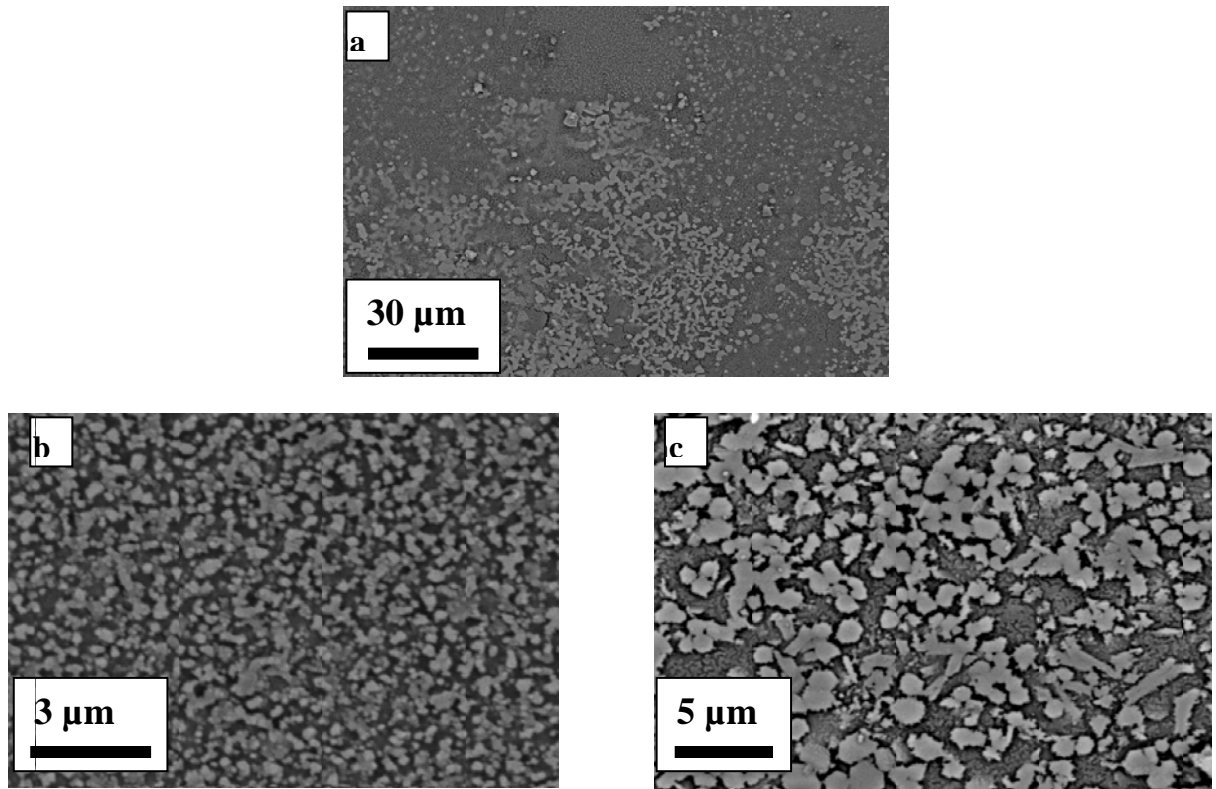


Fig. 7. SEM micrographs on the surface of F glass-ceramic glaze prepared with addition of a 90% of IGF frit; a) general view of the surface, b) hematite (Fe_2O_3) crystals and c) biotite ($\text{K}(\text{Mg},\text{Fe}^{2+})_3(\text{Al},\text{Fe}^{3+})_3\text{O}_{10}(\text{OH},\text{F})_2$) crystals.

Figure 8 shows the evolution of toughness versus Fe_2O_3 content in mica glazes. Glaze A, without addition of iron frit, shows a fracture toughness of $0.9 \text{ MPa m}^{1/2}$. This value is slightly increased in glazes B and D (1.0 and $1.2 \text{ MPa m}^{1/2}$, respectively), in which biotite starts to crystallize, and enhanced in glaze F (2.1 MPa m) where biotite is the main crystalline phase. The significant improvement of the mechanical properties of glaze F results from both high interlocking and alignment of mica plates, which can efficiently deflect crack propagation with branching and even blunting of microcracking.^{10,17}

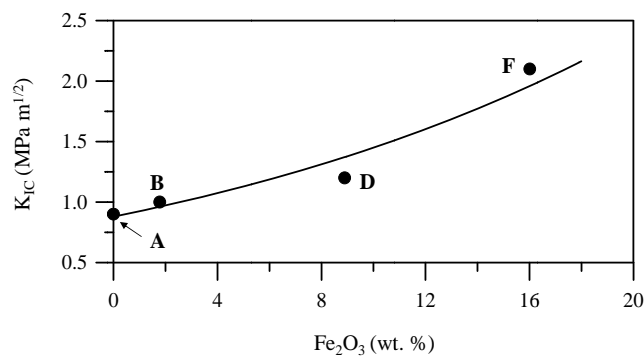


Fig. 8. Evolution of toughness versus Fe_2O_3 content in mica glazes

IV. Conclusion

The ability of an iron-containing frit as a precursor of mica crystallization in the production of glass-ceramic glazes has been established. SEM observations on the surface of glass-ceramic glazes have shown the presence of mica crystals with hexagonal and rectangular habits. The position of the 060 reflection in the XRD pattern (1.527 Å in glaze D), along with the absence of Li as a constituent, has allowed identification of this crystalline phase as biotite.

The effect of iron ions on the crystallization of biotite phase has been determined by comparison of the XRD patterns of different glazes. Increasing iron content up to 16.01% (glaze F) leads to a spatial orientation of biotite crystals with respect to the glaze surface, and the XRD pattern exhibits predominantly reflections from (001) planes.

The development of preferential crystal orientation in the mica glass-ceramic glaze, together with a high interlocking of crystals, has resulted in the improvement of mechanical properties. Thus, the value of fracture toughness of biotite glass-ceramic glaze F is 2.3 times greater than that of glaze A, which shows an amorphous behavior.

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