DEVELOPMENT OF NEW GLAZES FOR STONEWARE AND PORCELAIN TILE BODIES ADAPTED TO POLISHING PROCESSES AND HAVING GOOD TECHNICAL AND AESTHETIC PERFORMANCE

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ABSTRAT

A study has been undertaken of a new generation of glazes adapted to stoneware and porcelain tile cycles, which present high refractive indices (transparent glazes), as well as good chemical and mechanical resistance.

The study focuses on their formulation from the corresponding oxides, the prerequisite being the introduction of elements exhibiting the chemical and mechanical end properties required in the frit.

In this sense, SiO_2*,* ZrO_2*, CaO and ZnO have been studied as precursor oxides, amongst others. Rheological behaviour has been analysed, such as melt viscosity and thermal behaviour, in addition to phase transformation processes by means of DTA/TG, and crystal nucleation and growth processes in the glassy phase.*

The presence and/or absence of crystallisation has been characterised structurally and microstructurally in the glaze, as well as glaze dilatometric behaviour, to assure body/glaze compatibility.

Finally, the glaze has been subjected to the required quality controls with regard to resistance to chemical attack and stains. The glaze has furthermore been subjected to polishing processes, and the presence and/or absence of microporosity has been analysed to evaluate glaze end quality.

Particular attention has been devoted to the mechanical properties achieved in the development of the glaze, as well as analysis of glaze scratch resistance, toughness measurement by Vickers microhardness and Mohs hardness, and loss of surface quality through the PEI method.

After achieving all these objectives, we studied glaze design and developed different models with the glaze, analysing the parameters of chromatic compatibility and versatility, and also applying the refractive index methods.

Keywords: *ceramics, glazes, glass-ceramics, mechanical properties, optical properties.*

1. INTRODUCTION

In the ceramic sector there is currently a greater demand for glazed and polished porcelain tile, with an increased tendency to fabricate this type of product with good technical performance and aesthetic qualities. This requires designing new frit formulations to enable making the aesthetic qualities compatible with the technical performance demanded of these products.

One way of combining both properties has been by designing frits that yield glazes of a glass-ceramic nature, i.e., glaze compositions that are able to devitrify controlled crystalline phases in the fired glazes. This enables uniting the advantages of glassy and crystalline materials.

The greatest advantage afforded by glass-ceramic systems compared with traditional glazes, which consist of a glassy phase, is that they contribute greater chemical and mechanical resistance to the ceramic piece onto which they are applied. In addition, from an aesthetic point of view, the development of crystalline phases in the glass opens up a wide range of possibilities for making transparent or opaque, glossy or matt, and smooth or textured glazes, depending on the desired effect[1].

The fabrication of glass-ceramic materials is based on the controlled devitrification of one or more crystalline phases in a glass. For this, it is essential not only to control the applied heat treatment, but also the chemical composition of the glassy phase.

Devitrification occurs when the glassy substances, which are in an undercooled state with an energy exceeding that of their thermodynamic balance, evolve under certain favourable conditions to form stable crystalline species. This process is known as devitrification, because it is counter to the very nature of the glass itself[2].

Nucleation is the formation of stable crystalline seeds of the new phase in equilibrium with the melt and, depending on the origin of the nuclei, nucleation may be homogeneous or heterogeneous[3]. If the nuclei formed have the same chemical composition as the crystalline phase and originate from the components of the melt itself, homogeneous nucleation is involved. In contrast, if they form on already existing particles that have a different composition from that of the melt (impurities, interfaces, etc.), heterogeneous nucleation is involved.

If we consider homogeneous nucleation, when the crystalline phase forms, a variation occurs in the free energy of the system, in which the crystallization energy ($\Delta G<0$) per unit volume and the work needed to form the new surface ($\Delta G>0$) play a part.

Thermodynamic calculations indicate there is a critical radius up to which the nuclei are unstable. The seeds that are unable to reach this critical radius because they re-dissolve beforehand are known as embryos, whereas those that proliferate are termed crystallization nuclei. Figure 1 shows the variation of nucleation free energy versus seed ratio.

Crystalline growth is the process that occurs after nucleation, by which material is deposited on the formed primary nuclei. Crystalline growth can continue until the actual crystals have formed, and depends on the possibilities of transporting the chemical components to the developing crystal.

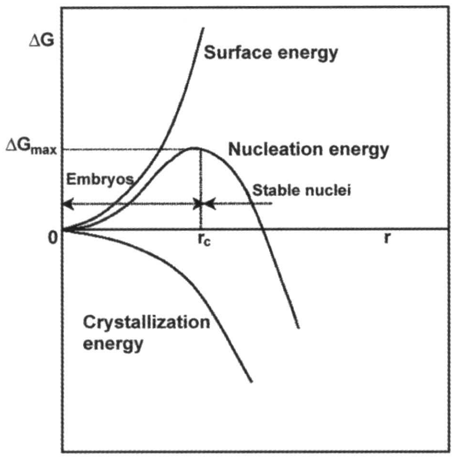

Figure 1. Variation of nucleation free energy with crystallization nuclei.

The size and quantity of the resulting crystals are largely controlled by nucleation and growth kinetics. If few crystals of large size are to be obtained, cooling must take place rapidly around the temperature corresponding to the maximum nucleation rate, and slowly in the maximum growth rate range of temperatures (figure 2). If a greater number of crystals are to be obtained, cooling must take place slowly at the maximum nucleation rate; crystal size can also be controlled in a similar fashion[4].

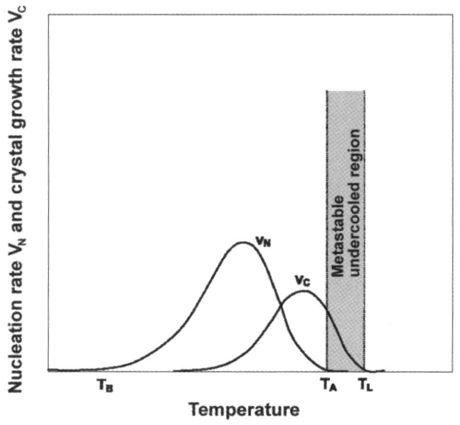

Figure 2. Plot of the variation of crystal growth and nucleation rate with temperature.

Studying the phase equilibrium diagram enables selecting the chemical composition of the glass that favours devitrification of the sought-after phase(s).

In this sense, it is necessary to realize that if a composition point is chosen next to the equilibrium line between two phases, the crystallization of one of these could favour devitrification of the other phase. This phenomenon, known as paragenesis, explains the coexistence of two or more phases whose devitrification would otherwise not take place at the same time[5].

In the present paper, a study has been undertaken of the development of glass-ceramic glazes that display good mechanical and chemical properties, in addition to control of glaze transparency.

Note that the transparency or opacity of a polycrystalline material or composite material containing different phases, which include glass-ceramic materials, depends on the internal refractions that occur in the material[6],[7]. For this reason, to develop a transparent material in these conditions it is important to use substances with similar refractive indices.

Assuming that the refractive index of the glass [8] is 1.5, to obtain a transparent glass-ceramic material it is advisable for this material to have crystalline phases with refractive indices close to 1.5, for instance such as tridymite and cristobalite, which are both polymorphic varieties of silica.

Thus, the study was performed in the system SiO_2-Al_2O_3-MO with a view to obtaining crystalline phases of silica, SiO_2. The most widely and thoroughly studied crystalline forms of silica are quartz, tridymite and cristobalite. The stability and transformation temperature ranges of each of these crystalline phases are detailed in the schematic illustration of Figure 3.

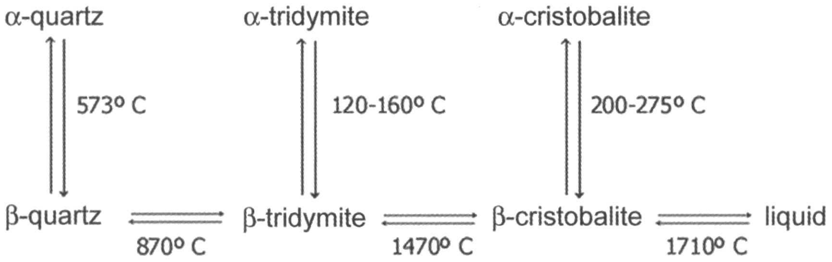

Figure 3. Stability ranges of SiO_2 polymorphic phases.

With regard to the properties of these crystalline phases, both tridymite and cristobalite display Mohs hardness between 6.5 and 7, while quartz has a hardness of 6. Table 1 sets out the formation conditions of the different polymorphic varieties of SiO_2, as well as the system in which they crystallize, together with their density and refractive index.

SiO_2	Crystalline system	Density g/cm³	Refractive index (n)	Formation conditions
α-Quartz	trigonal	2,65	1,55	T<573°C
β-Quartz	hexagonal	2,53	1,54	T>573°C
α-Tridymite	monoclinic	2,27	1,47	
β-Tridymite	hexagonal	2,26	1,47	T>870°C
α-Cristobalite	tetragonal	2,32	1,48	
β-Cristobalite	cubic	2,20	1,48	T>1470°C
Coesite	monoclinic	3,01	1,59	P>20kbar
Stishovite	tetragonal	4,35	1,81	P>80kbar
Opalo (SiO_2 aq)	amorphous	2,1 - 2,2		

Table 1. Properties of different polymorphous varieties of SiO_2

In the paper, we have studied the system SiO_2-CaO-ZnO-Al_2O_3 The equilibrium phase diagram of this system [9] (Figure 4) shows that tridymite and/or cristobalite crystallizations occur in compositions with high silica and low ZnO and CaO contents, thus avoiding the formation of calcium and zinc silicates like $CaAl_2Si_2O_8$ (anorthite) or Zn_2SiO_4 (willemite). In this sense, low percentages were also used of Al_2O_3, since this oxide inhibits silica devitrification in tridymite and cristobalite, favouring the formation of $3Al_2O_3{\cdot}2SiO_2$ mullite [10]. These phases have different refractive indices from the glass, giving rise to opaque or translucent glazes, depending on the resulting degree of crystallization [11], [12].

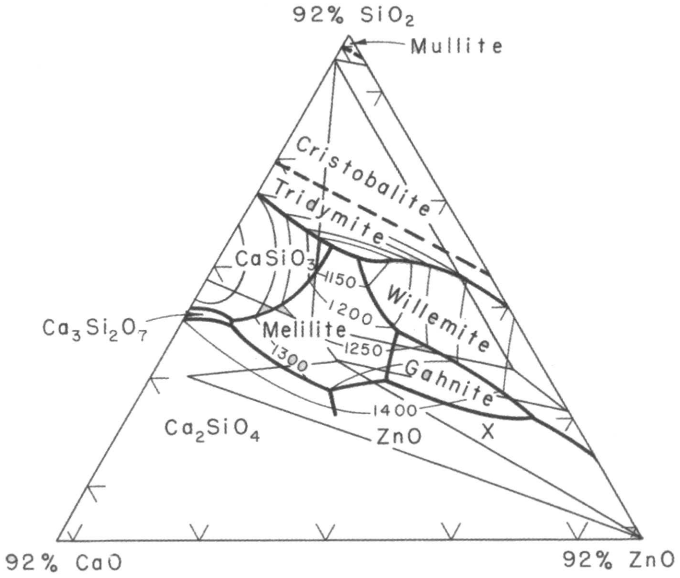

Figure 4. Equilibrium phase diagram of the system SiO_2-CaO-ZnO-Al_2O_3 at 10% Al_2O_3

Thus, the general objective of this paper has been to study and develop a family of glass-ceramic glazes adapted to stoneware and porcelain tile bodies, which are transparent and have good chemical and mechanical resistance to enable them to be polished in a subsequent process.

For this a series of concrete objectives has been set:

- Study and development of crystalline phases with good mechanical properties and refractive index similar to glass.
- Development of a family of frits in the system SiO_2-CaO-ZnO-Al_2O_3, which display good industrial adaptability.
- Obtaining glass-ceramic glazes from the developed frits adapted to stoneware and porcelain tile cycles, and having good chemical and mechanical properties.
- Study of the nucleation and growth capacity of the developed glass-ceramic materials.
- Adaptability of these glazes for polishing in a subsequent process.

2. EXPERIMENTAL

2.1. MATERIALS AND METHODS

2.1.1. Raw materials used

We designed different frits that enable nucleation and devitrification from the crystalline phases being studied, while also meeting the requirements for industrial adaptability, which exhibited appropriate melt viscosity, suitable coefficients of expansion for their bonding to the ceramic body as glazes, and matched the industrial single-firing cycles for stoneware and porcelain tile.

A family of frits has been designed, in which a greater amount of silica has progressively been added, from 65% to 80% by weight. Similarly, we have studied and monitored the effect of particle size of the added silica, using SiO_2 with two different particle-size distributions: 23 μm and 3 μm mean particle size.

Table 2 details the qualitative analysis of the family of developed frits. For the design of this family, the quantity of added silica and its particle size were both controlled.

Oxides	SiO_2	Al_2O_3	ZnO	CaO	Na_2O	K_2O
Wt%	65-80	1.5-5	6-10	8.5-12.5	2.5-3.5	1-2

Table 2. Qualitative analysis of the family of frits used in the study.

For this, the following raw materials were used, all of industrial quality (Table 3)

Raw materials	**Oxide content (% by weight)**
α-SiO_2	99% SiO_2
α- Al_2O_3	99% Al_2O_3
Na_2CO_3	58% Na_2O
KNO_3	46% K_2O
ZnO	99% ZnO
$CaCO_3$	60% CaO
Kaolin, $2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$	39% Al_2O_3 y 47% SiO_2

Table 3. Composition of the different raw materials used in making the frits.

Using these raw materials, the compositions referenced P1 to P4 (Table 4) were prepared, varying composition particle size (the samples referenced PF contained a smaller particle size, 3 μm) and SiO_2 content.

		SiO_2 Content (% by weight)			
		65%	**70%**	**75%**	**80%**
SiO_2 mean particle size	**23 µm**	P1	P2	P3	P4
	3 µm	P1F	P2F	P3F	P4F

Table 4 Samples prepared for this study.

2.1.2. Methodology adopted for making the frits

The frits developed were synthesized by means of a fritting process in a laboratory crucible kiln at a peak temperature of 1450°C, followed by quenching in water, as shown in Figure 5.

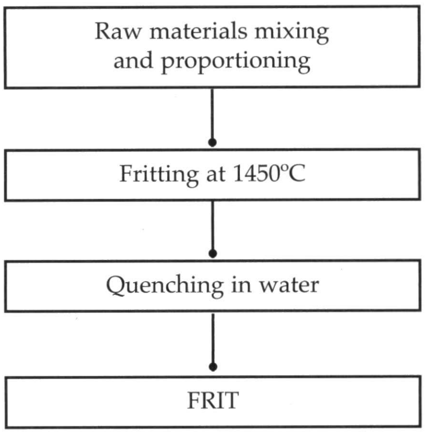

Figure 5. Scheme of the experimental procedure for making the frits in the study

2.1.3. Methodology followed for making the glass-ceramic glazes

The frits obtained by means of the process described in Figure 5 were used to develop a family of glass-ceramic glazes, following the general methodology outlined in Figure 6. These were applied as glazes onto stoneware and porcelain tile bodies.

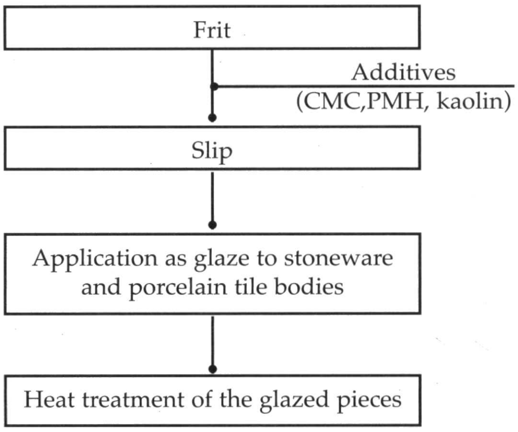

Figure 6. Synthesis methodology followed for making the glass-ceramic glazes.

2.2. HEAT TREATMENTS

2.2.1. Heat treatments conducted on the starting raw materials

To obtain the glassy material for generating the glass-ceramic glazes, the proportioned and homogenized raw materials were heat treated at 1450° C until they fused, followed by quenching in water.

Parallel to the development of the glass-ceramic glazes, to facilitate the study of the different crystallizations and nucleations that this material glassy could generate, the raw materials were subjected to different thermal cycles, varying the peak temperature from 900 to 1200°C, using a 30 min soak at peak temperature in every case and a heating rate of 5°/min, to encourage crystal development and growth.

2.2.2. Development of glass-ceramic glazes

The glazed ceramic pieces were subjected to industrial single-firing cycles at 1150°C for the stoneware body and 1200°C for the porcelain tile body, similar to the cycles used in industrial production. Figure 7 depicts these firing cycles, carried out in a gas-fuelled single-deck roller kiln for trials.

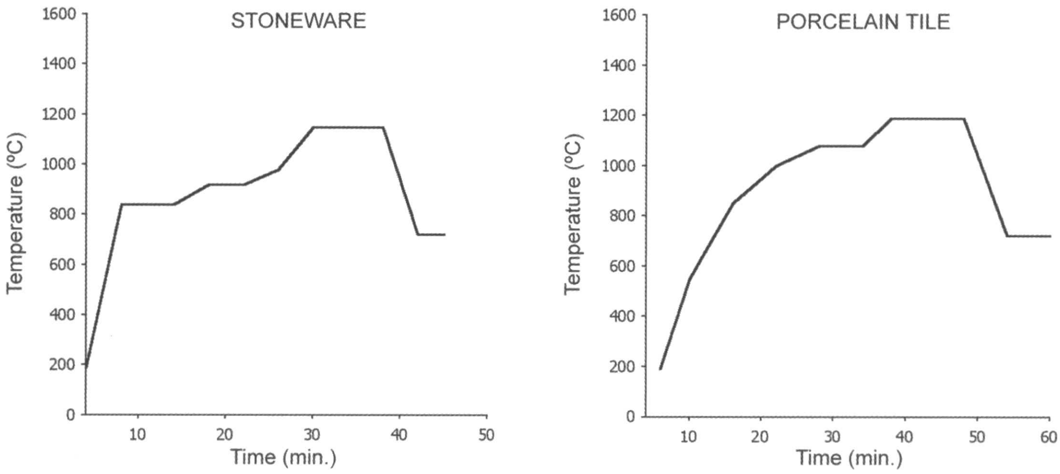

Figure 7. Stoneware and porcelain tile heat treatment cycles used.

2.3. CHARACTERIZATION TECHNIQUES USED

X-ray diffraction. (XRD): A Siemens model D5000 diffractometer with a copper anode was used. The measurements were conducted at an intensity of 20 mA and voltage of 40 kV, in a range of 2θ from 10 to 80°. A 10-second step was used for counts, and goniometer speed was 0.050° 2θ /s. This technique was used to determine the crystalline phases present in the studied materials.

Scanning electron microscopy (SEM) and microanalysis (EDX): A Leica Mod. LEO440i scanning electron microscope with energy-dispersive X-ray microanalysis, EDX, OXFORD model Link-ISIS with backscattered and secondary electron detector, was used. The conditions set for obtaining the different microanalyses were an acceleration voltage of 20.00 kV and filament current intensity of 2000 pA.

Differential thermal and thermogravimetric analysis (DTA/TG). This was used to study the thermal evolution of the materials. A Mettler-Toledo Mod. TGA/SDTA851e, simultaneous instrument was used, connected to a Balzers ThermoStar molecular mass spectrometer for reaction gas analysis. The working conditions set were a heating rate of 25°/min in a temperature range of 25 to 1500°C

Hot stage microscopy. A MISURA hot stage microscope with a heating rate of 50°/min was used. This technique enabled determining the characteristic temperatures of each frit.

Measurement of the CIE-L a* b* chromatic coordinates.* A Minolta CR200 colorimeter was used to measure the CIE-L* a* b* chromatic coordinates of the glazed pieces.

Scratch hardness of the surface according to Mohs. The Mohs hardness test was run on the glazed pieces according to standard UNE 67-101.

Vickers microhardness. The measurement of Vickers microhardness was performed according to standard UNE-EN ISO 6507-1. A Matsuzawa model MHT-1 instrument was used, conducting the test on the glazed pieces.

3. RESULTS AND DISCUSSION

3.1. THERMAL STUDY OF THE SAMPLES

3.1.1. *Hot stage microscopy*

Hot stage microscopy was used to determine the behaviour of the raw materials during the fusion process, enabling the melting temperature of the studied glasses to be established. The results obtained show that raising the quantity of silica in the formulation reduces frit fusibility, reaching temperatures up to 1530°C.

3.1.2. *Differential thermal and thermogravimetric analysis (DTA/TG)*

Differential thermal and thermogravimetric analysis has enabled monitoring the exothermic and endothermic processes of the system during heat treatment. This therefore allows establishing the phase transition, nucleation, crystallization and fusion temperatures.

In order to study the thermal process, a DTA/TG heating cycle was used, with a gradual rise at 25°/min to 1500°C. This was followed by cooling to 100°C, then heating again to 1200°C, followed by free cooling. In this way, in the first part of the cycle (heating to 1500°C), as all the samples display similar behaviour on belonging to the same family, nucleation and crystalline growth were favoured, as observed by hot stage microscopy. Figure 8 shows the DTA/TG and mass spectroscopy of a sample with an intermediate silica content (sample P3, 75% SiO_2).

As Figure 8 shows with respect to thermogravimetric analysis, the samples all exhibit weight losses around 10%. A small water loss can be observed around 100° C (presence of fragment 18 in the mass spectrum) and a greater loss, of the order of 10%, between 500°C and 900°C relating to the loss of CO_2 (presence of fragment 44 in the mass spectrum). Another loss of 1-2% around 600°C can be attributed to eventual nitrogen compounds. With respect to differential thermal analysis, an exothermic peak is observed at 573°C of α–β quartz transition.

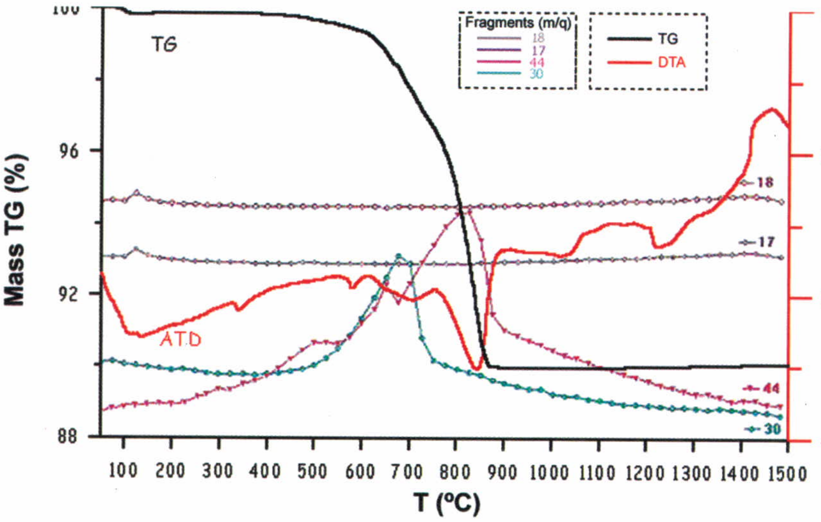

Figure 8. DTA/TG of sample P3 (75% SiO_2 content) from 25 to 1500°C and its corresponding mass spectrometry.

In the second cycle (Figure 9), the glass melting temperature (Tf) can be observed at temperatures above 1000°C, as well as the glass transition temperature (Tg) between 650 and 680°C, depending on the initial SiO_2 concentration. Raising the amount of SiO_2 was found to slightly increase the glass transition temperature. All the samples present an exothermic peak around 1000°C, which is related to the glaze nucleation and crystallization capacity. In this case, raising silica content favours a more defined peak, as does the introduction of SiO_2 with a smaller particle size, encouraging the nucleation and crystalline growth processes.

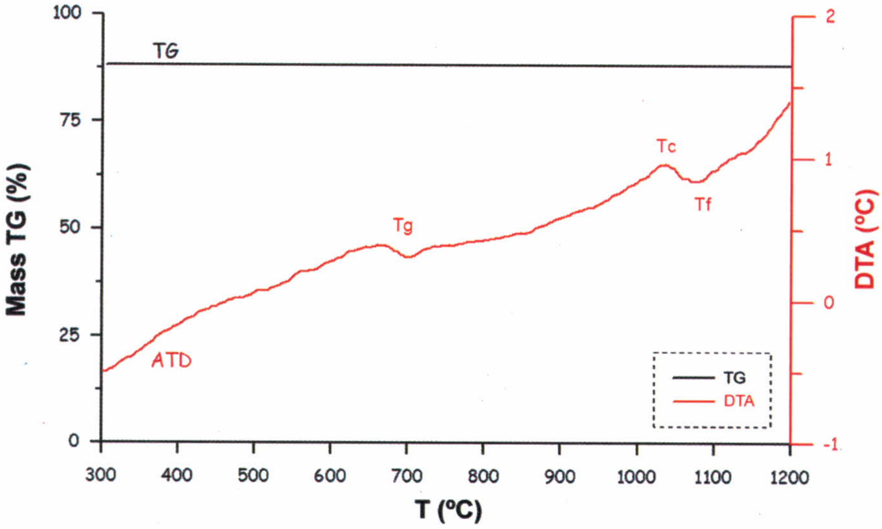

Figure 9. DTA of sample P3 (75% SiO_2 content) after fusion.

3.2. STRUCTURAL AND MICROSTRUCTURAL STUDY OF THE SAMPLES

3.2.1. Development of crystalline phases.

To better study the nucleation and crystalline phase development capacity, the starting compositions were subjected to different heat treatments to favour crystallization, while also studying the influence of initial SiO_2 particle size.

In order to observe the different behaviour that two analogous samples exhibit, Figure 10 shows the diffractograms of compositions P4 and P4F, as these have the greatest SiO_2 content (containing 80% SiO_2), and therefore more clearly evidence the effect of particle size.

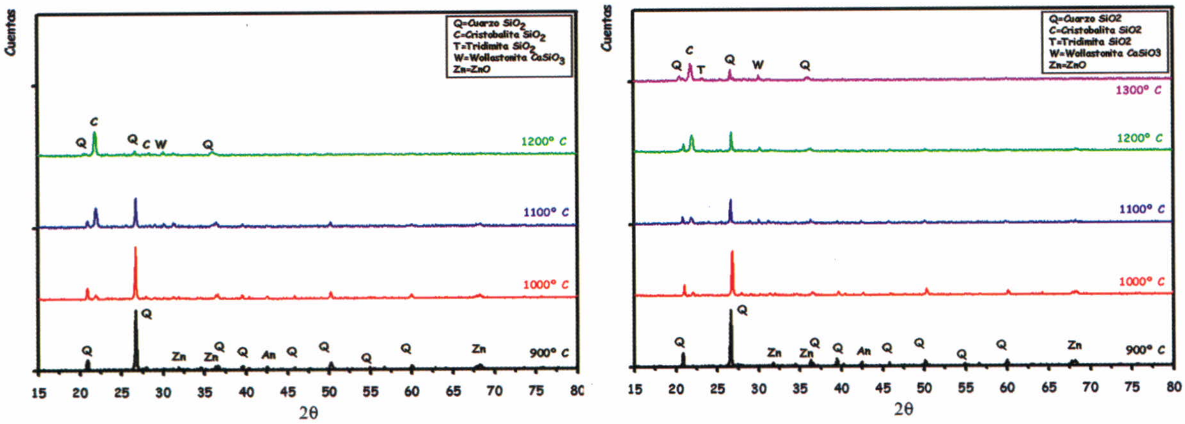

Figure 10. X-ray diffractograms of analogous samples P4 (diffractogram on the right) and P4F (diffractogram on the left) with 80% SiO_2 in their initial composition.

The results obtained show that the reduction in SiO_2 particle size favours sample reactivity, as well as the formation of SiO_2 cristobalite at lower temperatures, since at 1200°C the sample with the smaller particle size (P4F) displays almost a complete transformation of quartz in cristobalite, whereas in the case of SiO_2 of larger particle size (P4), this conversion does not happen until 1300°C. Similarly, it can be observed that the reduction of SiO_2 particle size in the initial composition encourages formation of the cristobalite crystalline phase instead of tridymite.

3.2.2. Study of the synthesized glassy material

The synthesized frits were characterized by X-ray diffraction, and by scanning electron microscopy and microanalysis. All the analyzed frits were glassy, and no crystalline phases were detected by XRD or SEM, as the diffractogram in Figure 11 shows, which depicts the diffraction spectrum of the frit with the largest SiO_2 content (sample P4), and therefore with the greatest tendency to crystallize or contain unmelted materials. Figure 12 shows the morphology of this frit.

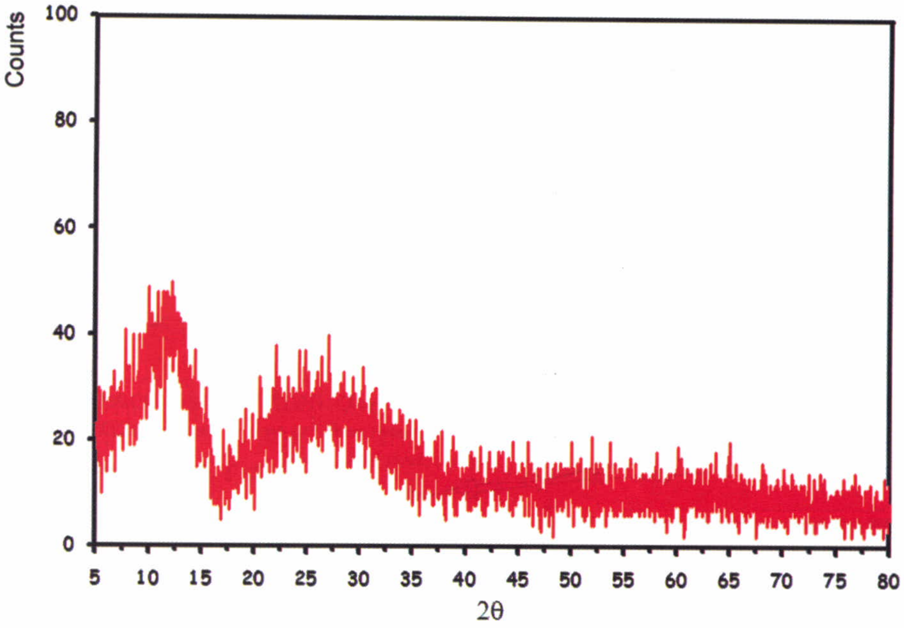

Figura 11. Difractograma de rayos X de la frita sintetizada a partir de la muestra P4

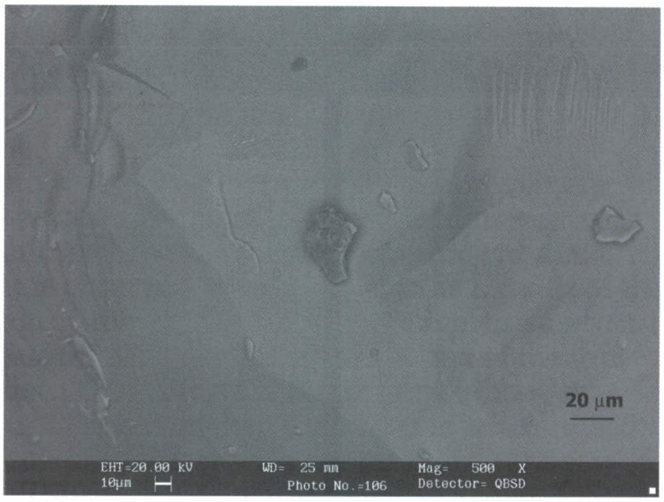

Figure 12. Micrograph of the glassy material synthesized from sample P4

3.2.3. Study of the synthesized glass-ceramic glaze family

As observed by scanning electron microscopy (SEM), raising the quantity of SiO_2 produces a greater devitrification of crystalline phase. Figure 13 shows micrographs of the same and greater magnifications of the glaze with the smallest SiO_2 concentration (sample P1) and of the glaze with the largest SiO_2 concentration (sample P4) in their initial composition. They evidence the different crystalline distribution existing in the two samples. Both cases show the morphology and homogeneity of the crystallizations, stemming from devitrification of the analyzed frits.

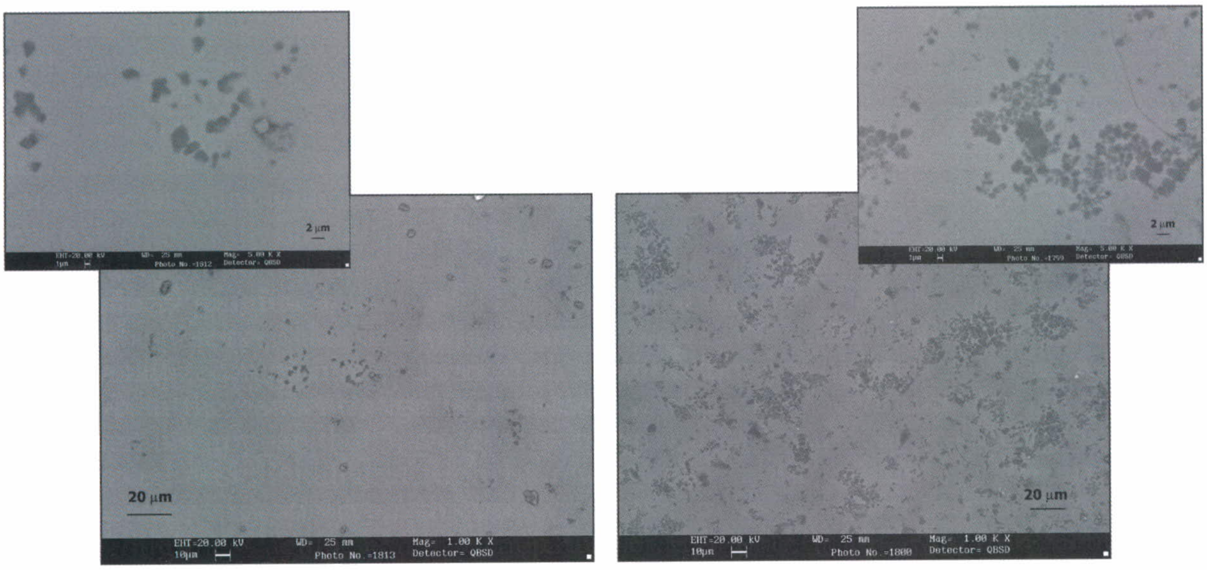

Figure 13. Micrographs of samples P1 (left) and P4 (right) and extent of the regions with crystallizations.

The X-ray diffraction study of the glass-ceramic glazes shows the presence of crystalline phases belonging to the SiO_2 system (Figure 14).

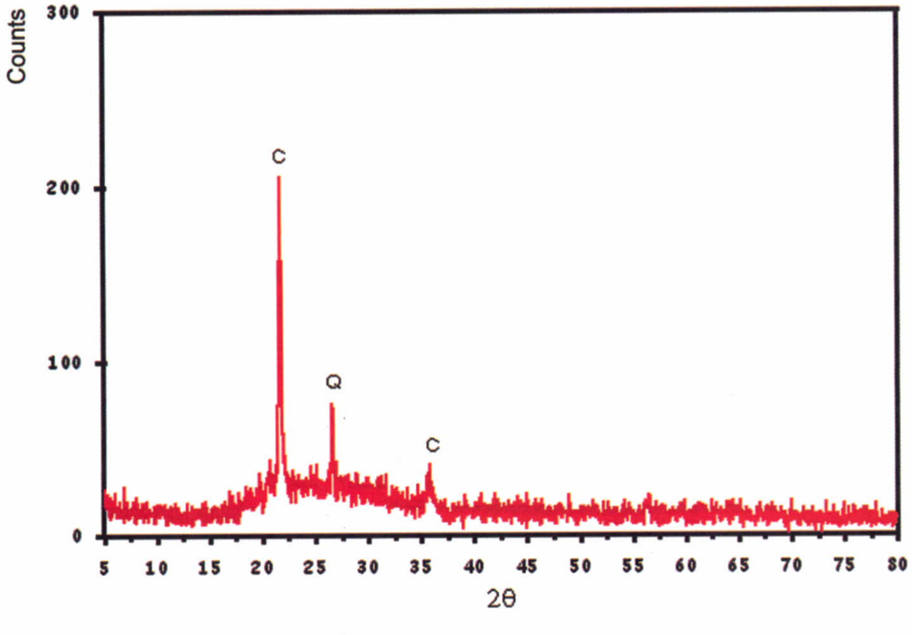

Figure 14. X-ray diffractogram of the surface of a glaze developed from glassy material with a 75% silica content by weight (sample P3). (C=SiO2, cristobalite, Q= SiO2 quartz).

Energy-dispersive X-ray microanalysis (EDX) of the studied samples (Figure 15) showed SiO_2 crystallizations and the presence of phase nucleations rich in Si and Ca, which were below the XRD detection limit, in all of these. The glassy matrix containing the arising crystalline phases can also be observed.

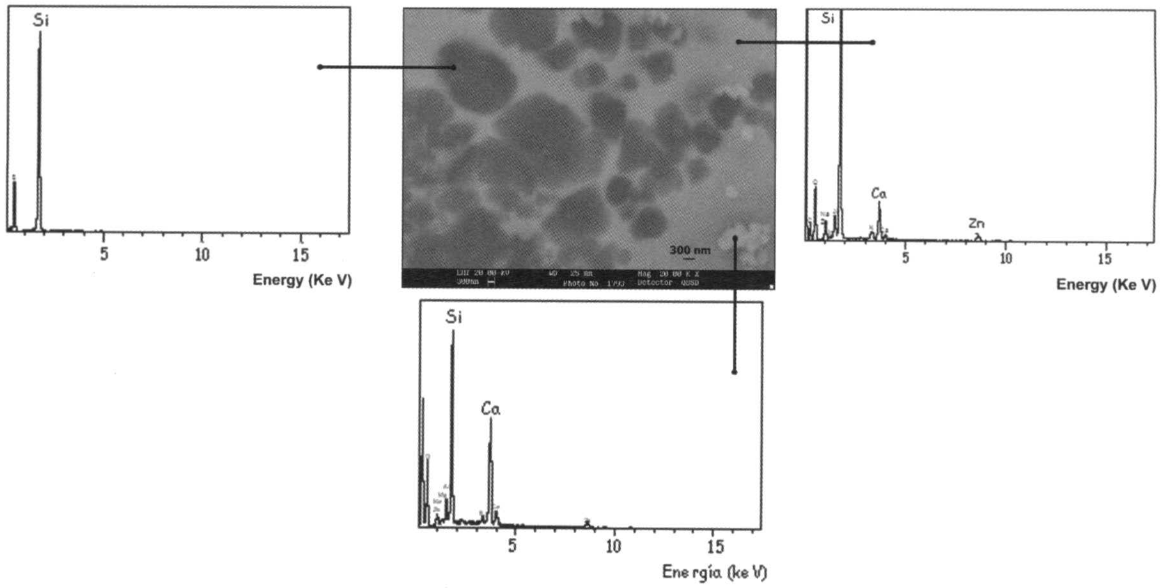

Figure 15. Micrograph and EDX microanalysis showing SiO_2 crystallizations, Si and Ca nucleation, and the glassy matrix.

To further study the development of these phases, scanning electron microscopy and microanalysis were run on the system when it began to fuse.

Figure 16 depicts a micrograph and its magnification of the sample with 75% SiO_2 in the initial composition (sample P3). They show the phase rearrangement and separation that this system undergoes during fusion (1450°C). Note the presence of three phases of different compositions, which correspond to the ones found in the glaze resulting from this sample, as the corresponding EDX microanalyses indicate: a Si-rich crystalline phase of the SiO_2 crystallizations and two glassy phases, distinguished fundamentally by the quantity of Si and Ca.

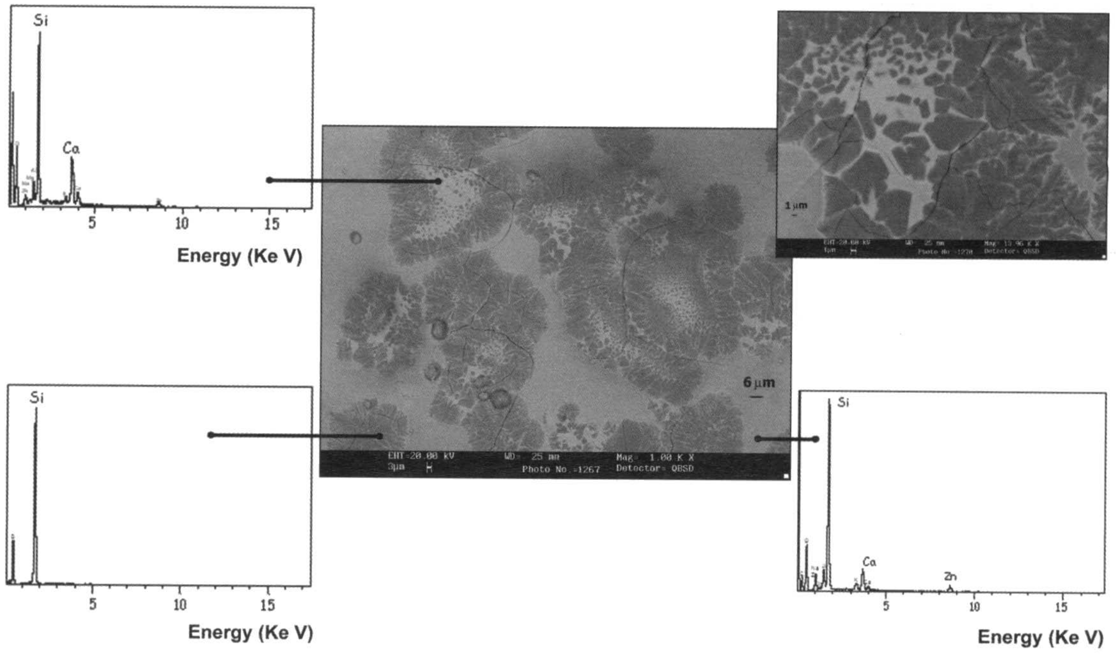

Figure 16. Micrographs and EDX microanalysis of the frit with 75% SiO_2 (sample P3) at fusion start

Therefore, comparing both micrographs (Figures 15 and 16), it can be observed that the Si-rich phase corresponds to the SiO_2 crystallizations developed in the glass-ceramic glaze, as well as the glassy phase with a smaller percentage of Ca, which is equivalent to the glassy matrix developed in glaze. It is important to note that the glassy phase with the greater Ca content is surrounded by SiO_2 crystalline particles, which can be identified as the nucleating phase of the crystallizations rich in Ca and Si observed in the resulting glass-ceramic glaze.

3.3. STUDY OF THE SURFACE PROPERTIES DEVELOPED IN THE POLISHED PIECES.

The transparent glass-ceramic glazes obtained were applied onto stoneware and porcelain tile bodies, after which the resulting glazes were polished. In the polished samples, no microporosity was detected, as image analysis of the optical microscopy photographs shows (Figure 17).

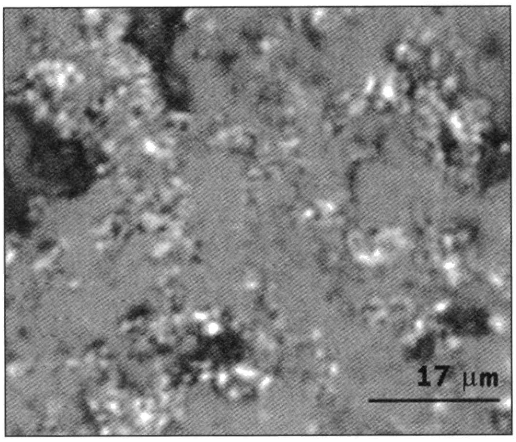

Figure 17. Optical microscopy photograph of sample P3 at a magnification of 1000x, representative of the developed sample.

With regard to surface properties, the resulting glazes exhibited Vickers microhardness values between 450 and 600 kg/cm^2, and Mohs hardness between 5 and 6, depending on the SiO_2 content. The highest values correspond to the glazes with the largest silica content in their initial composition, while the developed materials are transparent and have high gloss.

Quality tests were similarly conducted on the glazed and polished pieces. Table V details the most noteworthy results.

TEST	APPLIED STANDARD		CLASSIFICATION
Determination of chemical resistance	UNE-EN-ISO 10545-13	Acid attack Alkali attack	GHA GHB
Determinationn dof stain reesistance	UNE-EN-ISO 10545-14		Class 5 (no staining)

Table 5. Most noteworthy results of the quality tests performed on the glazed and polished pieces.

4. CONCLUSIONS

SiO_2-rich compositions were formulated in the vitrifying system SiO_2-MO-Al_2O_3.

These modified compositions have enabled obtaining glazes of a glass-ceramic nature, adapted to stoneware and porcelain tile bodies.

The glass-ceramic system is made up of crystalline phases of silica, SiO_2, with mean crystal sizes of 1 μm, which were homogeneous.

The glaze compositions, applied as glaze coatings and polished, display good industrial adaptability, with high mechanical strength and scratch resistance, and are transparent and glossy.

5. ACKNOWLEDGEMENTS

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