

EFFECT OF THE MAJOR DEVITRIFYING PHASE ON CERAMIC GLAZE MICROSTRUCTURE AND MECHANICAL PROPERTIES

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ABSTRACT

The composition of a ceramic glaze must match the firing cycles as well as the ceramic substrate it coats to achieve an appropriate response with regard to mechanical, bonding and optical properties. The composition of the glaze in these conditions produces devitrification of insoluble crystalline phases that decisively influence the microstructure of the material and, hence its mechanical properties. In this study we have analysed some microstructures of glossy glazes used on red and white ceramic stoneware floor tile and porcelain tile bodies, analysing composition-microstructure-mechanical properties. Seven standard microstructures were analysed, based on the major devitrifying phase: zircon, gahnite, anorthite, wollastonite, scheelite, powellite and diopside. The microstructures with acicular-shaped devitrified phases and high anastomosis (zircon, wollastonite, anorthite) displayed lower brittleness indexes than the pseudocubic ones (gahnite, diopside). The cluster-forming pseudocubic shapes that crystallised together with acicular shapes (devitrified powellite and scheelite lustres together with zircon) improved gloss (lustre effect) and maintained or slightly improved mechanical properties.

1. INTRODUCTION

Ceramic glazes are obtained by firing a ceramic frit modified by mill additions. The frit and the additions are homogenized and added from the point of view of particle size, either by wet milling in aqueous medium or dry milling. The resulting slip is deposited by different methods on a metallic or ceramic substrate.

The nature of the ceramic glazes is therefore of a crystalline, glass-ceramic or in more general terms of a "glass-ceramic composite material" type, as in general four types of constituents can be found in glazes ^[1].

- (a) Glass or glassy phase, which makes up the structural matrix of the glaze, and which can be homogeneous or display different phases when phase separation occurs by formation of insoluble glass.
- (b) Nanocrystals or ceramic phase generated by devitrification of the glass with sizes between 500 and 2000 nm.
- (c) Microcrystals or ceramic phase added to the glaze in the mill, which because of its insolubility, appears in the fired glaze.
- (d) Porosity or occluded air phase (closed porosity), not eliminated in the firing process.

The glassy network-forming elements that exhibit high ionic potentials, such as Ti, Zr, Sn or Al, can be expected to present a certain tendency to form MO_n structural units given their relative acidity, and therefore leave the glassy network and crystallize nanocrystals in the network. These usual crystallization phases in ceramic glazes are listed in Table I. Thus Zn crystallizes willemite, Ti rutile, anatase and sphene, Zr zirconia and zirconium silicate (zircon), Sn cassiterite and tin sphene, and Al corundum, gahnite, anorthite, gehlenite, spodumene or celsian. Under certain conditions, calcium also devitrifies a wide group of crystalline phases, such as wollastonite, diopside, scheelite or powellite ^{[2], [3]}.

These materials can give rise to glossy white glazes in the appropriate thermal conditions for firing vitrified materials (red or white stoneware and porcelain tile), which are widely used because of their smoothness and aesthetic quality.

2. OBJECTIVES AND CHARACTERIZATION METHODS

The mechanical and optical properties of a devitrified ceramic glaze are the result of the composition and microstructure it adopts. The objective of this work is to analyze the mechanical and optical relation between composition, microstructure and properties of a family of glossy white ceramic glazes of the system ZnO-CaO-SiO₂, which devitrify different major crystalline phases:

- 1) glazes that devitrify zircon and/or diopside.
- 2) lustres of scheelite and powellite with zircon as secondary phase.
- 3) glazes that devitrify wollastonite.
- 4) glazes that devitrify in the system willemite-gahnite-anorthite.

Knowing the composition of the starting glazes, these were characterized by the following techniques:

- (a) The morphological, microstructural and compositional characterization of the samples was performed by scanning electron microscopy (SEM) in a Leyca-400 microscope, and microanalysis was done by X-ray energy dispersion (EDX) with an Oxford instrument.
- (b) The devitrified crystalline phases were identified by X-ray diffraction with a Siemens model D5000 diffractometer with Cu K α radiation and graphite monochromator, with a goniometer rate of 0.05 °2 θ /s, having a voltage of 40 kV and 20 mA intensity.
- (c) The optical gloss and whiteness properties were respectively determined with a Multi-gloss 268 portable reflectometer (conforming to DIN 67 530, ISO 2813 and ASTM D523) and a Perkin Elmer Lambda 19 spectrophotometer, scanning in the diffuse reflectance visible wavelength range (between 380 and 780 nm).
- (d) The following mechanical properties were analyzed:
 - (i) The abrasion study was conducted according to the PEI (Porcelain Enamel Institute) method with a wet abrasive charge. Test specimens were used of ceramic tiles fired in a fast laboratory kiln, cut to size 100x100 mm in accordance with standard UNE-67-154-85 or EN 154 for ceramic tiles with a Gabrielli abrasion tester of the PEI type.
 - (ii) The Vickers microhardness test uses a pyramidal diamond indenter that is pressed against the surface of the metal (traditionally it is a metallographic test) under a load of W kg, measuring the length of the diagonal d of the resulting indent notch and averaging the values of several tests.
 - (iii) Fracture toughness was measured by the critical stress intensity factor for flat geometries type I (K_{Ic}) from the measurement of a resulting lateral crack or by the deformation stress of a Vickers indenter. Material toughness is determined from Equation 1, in accordance with the application of the ideas of Lawn and Fuller developed by Roesler for lateral cracks:

$$K_{Ic} = 0.0513 P c^{(-3/2)} \quad (\text{Eq. 1})$$

where K_{Ic} is the critical stress intensity factor, P the charge applied in N, and c lateral crack front. The units of K_{Ic} toughness are from the equation in (GPa m^{1/2}).

- (iv) The brittleness index B is the relation between Vickers microhardness (resistance to plastic deformation) and fracture strength (K_{Ic}): the material is more brittle if it displays high resistance to plastic deformation and fracture strength.
- (v) The determination of the scratch hardness of the surface according to the Mohs' scale was conducted by scratching the surface with the collection of minerals from the scale according to standard EN 101.

3. EXPERIMENTAL

The glazes were chosen from commercial frits of different suppliers, except glazes PO and SC. These were prepared by mill additions of WO₃ and MoO₃ supplied by PANREAC S.A., to glazes DI and OR respectively.

The frits were milled to the oversize preset by the supplier in a ball mill. The material sieved at 125 μ m was dried and subsequently used in portions of 100 g, mixing in carboxymethylcellulose adhesive and water until obtaining a slip with a bulk density of 1.6 g/ml by homogenizing in a ball mill. The slip was deposited by the Doctor Blade or slider method.

The composition of the six glazes is listed in Table II. Boron is not used in any of the compositions. From a compositional point of view, all the glazes belong to the ZnO-CaO-SiO₂ system. The first is used as a flux for stoneware bodies, as it promotes the fusion of the glaze at temperatures above 1050°C when its concentration in the glaze is moderate. Calcium also improves fusibility by reducing viscosity above 1000°C, and in these glazes acts as a hardening agent, improving glaze mechanical properties. Finally, SiO₂ is the glassy network former ^{[4], [5]}. On the other hand, on moving from glaze family group 1 to 4 in this characteristic set of glazes, we can observe the following changes in composition:

- i) the main modifiers change in reverse form on going from group 1 to 4: ZnO increases (almost duplicates) and CaO decreases (almost halves).
- ii) Al₂O₃ goes from values around 13% to just 5 in the glaze that devitrifies wollastonite, and it rises to 22% in gahnite glazes. Aluminium stabilizes the glassy network, increasing mechanical strength. However, it raises melt viscosity, so that it reduces the tendency of the glazes to devitrify.
- iii) The alkaline fluxes, basically K₂O because Na₂O is of little significance, increase from 2.5 in the zircon glazes to almost double in the gahnite glazes. In addition to fusibility, the greater presence of alkalis in the network lowers mechanical strength in the gahnite glazes, counteracted by the strong presence of aluminium.
- iv) In the glazes that devitrify zircon, powellite or scheelite the presence is respectively found of ZrO₂, MoO₃ and WO₃.

COMPOUND	MOHS	n
Willemite Zn ₂ SiO ₄	6	1.7
Rutile TiO ₂	6-61/2	2.8
Anatase TiO ₂	51/2-6	2.5
Sphene CaSiTiO ₅	5-51/2	1.91
Zircon ZrSiO ₄	71/2	1.9
Baddeleyite ZrO ₂	61/2	2.2
Cassiterite SnO ₂	6-7	2
Sphene CaSiSnO _{4.5}	6	1.8
Corundum Al ₂ O ₃	9	1.77
Gahnite ZnAl ₂ O ₄	6	1.9
Anorthite CaAl ₂ Si ₂ O ₈	6	1.58
Gehlenite Ca ₂ Al ₂ SiO ₇	5-6	1.7
Spodumene LiAlSi ₂ O ₆	6-7	1.67
Celsian BaAl ₂ Si ₂ O ₅	6	1.59
Wollastonite CaSiO ₃	5-51/2	1.63
Diopside CaMg(SiO ₃) ₂	6	1.7
Scheelite CaWO ₄	41/2-5	1.9
Powellite CaMoO ₄	31/2-4	1.97

Table I. Scratch resistance and refractive index of opacifiers and common devitrifying phases in ceramic floor tile glazes.
(Source: Dana (2) and ASTM X-ray diffraction files).

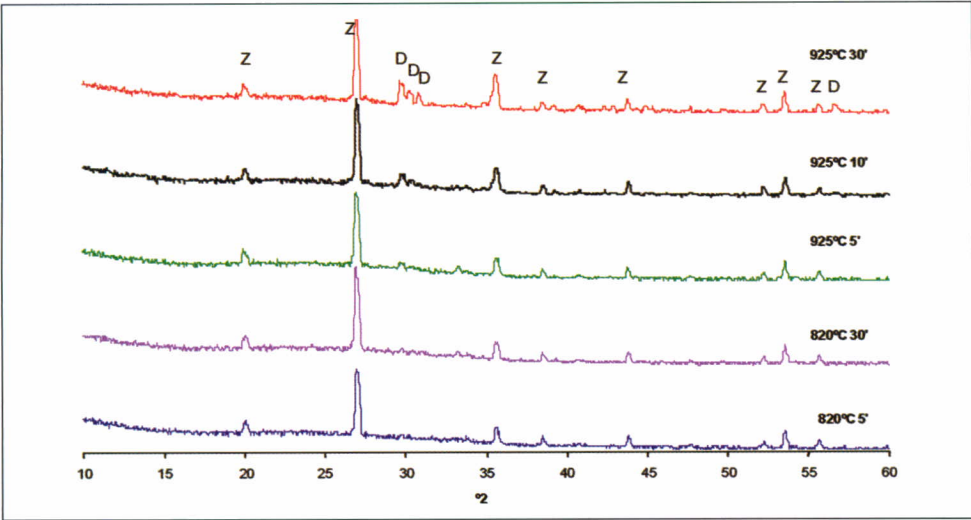
4. GLAZES THAT DEVITRIFY ZIRCON AND/OR DIOPSIDE

These glazes have undergone great development owing to their gloss, whiteness, appropriate mechanical properties and chemical resistance. They are used in formulations of both porous single-fired tile and stoneware.

When the composition of the glaze contains MgO, melt viscosity increases, so that depending on the type of heat treatment, the glaze can devitrify diopside with prolonged treatments and/or high temperatures. Figure 1 shows the evolution of the diffractograms of glaze OR on being recalcined. It can be observed that recalcination at 820°C does not yield diopside, but at 925°C diopside peaks are detected that grow progressively: 27 cps at 5 min, 50 cps at 10 min and 70 cps at 30 min, while the zircon intensity remains constant around 1200 cps.

	OR Zircon (red)	DI diopside (red)	SC scheelite (red)	PO powelite (red)	WO wollastonite (porcel)	AN anorthite (porcel)	GA gahnite (porcel)
ZnO	10,0	9,7	9,3	9,7	13,0	18,0	17,5
CaO	19,8	19,1	18,4	19,2	16,0	10,7	7
MgO	1,0	4,3	3,9	1	1,0	5	5
K ₂ O	2,3	2,2	2,1	2	5,0	4	4
Na ₂ O	0,2	0,2	0,2	0,2	-	-	-
Al ₂ O ₃	8,0	7,7	7,4	7,8	5,0	22	22
SiO ₂	52,5	50,7	48,8	51	59	43	47,1
ZrO ₂	4,6	4,6	4,4	4,5	-		-
WO ₃	-	-	4	-	-	-	-
MoO ₃	-	-	-	2,9	-	-	-
LOI	1,6	1,5	1,5	1,5	1,0	1,2	1,5

Table II. Centesimal composition of the six glazes together with the major devitrifying phase and body used (Red: red body 1140°C, porcel: porcelain 1200°C).



CRYSTALLINE PHASES: Z Zircon ZrSiO_4 ($2\theta=27$), D Diopside $\text{CaMgSi}_2\text{O}_6$ ($2\theta=30$).

Figure 1. Recalcinations of glaze OR at different temperatures and residence times with a modified fast cycle of porous single-fired tile.

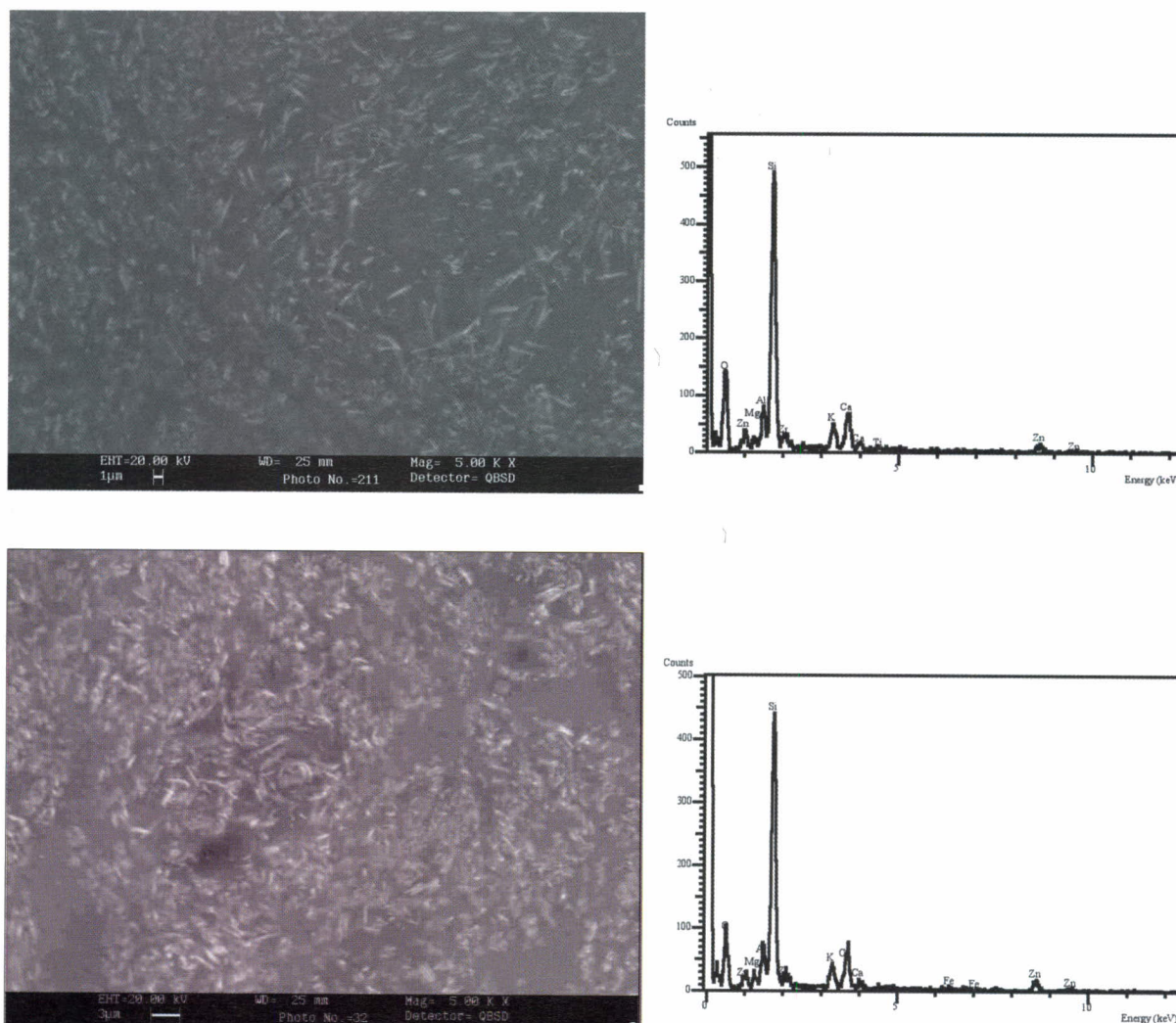


Figure 2. SEM micrographs and related EDX spectrum for sample OR recalcined at: (a) 820°C/5 min, (b) 925°C/30 min.

Figure 2 depicts the evolution of the microstructure of glaze OR after recalcination. At 820°C the glaze remains homogeneous; at 925°C diopside crystallizations appear in the form of darker cubes than the glassy matrix. This is because the image, made with a backscattered electron detector, displays a smaller absorption for the smaller diopside, which has a lower backscattering power on having a smaller molecular mass relative to the matrix.

Figure 3 shows a SEM micrograph of glaze OR and the SEM spectra associated with the overall field and the crystals. Figure 4 shows the X-ray diffractograms of the glazed surface with OR and DI respectively.

The microstructures observed in these glazes allow inferring that glazes of high homogeneity are involved in the case of OR, with acicular zirconium silicate precipitate oriented in the $27^\circ 2\theta$ ($hkl=200$) direction, which is observed to be of very high intensity compared with the other orientations. The particle sizes range from 1-5 μm and display a certain coarsening with temperature. The crystal volume fraction is around 20%, if considered proportional to the surface occupied by the crystalline phase in the micrographs.

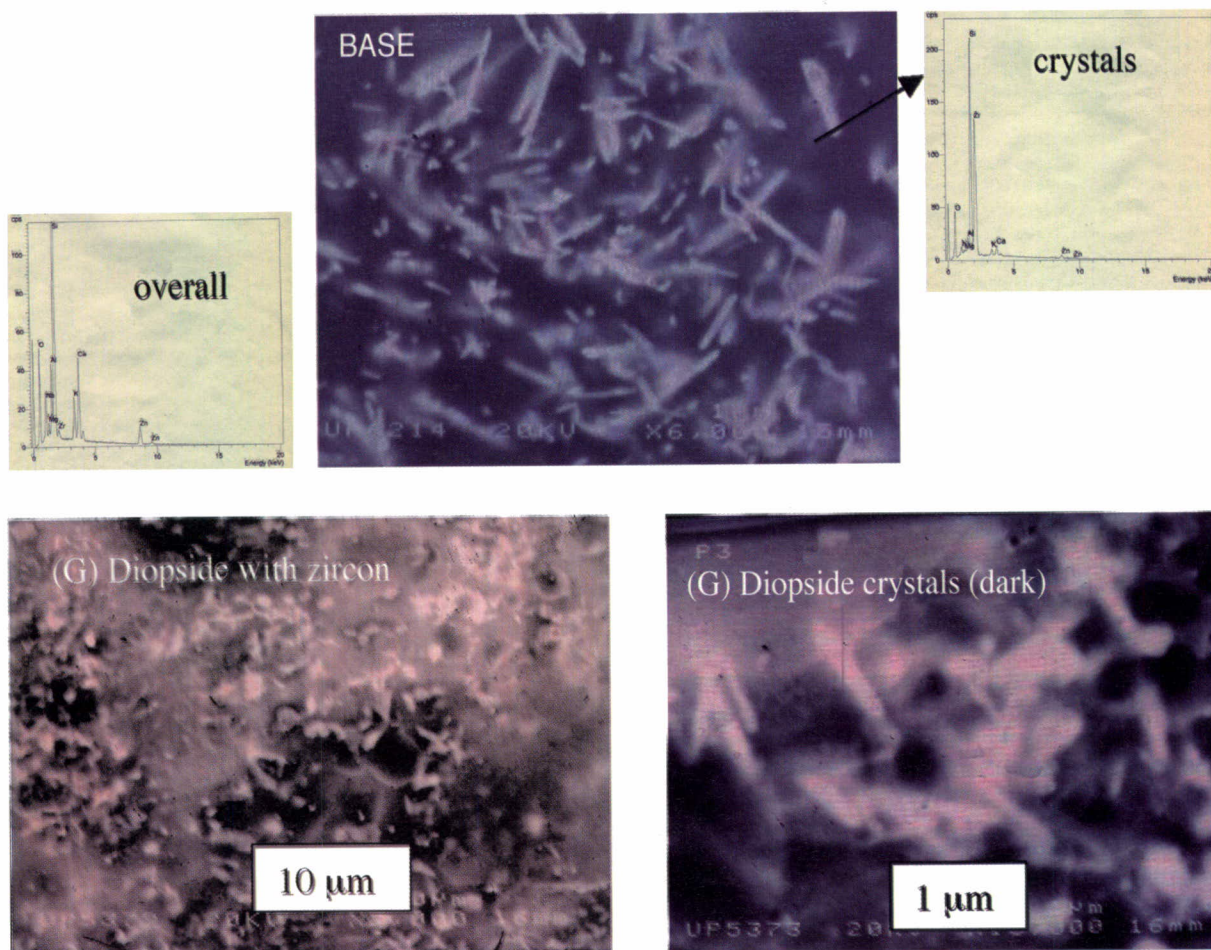
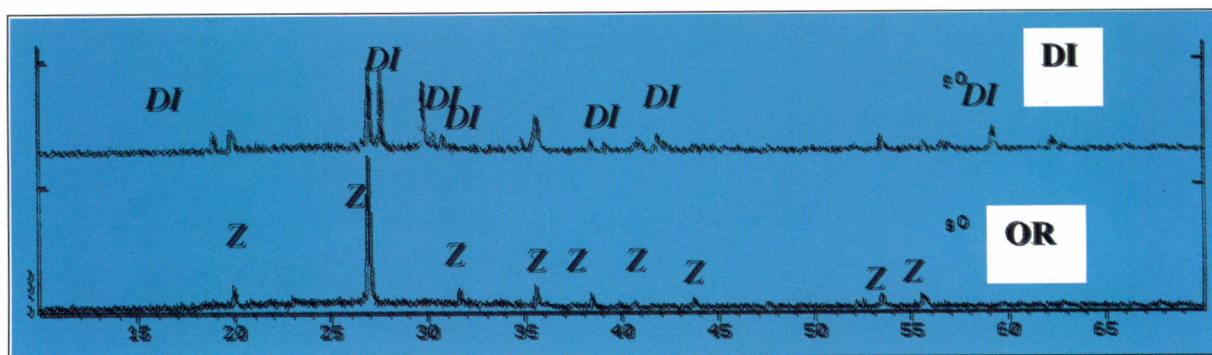


Figure 3. SEM micrographs with backscattered electron detector: (a) OR: devitrification of zircon ZrSiO_4 , (b) DI: crystallization of diopside with zircon and diopside crystals (dark) together with acicular zircon crystals (white).



CRYSTALLINE PHASES: Z Zircon ZrSiO_4 ($2\theta=27$), DI Diopside $\text{CaMgSi}_2\text{O}_6$ ($2\theta=30$).

Figure 4. XRD of samples OR and DI.

The preferential devitrification of diopside in sample DI gives rise to a heterogeneous microstructure.

As the data detailed in Table III indicates, the microstructure with heterogeneities in DI leads to reduced gloss, even though whiteness is similar, while microhardness and toughness increase, but the brittleness index rises, so that

although PEI IV is held, the mass losses measured in the PEI test at 12,000 revolutions indicate higher losses in DI.

5. SCHEELITE AND POWELLITE LUSTRES WITH ZIRCON AS SECONDARY PHASE

The WO_3 and MoO_3 mill additions respectively in frits DI and OR give rise to devitrification of tetragonal shapes of scheelite CaWO_4 and powellite CaMoO_4 respectively.

Figure 5 shows the SEM micrographs of the glazed surfaces with the red stoneware cycle at 1140°C . Figure 6 depicts the diffractograms obtained of the glazed surfaces.

Scheelite and powellite are isostructural, and exhibit a very similar diffractogram in Figure 6, which shows that the devitrified zircon phase continues to display the typical crystalline orientation evidenced by the high intensity of the peak at $27^\circ 2\theta$.

The microstructure of the devitrifications is also very similar in both samples: the tetragonal crystals occur in the form of clusters or aggregates of $20\text{--}10\text{ }\mu\text{m}$ of $2\text{ }\mu\text{m}$ edge. Moreover, the zircon crystals are smaller than those observed in OR and DI, reaching submicrometric sizes, making it difficult to observe them as they are masked by the intense crystallization of powellite or scheelite. Diopside devitrification is not detected, which has been inhibited by scheelite devitrification, as is also partly the case with zircon.

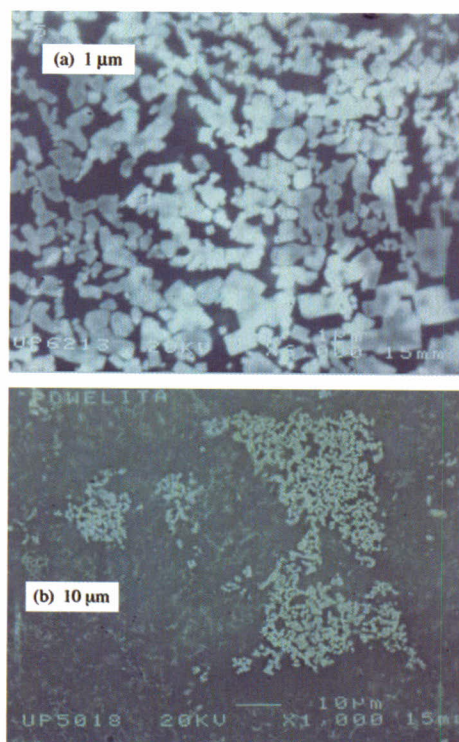
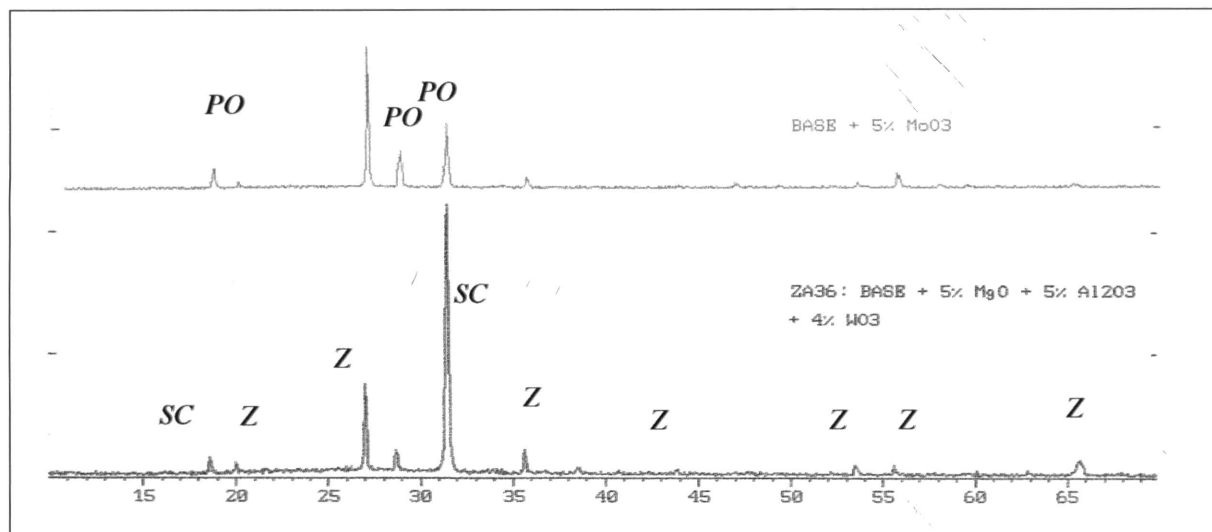


Figure 5. SEM micrographs with backscattered electron detector: (a) SC: crystallization of scheelite CaWO_4 , (b) PO: crystallization of powellite CaMoO_4 forming crystal clusters.



CRYSTALLINE PHASES: Z Zircon ZrSiO_4 , PO Powellite CaMoO_4 .

Figure 6. XRD of scheelite and powellite lustres

The microstructure in clusters of scheelite or powellite microcrystals raises gloss (Table III) owing to the high refringence of the devitrified phases (Table I), while the whiteness index is also held.

The scheelite glaze has held or even improved the mechanical properties compared with DI. Its brittleness index has decreased and so have the mass losses at 12,000 revolutions, although it keeps PEI IV. Powellite holds the values of base OR.

6. GLAZES THAT DEVITRIFY WOLLASTONITE

In glaze WO, the increase in alkaline fluxes in the system ZnO-CaO-SiO_2 produces the devitrification of wollastonite CaSiO_3 [6].

Figure 7 shows the microstructure of the glaze fired in the porcelain tile cycle at 1200°C. Crystallization can be observed of dark acicular wollastonite crystals around regions of the glaze that appear whiter, enriched in zinc, probably due to the development of liquid immiscibility prior to crystallization. The size of the acicular crystals is of the order of 2-4 μm .

The anastomosed acicular microstructure of wollastonite is whiter than that of zircon (Table II) although it loses gloss and the mechanical properties suffer: scratch resistance decreases although it is

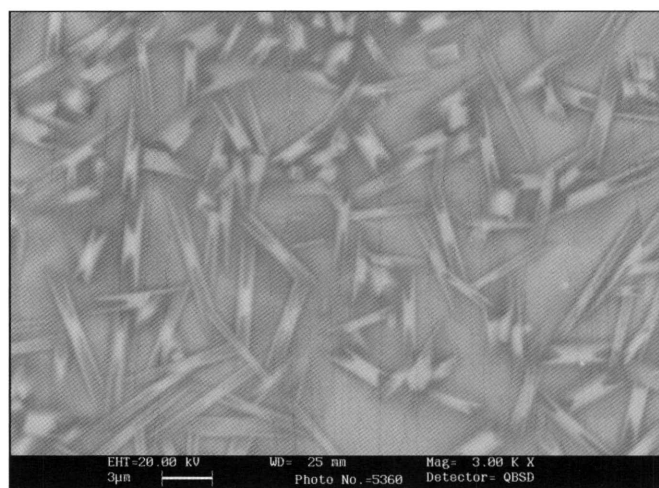


Figure 7. SEM micrographs with backscattered electron detector, WO devitrification of wollastonite CaSiO_3 .

measured at a greater microhardness, which results in higher brittleness indices. It holds classification IV in the PEI test.

7. GLAZES THAT DEVITRIFY IN THE SYSTEM WILLEMITE-GAHNITE-ANORTHITE

Glazes GA and AN in Table II exhibit high proportions of ZnO and Al_2O_3 with the presence of alkaline fluxes that enable devitrification of willemite Zn_2SiO_4 , $\text{CaAl}_2\text{Si}_2\text{O}_8$ anorthite or ZnAl_2O_4 gahnite or a mixture of the three.

Figure 8 shows the microstructures of both glazes in a surface and cross-sectional view. Figure 9 depicts the corresponding diffractograms.

The devitrification of anorthite in this type of glaze is always accompanied by that of gahnite, which behaves as a final phase, while the same occurs more or less with willemite and forsterite. Furthermore, depending on the firing cycle, gahnite can retain crystallized anorthite residual phase.

The gahnite devitrification microstructure is homogeneous, as it corresponds to a homogeneous nucleation mechanism and displays submicrometric particle sizes (between 400-600 nm, Figure 8). In contrast, anorthite exhibits clustered crystallizations around glaze particle interfaces in the sintering process.

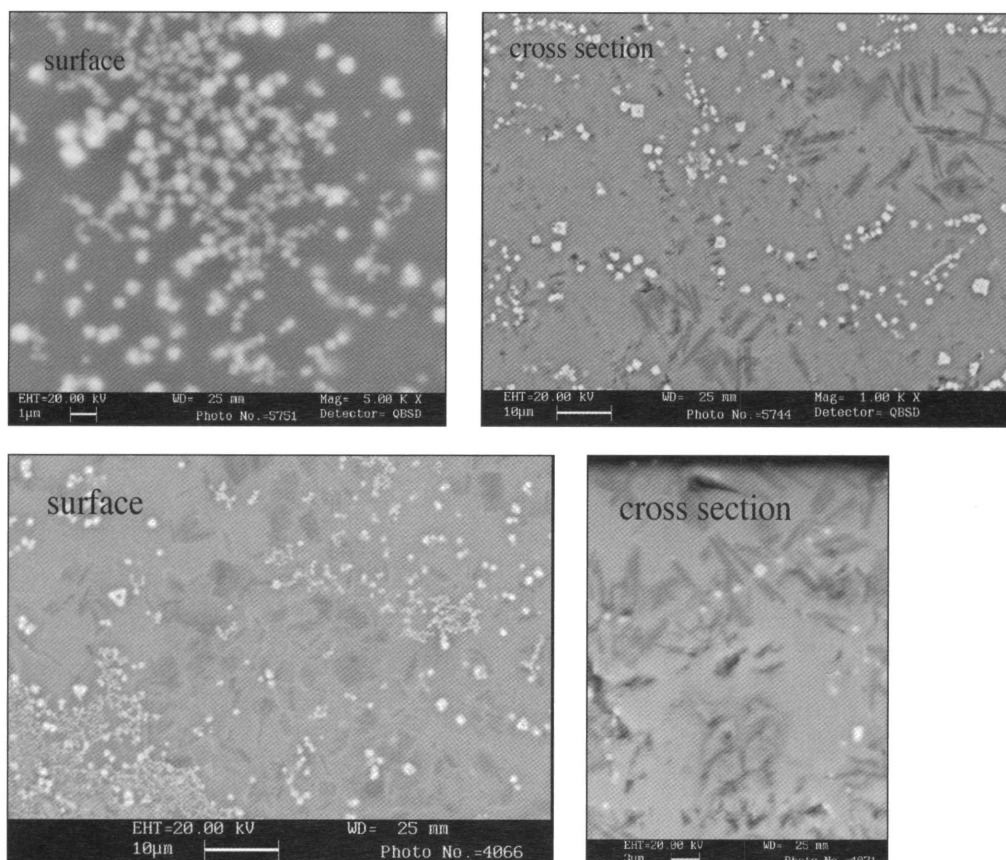
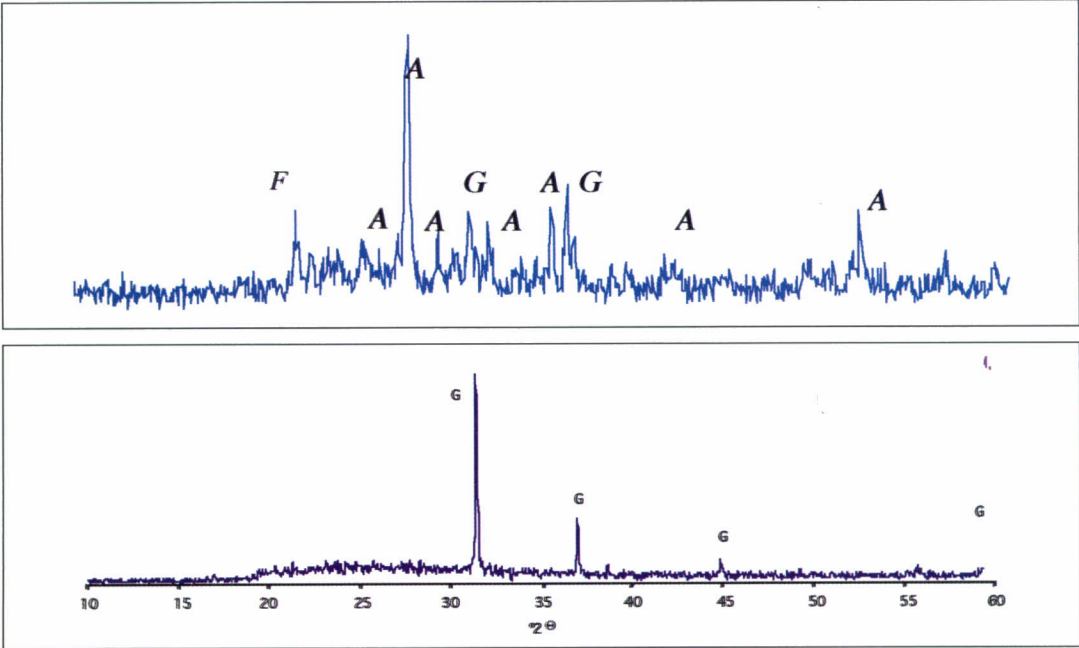


Figure 8. SEM micrographs with backscattered electron detector: (a) GA: crystallization of gahnite ZnAl_2O_4 together with secondary anorthite crystallization $\text{CaAl}_2\text{Si}_2\text{O}_8$ observed at the surface of the piece and in a polished cross section (b) AN: crystallization of anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ together with secondary gahnite crystallization ZnAl_2O_4 observed at the surface of the piece and in a polished cross section.

The material that devitrifies anorthite is matt (Table II). In contrast, the glaze that devitrifies gahnite is very glossy. Both raise microhardness, but anorthite is tougher than glaze OR which devitrifies zircon, while gahnite is not as tough as this glaze [7]. However, both have a smaller brittleness index and although they keep the PEI classification, in the test with 12,000 revolutions with the abrasive charge, the losses are larger than in base OR.



CRYSTALLINE PHASES: G Gahnite ZnAl_2O_4 , A Anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$, F Forsterite Mg_2SiO_4 .

Figure 9. X-ray diffraction of samples AN and GA.

SAMPLE	Mohs	HV (± 7) (Kg/mm ²)	$K_{IC}(\pm 0,1)$ (Mpa.m ^{1/2})	$B(\pm 0,1)$ ($\mu\text{m}^{-1/2}$)	Δm (1200v) mg	PEI	Whiteness index (Gloss 60°)	XRD
OR	5	502	2,2	2,2	260	IV	6,4 (91)	Z(1240)
DI	7	620	2,3	2,6	280	IV	6 (80)	Z(490) DI(632)
SC	7	542	2,5	2,1	220	IV	6,0 (95)	SC(1300) Z(400)
PO	5	560	2,4	2,3	260	IV	7 (93)	Z(1166) PO(656)
WO	5	572	2,2	2,5	280	IV	80,1 (3,4)	WO(825)
AN	6	668	2,4	2,7	330	IV	67,7 (33,7)	AN(370) GA(50)
GA	5	653	2,0	3,2	390	IV	16,8 (95,7)	GA(470) AN(50) F(40)

FASES CRISTALINAS: Z Zircon ZrSiO_4 ($2\theta = 27$) GA Gahnite, ZnAl_2O_4 ($2\theta = 31$); WO Wollastonite CaSiO_3 ($2\theta =$); AN Anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$ ($2\theta = 28$); MO Baddeleyite, ZrO_2 ($2\theta = 28,2$); AD Diopside, $\text{CaMgSi}_2\text{O}_6$ ($2\theta = 30$), PO Powellite CaMoO_4 ($2\theta = 31,5$); SC Scheelite CaWO_4 ($2\theta = 31,5$), Forsterite (Mg_2SiO_4 , peak $22^\circ 2\theta$).

Table III Characterization results of the samples with different major phases.

8. CONCLUSIONS

The study allows drawing the following conclusions on analysing the opaque, glossy ^[8], white glazes of the system $\text{ZnO}_2\text{-CaO-SiO}_2$:

a) The glazes that devitrify zircon display a homogeneous microstructure with volume fractions of the order of 20% of devitrified phase in the form of a homogeneous precipitation of acicular zircon microcrystals, 1-4 μm long, with crystalline orientation. The materials are of high whiteness, gloss and with moderate-high mechanical properties, microhardness around 500 kg/mm^2 , low toughness around 2.2 $\text{MPa.m}^{1/2}$, though with relatively high abrasion resistance (PEI IV and brittleness index of 2.2 $\mu\text{m}^{-1/2}$).

b) If the formulation contains magnesium, the pyroxene phase diopside $\text{CaMgSi}_2\text{O}_6$ is readily detectable, which appears as the major phase when the system is enriched with MgO . The two-phase materials diopside-zircon have a heterogeneous microstructure, and display a smaller abrasion resistance despite the increase in both microhardness and toughness.

c) The addition of tungsten and molybdenum oxides to the glazes that devitrify diopside-zircon gives rise to glossier glazes, while holding the mechanical properties with a scheelite or powellite microstructure that devitrifies, forming clusters or aggregates of tetragonal crystals of 2 μm edge. This devitrification inhibits zircon and diopside crystallization.

d) The formulations with alkalis and equilibrium CaO-ZnO devitrify wollastonite as acicular crystals of 2-4 μm in an anastomosed acicular microstructure that gives rise to greater whiteness than that of zircon, although it loses gloss and the mechanical properties suffer.

e) With high proportions of aluminium in the system $\text{ZnO}_2\text{-CaO-SiO}_2$, crystallization occurs of anorthite-gahnite, the former in a heterogeneous and the latter in a homogeneous form, with submicrometric crystals. Anorthite tends to have a matting effect, while gahnite increases gloss. Although microhardness increases, abrasion resistance decreases notably.

9. ACKNOWLEDGEMENTS

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