DEVELOPMENT OF GLASS-CERAMIC GLAZES WITH ANTI-SLIP PROPERTIES FOR PORCELAIN TILES

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ABSTRACT

Slip resistance is a mechanical performance feature that is to be evaluated in the selection of ceramic flooring, always considering the flooring's intended application. The increase in the use of ceramic floorings in building areas of public use, exterior and/or wet ambients, has led the market to demand increasingly higher slip resistance as a basic safety requirement, from which civil liabilities are derived.

In order to try to solve these problems, glazes have been developed that allow the surface finish of floorings to be modified, adapting their slip resistance performances to the demands established for any type of application. Their anti-slip effect has originated partly by the devitrification in the glass-ceramic glaze of crystalline phases in the quaternary system, $CaO – MgO – Al_2O_3 – SiO_2$. *The devitrified phases and the crystal quantity have been studied and controlled by XRD, SEM and DTA–TG.*

Once the selected glass-ceramic systems had been characterised, they were applied to stoneware tiles and porcelain tiles using the wet method (screen printings and slips) and the dry method (grits), and the surface properties of these systems were determined.

1. INTRODUCTION

Recent years have witnessed increased attention and interest in the ceramic production sector towards the obtainment of new glass-ceramic materials that display better technical performance and aesthetic features in comparison with other types of traditional glazes, thus allowing products of greater quality to be obtained and, hence, with greater added value.

Starting off with the development of certain base glass-ceramic frits, it has been possible to prepare a series of materials with innovative characteristics that combine high technical performance with aesthetic characteristics that are capable of addressing current trade demands, focusing on the need to create added value by means of highly customised porcelain tiles.

One of the demanded technical performances at the present time is the anti-slip effect of the materials, since new regulations have recently appeared on uses in public floors with heavy traffic. [1,2]

The so-called glass-ceramic glazes cover that need, since they are a type of material that, by their nature, combine the properties of crystals and glasses, improve mechanical properties and allow different aesthetic aspects to enter into play. That is, they constitute a new generation of glazes in which crystals form in the glassy phase itself, after they are subjected to the corresponding thermal treatments. In addition, the most important aspect in the development of the glass-ceramic systems compatible with the technological characteristics of porcelain tile production is that relative to the thermal and chemical stability of the crystalline phases that form during the crystallisation process. [3,4]

In this sense, it is possible to design and improve the technological performance features of these materials, controlling the nucleation and crystallisation processes of the glassy compositions, thus relating the technical performance to the nature, number, and size of the resulting crystals [5]. The controlled devitrification of crystalline phases takes place in two steps: the nucleation step in which the crystalline seeds form on which the crystalline phase grows by material deposition on the seeds in the growth step. [4]

Depending on the nature of the nuclei, homogeneous nucleation may be involved, when the nuclei originate from the own melt, having same chemical composition as the formed crystalline phase; or heterogeneous nucleation, when the crystals grow from particles or interphases foreign to the melt. In fact, every phase contains some defect which is why homogeneous nucleation is very difficult to achieve.

The obtained crystal size and quantity can be controlled by adjusting the nucleation and growth rates. Thus, if it is desired to obtain many small crystals, the nucleation rate shall be favoured over the growth rate; however, if instead it is desired to obtain few large crystals, the nucleation rate needs to be encouraged. [5]

In view of the foregoing, to obtain a controlled glass devitrification it is essential to control both the chemical composition of the glaze, through the study of the equilibrium diagram of phase stability, and the applied thermal treatment.

The devitrification of a glaze may be favoured by the introduction of nucleating agents. Nucleating agents are substances of high solubility in the glass at high temperature, but whose solubility, during the cooling, decreases, facilitating their segregation and forming discontinuities in the glassy network that will give rise to crystallisation nuclei on which the major crystalline phase is deposited. [6]

The main objective of the present work has been the synthesis and characterisation of glass-ceramic glazes based on the systems SiO_2-Al_2O_3-CaO-MgO (CMAS) and SiO_2-Al_2O_3-MgO (MAS) owing to their capacity to develop the crystalline phase α-cordierite ($2MgO$-$2Al_2O_3$–$5SiO_2$), also known as Indialite, which improves surface friction properties, thus obtaining anti-slip glazes. This phase has been widely studied by various authors owing to its capacity to improve the mechanical and chemical properties of the glazes in which it develops [7-13]. Cordierite, according to the literature surveyed, is an important technical material that is applied in a great variety of areas; this material and the glass-ceramic glazes based on it are well known for their low dielectric constant, high resistivity, high thermal and chemical stability, and very low coefficient of thermal expansion.

It is has been sought to study the effect of the nucleating quantity, in this case of the titanium oxide, on the development of glass-ceramic glazes based on cordierite, mainly in order to obtain the largest quantity of cordierite, without any secondary crystalline phase, in addition to fine crystals with well-defined morphologies.

For the achievement of this main objective a series of particular objectives have been considered, namely:

- Study of the crystalline phase cordierite $2MgO\cdot 2Al_2O_3\cdot 5SiO_2$ in the foregoing phase diagrams.
- Study and characterisation of frits.
- Development of glass-ceramic glazes from the obtained frits, as well as the study and characterisation of these glass-ceramic materials.
- Study of the influence of the titanium oxide quantity in the quantity of developed crystalline phase.
- Application of glazes prepared on porcelain tiles and characterisation of their physical and chemical properties, as well as the quality parameters that allow their industrial use.
- Characterisation of the anti-slip properties of the systems developed, according to the standards.

2. EXPERIMENTAL METHODOLOGY

2.1. SYNTHESIS OF THE FRITS

2.1.1. Studied compositions.

Based on the study of the phase equilibrium diagrams of each oxide system [14], the range of compositions has been established in which this work is framed. The nucleating agents and fluxes selected were titanium oxide and boron and sodium oxide, respectively, in low percentages in the formulation, with a view to reducing the nucleation temperatures of the phases to be synthesised and to favouring the formation of cordierite crystals after controlled thermal treatment.

Table 1 presents the compositions of the frits formulated for the development of glass-ceramic glazes with the ability to devitrify cordierite in which work was conducted for each oxide system. The frits formulated from the MAS system have been referenced F1-3-5-6-7-9, and those of the CMAS system F2-4-8-10, these differing in each system owing to their titanium oxide and sodium oxide content.

Oxide	**MAS (% by weight)**	**CMAS (% by weight)**
SiO_2	60-70	50-60
Al_2O_3	20-25	20-30
CaO	0-5	0-5
MgO	9-15	9-15
TiO_2	1-5	1-5
Na_2O_3	0-3	0-3
B_2O_3	1-5	1-5

Table 1. Frit compositions expressed in wt% oxide.

2.2. OBTAINMENT OF GLASS - CERAMIC GLAZES

The methodology used in the development of the different glazes is summarised in Figure 1.

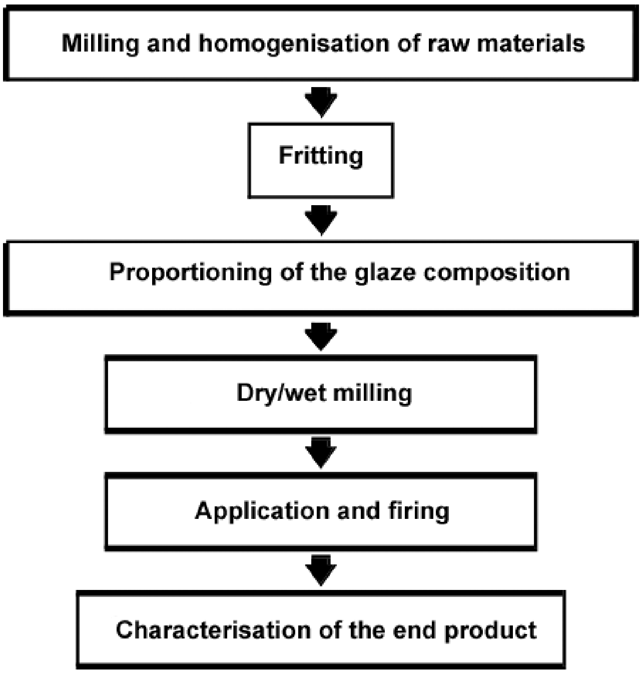

Figure 1. Flow chart of the development of the glass-ceramic glazes.

Starting with the base glass-ceramic frits, the glazes were prepared in two different ways depending on their later form of application. On the one hand, the frits were dry milled until a powder with a particle size below 90 μm was obtained; these powders were then applied on to porcelain tile bodies by means of a pressing process. On the other hand, the frits were wet milled together with different additives and the resulting slip was applied on to the body. The series of glazes that were applied dry were referenced ES, and those that were applied wet, EH.

2.3. THERMAL TREATMENTS

2.3.1. Thermal treatments conducted on the synthesised frits

The most refractory frits (according to the fusion tests) were milled and, under pressing at a pressure of 100 MPa, used to form test pieces. These test pieces were then subjected to a series of calcinations under different temperatures with a view to studying the capacity of the frits to generate the desired crystalline phases. For this, the applied thermal cycle was heating in an electric furnace at a rate of 25º/min up to, depending on the cases, maximum temperatures of 900, 1000, 1050, 1100 and 1200ºC, with a 5 minute residence time at peak temperature, followed by cooling at 25º/min.

2.3.2. Development of the glass-ceramic glazes

The ceramic pieces glazed with glazes EH1-EH10 were subjected to industrial porcelain tile single-firing cycles, i.e. to a peak temperature of 1200ºC and a total time of 50 minutes. In contrast, the test pieces glazed by dry pressing in the laboratory with glazes ES1-ES10 were subjected to a thermal cycle in an electric laboratory furnace that simulated an industrial porcelain tile thermal cycle to a peak temperature of 1185 ºC.

2.4. CHARACTERISATION TECHNIQUES USED

For the correct characterisation of the materials developed in the present work on a laboratory scale, as well as for the measurement of their properties, the following instrumental and analytical techniques were used:

- *X-ray diffraction (XRD)*: the instrument used was a model D4 Endeavor diffractometer (Bruker-AXS) with copper anode. The measurements were performed at an intensity of 20 mA and voltage of 40kV, in a 2θ range of 5 to 70º. The count collection time was 3 seconds per step and the goniometer speed was 0.03º 2θ/s. This technique has been used for the determination of the crystalline phases present in the materials used.
- *Scanning electron microscopy (SEM) and energy-dispersive X-ray microanalysis (EDX)*. A model LEO 440i scanning electron microscope was used with an Oxford Link ISIS energy dispersive X-ray microanalysis system with backscattered and secondary electron detector. The conditions used for the obtainment of the different microanalyses were an alteration voltage of 20,000kV and current intensity in the filament of 2000pA.
- *Differential thermal and thermogravimetric analysis (DTA/TG)*. For the study of the thermal evolution of the frits, a Mettler-Toledo model TGA/STDA851e simultaneous instrument was used.

- *Dilatometric analysis*: A BÄHR Thermo Analyse DIL 801 L dilatometer was used to obtain the dilatometric coefficients of the frits.
- *Hot stage microscopy*: a MISURA HSM 1600-80 was used for the study of the evolution of the frits with T (from 25º to 1400º C).

The following quality parameters of the developed materials were evaluated on a larger scale:

- Slip resistance by means of the TRRL pendulum method.
- Resistance to surface abrasion of glazed tiles or PEI according to standard ISO 10545-7 [2].
- Chemical resistance according to standard ISO 10545-13 [2].
- Stain resistance according to standard ISO 10545-14 [2].
- Scratch hardness of the surface (Mohs hardness) according to standard UNE 67101 [2].

3. RESULTS AND DISCUSSION

3.1. CARACTERIZACIÓN OF THE SYNTHESISED FRITS

Differential thermal and thermogravimetric analyses were used to follow the endothermic and exothermic processes that the frits underwent when they were subjected to a thermal cycle. For this, a heating rate of 25ºC/min was applied from 25 to 1200ºC, followed by free cooling.

The dilatometric and the hot stage microscopy studies were then performed. The most noteworthy results relating to these frits are given in Table 2.

SAMPLE	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10
T_G (ºC)	756	751	753	742	733	704	737	723	729	720
$T_{sintering}$ (ºC)	888	936	904	944	888	872	912	952	912	944
T_{sphere} (ºC)	1176	-	1216	-	1232	1216	1232	-	1244	1304
T_{fusion} (ºC)	1272	1384	1288	1368	1288	1296	1320	>1400	1304	1376
Dil. Coeff. (50-300)	51,6	40,9	44,5	42,1	51,3	59,9	55,8	78,0	51,5	61,9

Table 2. Characteristic temperatures and coefficients of the frits.

3.2. STRUCTURAL STUDY OF THE DEVELOPED GLASS-CERAMIC GLAZES

Both the test pieces treated at different temperatures and the glazes developed on porcelain tile bodies (series ES and EH) were structurally characterised by XRD, the formation of crystallisations in the glaze being observed.

The influence of the thermal treatment temperature on the crystallisation of a given composition and of the titanium oxide and flux content (sodium oxide) for a same firing temperature was then studied.

The most significant X-ray diffraction spectra as a function of temperature can be observed in Figures 2 and 3, in which the crystalline phases present are identified in each case.

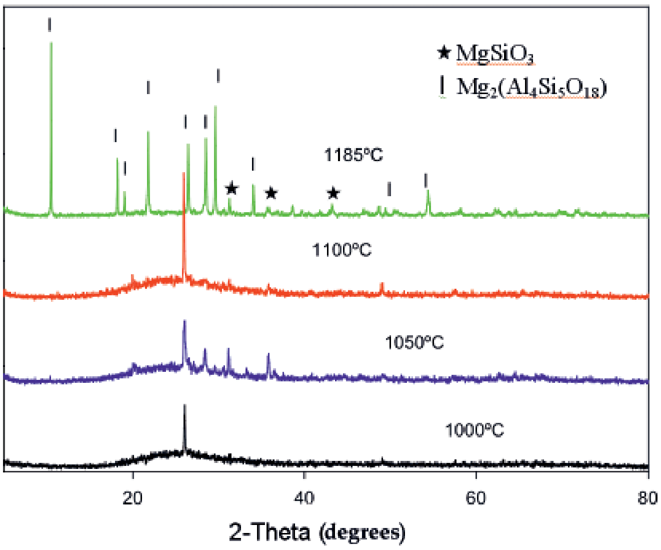

Figure 2. XRD of the F3 frit treated at different temperatures.

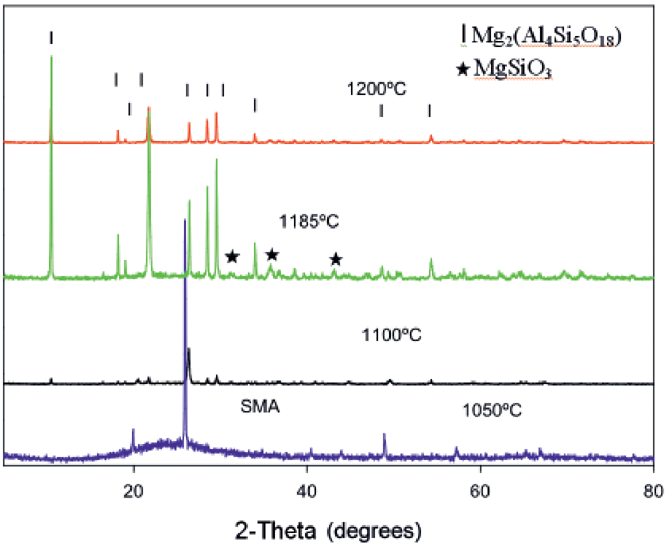

Figure 3. XRD of the F4 frit treated at different temperatures.

In F 4, pertaining to the MAS system, it may be observed that at 1050ºC only a magnesium and aluminium silicate appears, identified as SMA ($MgAl_2Si_4O_{12}$) from which the Indialite (I, $Mg_2Si_5Al_4O_{18}$) phase forms, which begins to form at 1100ºC. At 1200ºC, Indialite appears as a sole phase, and at 1185ºC magnesium silicate (★,$MgSiO_3$) appears as a minor phase.

On the other hand, in F 3, which belongs to the CMAS system, the evolution of the crystalline phases is similar to the foregoing one; at 1185 ºC Indialite appears as the major phase, though it begins to form at a temperature above 1100ºC.

The comparison of the XRD spectra of the frits at the same calcination temperature as a function of the titanium oxide and sodium oxide content is given in the following figures.

Figure 4 shows that the glaze that has the largest titanium oxide content (EH2) has Indialite ($Mg_2Si_5Al_4O_{18}$) as main phase, and Cristobalite (α-SiO_2) and Sapphirine $(Fe,Mg)_2Al_4O_6SiO_4$ as secondary phases. As the titanium oxide content decreases (glazes EH4 and EH8), the quantity of Cristobalite increases, the Indialite phase decreases and traces of Mullite ($3Al_2O_3$ $2SiO_2$) appear.

The diffractogram of glaze EH10, with the same titanium oxide content as EH8 but with a small sodium oxide quantity, displays more amorphous behaviour, though Mullite is equally observed to devitrify, in this case, as main phase, in addition to Indialite, Sapphirine and Cristobalite. This was corroborated by SEM observation.

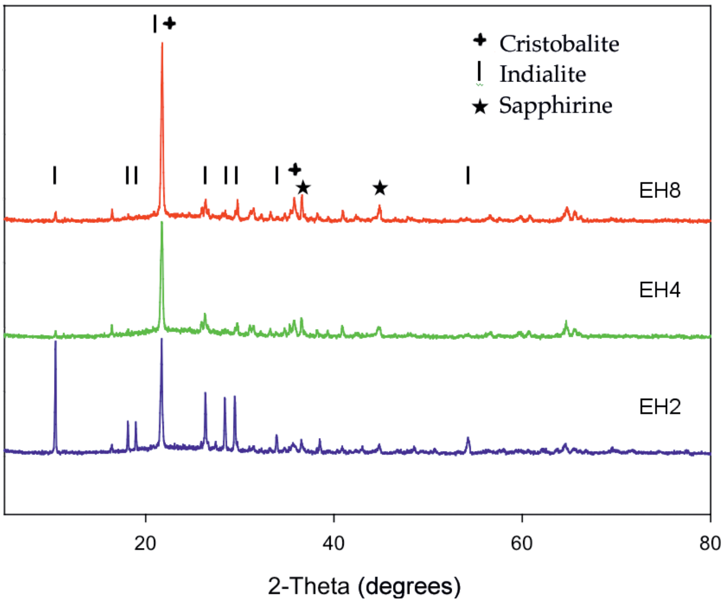

Figure 4. XRD of glazes EH2, EH4 and EH8 (cycle 1200ºC).

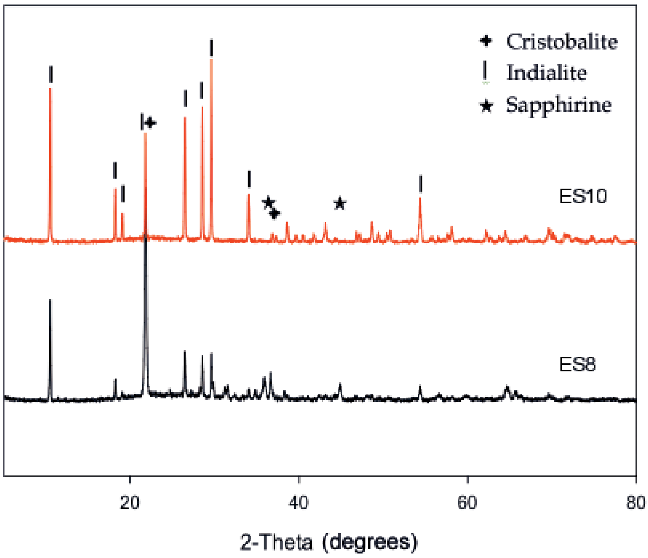

Figure 5. XRD of glazes ES8 and ES10 (cycle 1185°C).

Figure 5 shows that at the same titanium oxide content, the glaze (ES10), which has sodium oxide as a flux in addition to boron oxide, has a greater quantity of Indialite crystalline phase and a smaller Cristobalite content than the one that has no Na_2O (ES8). In glaze ES8 Sapphirine appears as a minor phase.

Comparing the glazes applied by the dry and wet methods, it may be stated that the ones pertaining to the MAS system crystallise the largest quantity of Indialite or α-cordierite when they are applied dry. When they are applied wet, this phase decreases and other phases appear, such as Cristobalite, Sapphirine, and Mullite. Of the glazes formulated from the CMAS system, EH7 and EH9 have a larger quantity of Indialite phase than the corresponding dry applied ones; the remainder have a greater crystallinity when they are applied dry.

3.3. MICROSTRUCTURAL STUDY OF DEVELOPED GLASS-CERAMIC GLAZES

In the first place, a morphological characterisation of the glazed surface, applied by the dry and wet method on already fired small slabs of porcelain tile, was conducted by SEM. The micrographs displayed regularly distributed crystallisations in all the observation area of the glassy matrix and in all the prepared compositions.

EDX microanalysis was used to identify the composition of the crystals developed in the glassy matrix of the glaze.

Figures 6 and 7 exhibit some micrographs corresponding to glazes ES3 (CMAS system) and ES4 (MAS system) calcined at 1185°C which devitrified α-cordierita ($5SiO_2$-$2MgO$-$2Al_2O_3$), a phase with a hexagonal structure.

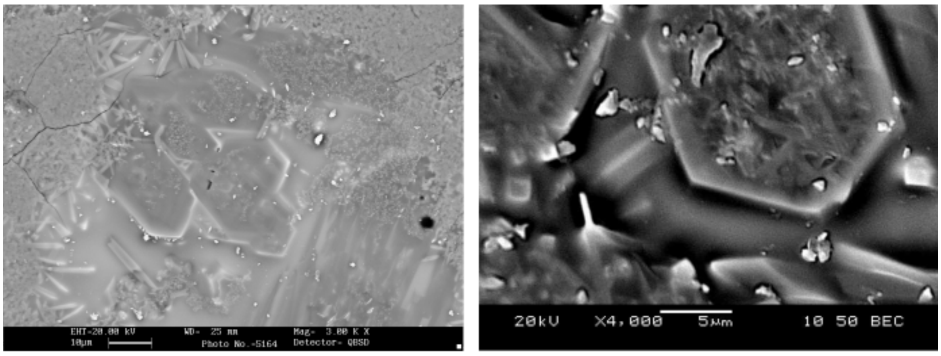

Figure 6. Micrographs of glazes ES3 (cycle 1185ºC).

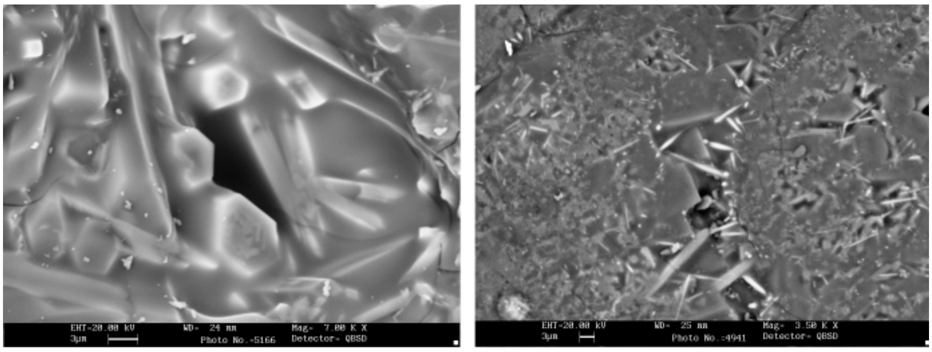

Figure 7. Micrographs of glazes ES4 (cycle 1185ºC).

Through EDX, it was deduced that the long glossier crystals corresponded to a Mg silicate where Al entered into solid solution replacing Mg^{2+} and Si^{4+} in its orthorhombic structure, i.e. it is a phase richer in Si and Mg and less rich in Al than the Indialite, from which this is formed, corroborating the results obtained by XRD for frits F3 and F4. This is shown in Figure 8.

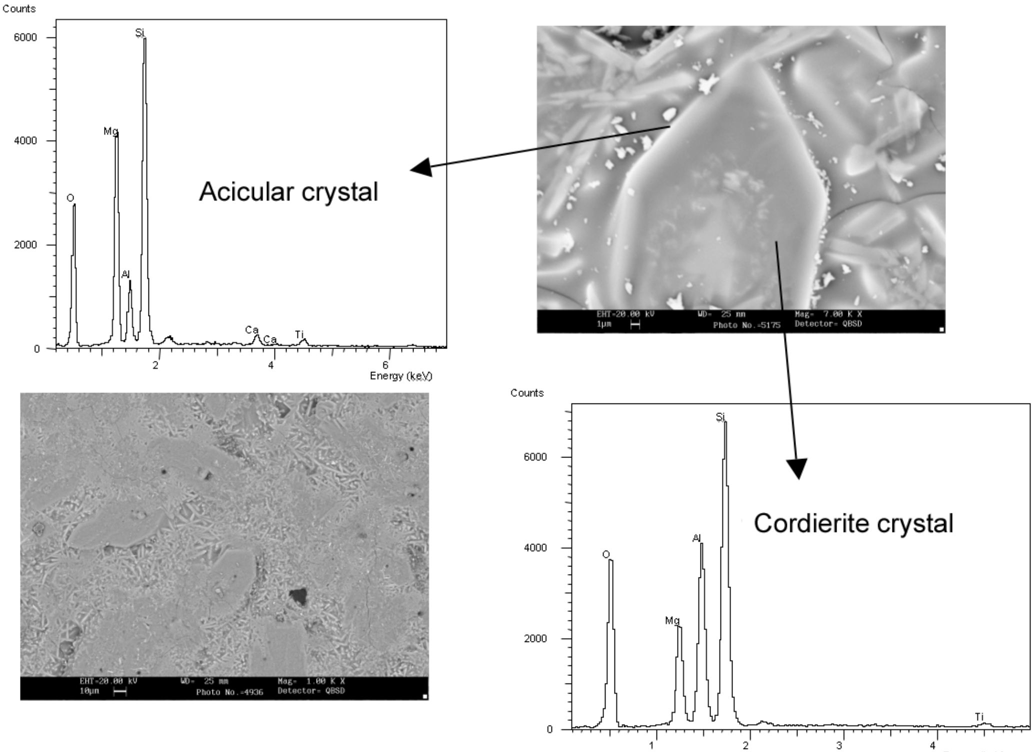

Figure 8. EDX of glazes ES3 and ES4 (cycle 1185ºC).

It may be said that Indialite forms through a heterogeneous nucleation mechanism from a Mg and Al silicate, and coexists at 1185ºC with a Mg silicate that has inclusions of Al and of Ca (in the case of F3) originating from the glassy matrix.

In the micrographs of the wet applied glazes, the greatest quantity of cordierite crystals is observed in glaze EH7 (Figure 9), as shown by XRD. In the cordierite crystals other very small crystals are observed, which are richer in magnesium (according to EDX), from which cordierite forms.

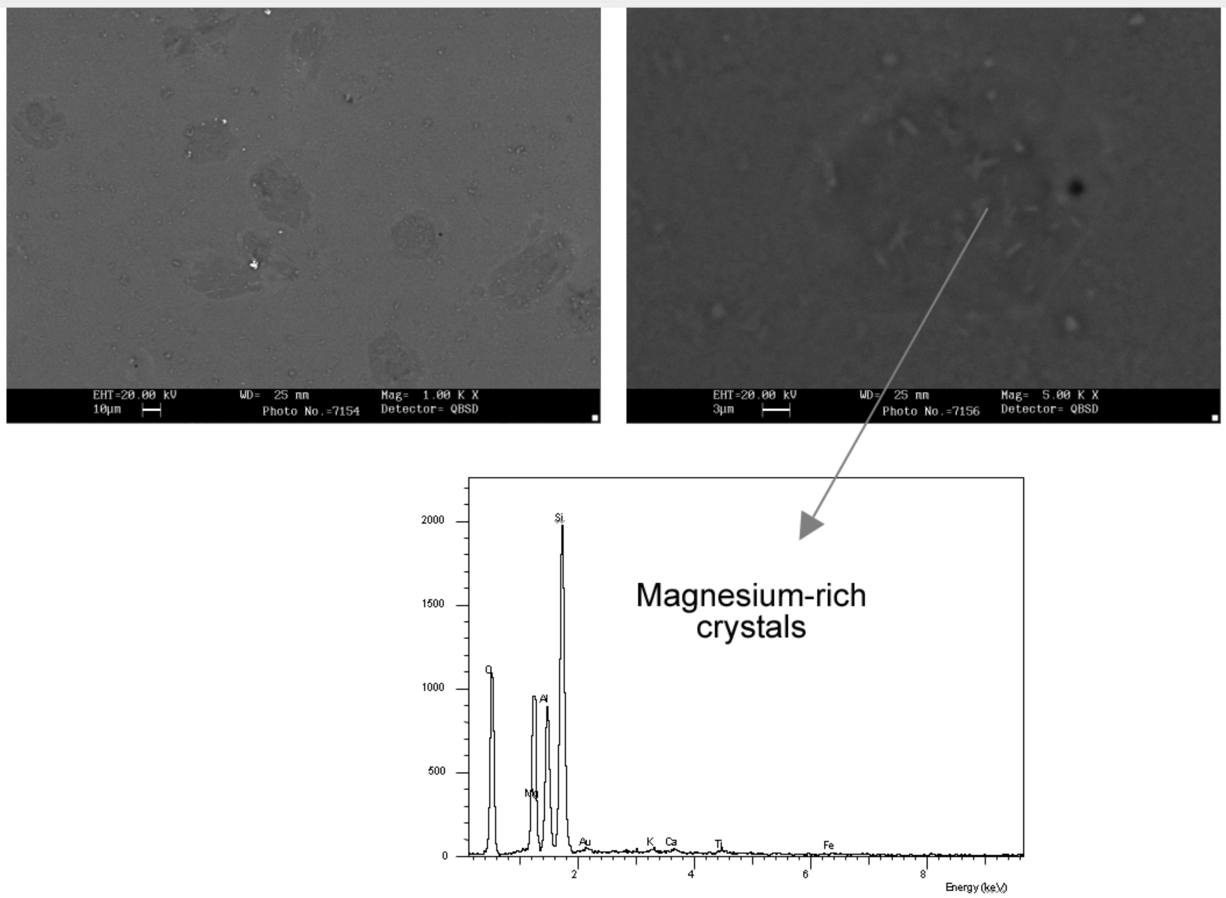

Figure 9. Micrographs and EDX of glaze EH7.

Glaze EH10 displays three different phases: long crystals rich in Mg, probably corresponding to the composition $Mg_2Al_{3,96}Si_{5,04}O_{18}$, a mixed silicate of magnesium and aluminium, present in the diffractograms. Sapphirine also appears (a phase rich in aluminium) and Cordierite. XRD shows traces of Mullite, which SEM was not able to identify. The micrographs and their corresponding EDX are shown in Figure 10.

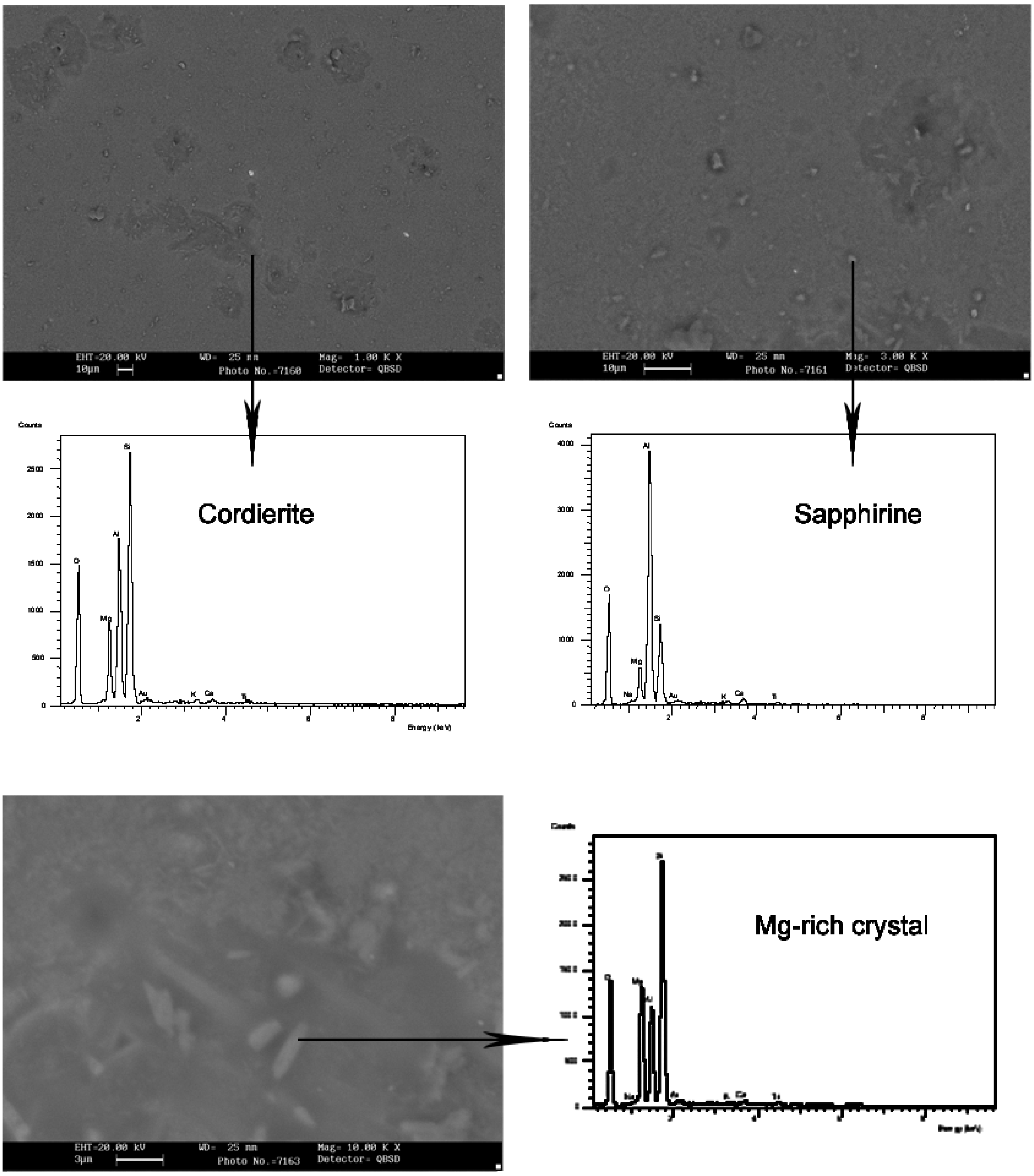

Figure 10. Micrographs and EDX of glaze EH10.

Glaze EH8 exhibits two main phases, Cristobalite and Mullite. The micrographs and their corresponding EDX are in shown in Figure 11.

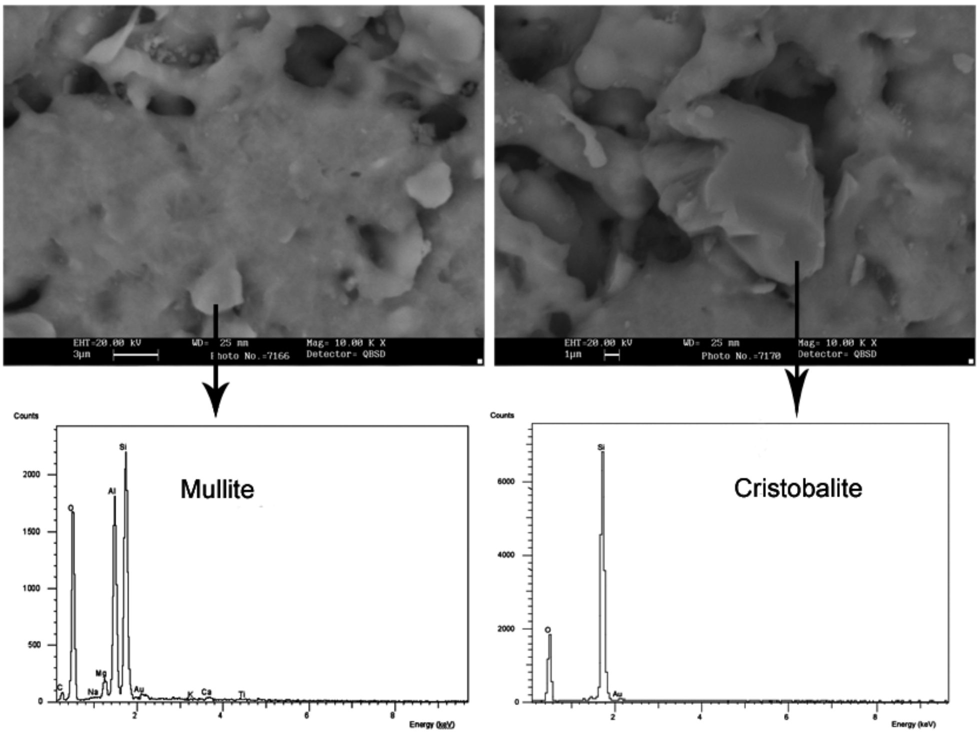

Figure 11. Micrographs and EDX of glaze EH8.

3.4. DETERMINATION OF THE APPEARANCE AND SURFACE PROPERTIES OF THE GLAZED PORCELAIN TILES

Taking into account the results of the structural and microstructural study of the glass-ceramic glazes conducted on a laboratory scale, and also taking into account their visual and aesthetic appearance, it was decided to determine the quality parameters of the materials developed from frits F4, F8 and F10, corresponding to the MAS system, on larger scale.

The application was carried out in two different ways: in the first place, grits from the selected frits were obtained, with a particle size below 250 µm, by dry grinding. Secondly, screen prints were prepared by wet grinding and subsequent drying and refining of the prints.

These materials were applied on to porcelain tiles and subjected to the corresponding firing cycle with a T_{max} of 1195º C. The visual appearance of the materials corresponds to transparent and glossy glazes, which enhance the initial colour of the ceramic models.

The technical results obtained in the characterisations of these pieces, for the materials prepared with the three frit compositions are summarised below:

MOHS HARDNESS	ABRASION RESISTANCE	ACID RESISTANCE	ALKALI RESISTANCE	STAIN RESISTANCE
7-8	IV	GLA-GHA	GLA-GHA	5

Table 3. Technical properties of the glazes

With respect to their anti-slip character, two different behaviours may be noted, depending on the way the material was applied. The glazes obtained from the screen prints slightly increased the slip resistance in regard to the pieces considered standard (of the order of a magnitude for the pendulum test). In contrast, the grits provided a rough surface similar to the industrial applications of sands or corundums, with quite larger increases of the anti-slip character of the surfaces (by two to three magnitudes).

4. CONCLUSIONS

This study has demonstrated that it is possible to formulate and use glazes or glass-ceramic glazes included in the system $CaO – MgO – Al_2O_3 – SiO_2$ for the surface protection of porcelain tiles. In addition, the use of these materials as grits can replace the application of corundums and sands on the surface for the obtainment of rustic anti-slip finishes.

These first results open a horizon of possibilities when it comes to formulating new compositions belonging to this oxide system, with a view to improving the final performance offered by the materials at issue in this study.

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