SYNTHESIS AND CHARACTERISATION OF GLAZES WITH A HIGH REFRACTIVE INDEX AND HARDNESS

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ABSTRACT

The present study proposes using technologies proper to other fields, like sol-gel processing, to produce nanometric crystals that can be used in the industrial glaze manufacturing process as seeds to generate the desired crystalline phases, avoiding the use of nucleants like titanium or zirconium oxides.

The processing of ceramic or glass-ceramic materials with high added value and engineered properties (texture, structure and morphology) has suffered the disadvantage of needing high temperatures to obtain acceptably homogeneous glass precursors.

Alternative technologies to traditional ones are currently available, which allow saving energy and are more compatible with the environment. Notable examples are the physical and chemical vapour deposition techniques (PVD and CVD), thermal projection methods (electrospray and thermospray techniques), laser fusion and the sol-gel methods. Among these techniques, sol-gel processing provides greater homogeneity of the materials on a molecular scale and, consequently, energy saving by reducing both phase formation temperature and reaction time.

However, the sol-method entails disadvantages regarding its industrial applicability, such as the handling of large volumes of liquids, the high cost of the precursors used and the long sample preparation times needed. One of the ways of getting around these disadvantages is by preparing sol-gel solutions (xerogels), which give rise to crystals of the phases of interest, which can then be added as nucleants or seeds when they are incorporated into a glassy matrix.

The present study has been undertaken on seeding systems based on the oxides LiO_2-SiO_2-Al_2O_3, MgO-SiO_2-Al_2O_3 and CaO-MgO-SiO_2-Al_2O_3 to obtain xerogels capable of developing, after the corresponding heat treatment, the phases β-eucryptite, β-spodumene and α-cristobalite in commercial glazes for porcelain tile. After these had been obtained and characterised, glazes were seeded, and the capacity was studied of generating crystalline phases in these glazes. Finally, the degree of crystallinity generated in the resulting glass-ceramic glazes has been evaluated, characterising these glazes structurally and microstructurally, as well as determining their mechanical properties.

1. INTRODUCTION.

At present, the ceramic sector is seeking new materials with improved technological performance, which are compatible with the demanded aesthetics features. In this sense, glass-ceramic glazes are a type of material that fulfils these needs by their nature, as they combine the properties of crystals and glasses, improve mechanical properties and facilitate different aesthetic options.[1]

Glass-ceramic materials are materials capable of generating one or more crystalline phases in a controlled form in a glassy matrix. The controlled devitrification of crystalline phases is carried out in two stages: a nucleation stage, in which the crystalline seeds form, on which the crystalline phase then grows by depositing material on these seeds in the growth stage.[2]

Depending on the nature of the nuclei, homogeneous nucleation can be involved, when the nuclei originate from the melt itself, having the same chemical composition as the precipitated crystalline phase; or heterogeneous nucleation may be involved, when the crystals grow from particles or interphases foreign to the melt. In fact, every phase contains some defect so that it is very difficult for homogeneous nucleation to occur.

The size and quantity of the crystals obtained can be modulated by adjusting the nucleation and growth rates. Thus, if it is desired to obtain many small crystals, the nucleation rate needs to be encouraged, as opposed to the growth rate; in contrast, if few, larger-sized crystals are to be produced, the nucleation rate needs to be favoured.[3]

In view of the foregoing, to obtain 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 heat treatment.

Glaze devitrification can be favoured by introducing nucleants. Nucleants are substances with high solubility in the glass at high temperature, but whose solubility diminishes during cooling, facilitating segregation and forming discontinuities in the glassy network, which will give rise to crystallisation nuclei on which the major crystalline phase is deposited. In the ceramic industry titanium and zirconium oxides are among the most widely used nucleants, but these oxides usually lead to opacification and, in the case of titanium, to yellow shades in the glaze.[4]

In order to avoid these undesired aesthetic effects, an alternative to the use of nucleants is the seeding of the glass with particles that are isostructural with the crystalline phase to be developed. Thus, the activation energy of the nucleation stage is diminished, since the introduction of heterogeneities creates preferential positions for nucleation in the form of low-energy epitaxial interphases, therefore increasing the nucleation frequency.

The nucleation work in a heterogeneous nucleation process (G^*_{Het}), as is the case in seeding, can be defined as a function of the work required in a homogeneous nucleation process (G^*_{Hom}), by means of a proportionality factor f(ϕ), as in equation 1:

$$G^*_{Het} = f(\phi) \cdot G^*_{Hom}$$

Ecuation 1

The proportionality factor f(ϕ) is a function of the contact angle (ϕ) (equation 2) forming between the crystallisation embryo and the heterogeneity on which it is generated in a glassy matrix (figure 1):

$$f(\phi)=\frac{(2+\cos\phi)\cdot(1-\cos\phi)}{4}$$

Ecuation 2

This angle can be defined from the relation of surface tensions, in the case of a system formed by a spherical embryo of phase α, nucleated on substrate θ and in contact with the matrix β . (Figure 1). Where $\gamma_{\alpha\beta}$, $\gamma_{\alpha\theta}$ and $\gamma_{\beta\theta}$ are the surface tension vectors of phase α and matrix β, of phase α and substrate θ , and of substrate θ and matrix β, respectively.

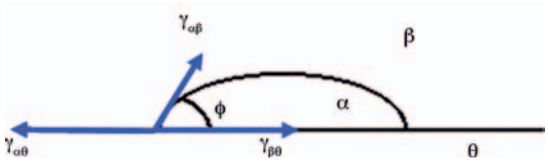


Figure 1. Scheme of the start of heterogeneous nucleation.

Defining the energy per unit area of the system (g_A) as, equation 3:

$$g_A = \gamma_{\alpha\beta} - \gamma_{\theta\beta} + \gamma_{\alpha\beta} \cdot \cos\phi$$

Ecuation 3

By imposing the equilibrium condition, i.e. setting the equation 3 equal to zero, cosϕ is defined as (equation 4):

$$\cos\phi = \frac{\gamma_{\theta\beta} - \gamma_{\alpha\theta}}{\gamma_{\alpha\beta}}$$

Ecuation 4

For the nucleation work (G^*_{Het}) to tend to zero, and the nucleation activation to decrease, the proportionality factor f(ϕ) should tend to zero (equation 1); this occurs when cosϕ tends to 1. For this to be so, the following must be obeyed: $\gamma_{\beta\theta} \cong \gamma_{\alpha\beta} >> \gamma_{\alpha\theta}$, a condition that is met when the network structure and parameters of the seed and of the nucleating phase are the same[5].

In the present work, a study has been undertaken of the oxide systems LiO_2–Al_2O_3–SiO_2 (LAS), CaO-MgO–Al_2O_3– SiO_2 (CMAS) and MgO–Al_2O_3–SiO_2 (MAS), which have drawn great interest for their capacity to develop crystalline phases such as β-spodumene ($LiAl_2Si_2O_6$), α-cordierite (2MgO-2Al_2O_3–5SiO_2), diopside (CaO-MgO–2SiO_2) and α-cristobalite (SiO_2). These phases have been widely studied by various authors because of their capacity to improve the chemical and mechanical properties of the glazes in which they develop.[6-12]

Thus, the main objective of this work has been the study and development by sol-gel processing of the seeding of β–spodumene, α–cordierite, diopside and cristobalite phases for their introduction into glazes, to enable obtaining glass-ceramic glazes with improved mechanical and chemical properties.

2. EXPERIMENTAL

2.1. XEROGEL SYNTHESIS

2.1.1. Studied compositions and raw materials used.

The phase equilibrium diagrams of each of the oxide systems[13] were used to establish the range of compositions for the study. Cerium oxide and boron oxide were selected as modifier and flux, respectively, in low percentages in the formulation, with a view to reducing the nucleation temperatures of the phases to be synthesised.

Table 1 sets out to the nominal compositions used for each oxide system, indicating the expected crystalline phase for each composition.

	LAS (wt%)	MAS (wt%)	CMAS-1 (wt%)	CMAS-2 (wt%)
SiO_2	60-65	40-50	55-65	65-75
Al_2O_3	20-25	25-35	5-10	5-10
CaO	----	----	10-15	5-10
MgO	----	5-15	5-10	1-5
Li_2O	5-10	-----	----	----
Ce_2O_3	3-6	3-6	3-6	3-6
B_2O_3	0-5	0-5	0-5	0-5
Expected crystalline phases	β–spodumene	α–cordierite	diopside	α–cristobalite

Table 1. Studied compositions.

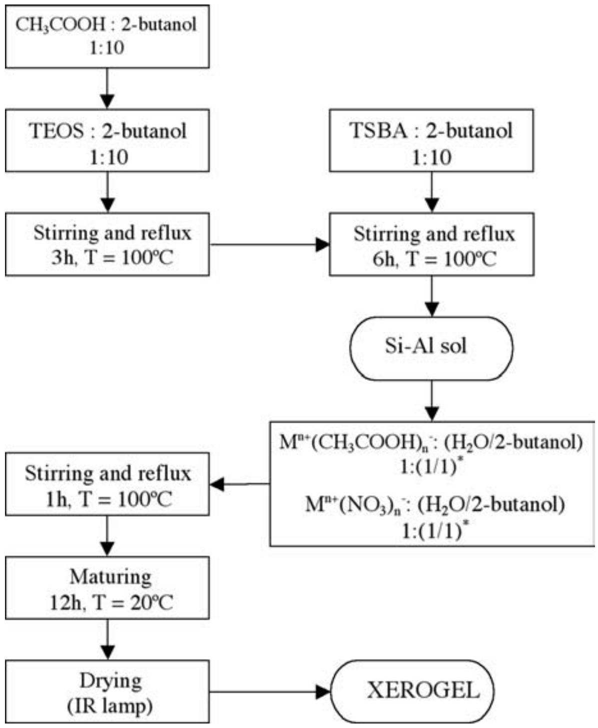
The raw materials used for each oxide are listed in table 2; each of which was analytical grade.

OXIDE	RAW MATERIAL
SiO_2	Tetraethyl orthosilicate (TEOS) $Si(C_2H_5O)_4$
Al_2O_3	Aluminium sec-butoxide (TSBA) $Al(C_2H_5CH(CH_3)O)_3$
CaO	Calcium nitrate tetrahydrate $Ca(NO_3).4H_2O$
MgO	Magnesium acetate tetrahydrate $Mg(CH_3COO)_2$ $4H_2O$
Li_2O	Lithium acetate dihydrate Li(CH3COO) . $2H_2O$
Ce_2O_3	Cerium nitrate hexahydrate $Ce(NO_3)_3.6H_2O$
B_2O_3	Boric acid H_3BO_3

Table 2. Raw materials used in gel synthesis.

2.1.2. Methodology for obtaining the xerogels.

The xerogels were obtained by means of the sol-gel method, as indicated in the flow chart of Figure 2, using 2-butanol as a solvent and acetic acid as a catalyst. The additions of each to the dissolutions were made very slowly to avoid any possible undesired precipitation and, therefore, to assure the homogeneity of the resulting gel.



* Volumetric ratios

Figure 2. Xerogel preparation process.

2.2. OBTAINMENT OF GLASS-CERAMIC GLAZES

After the xerogels had been synthesised, they were added in a percentage of 3% by weight to a commercial glossy transparent frit (crystalline frit) for porcelain tile, commercialised by QUIMICER S.A., referenced FAT60. The glass-ceramic glazes have been developed as shown in figure 3:

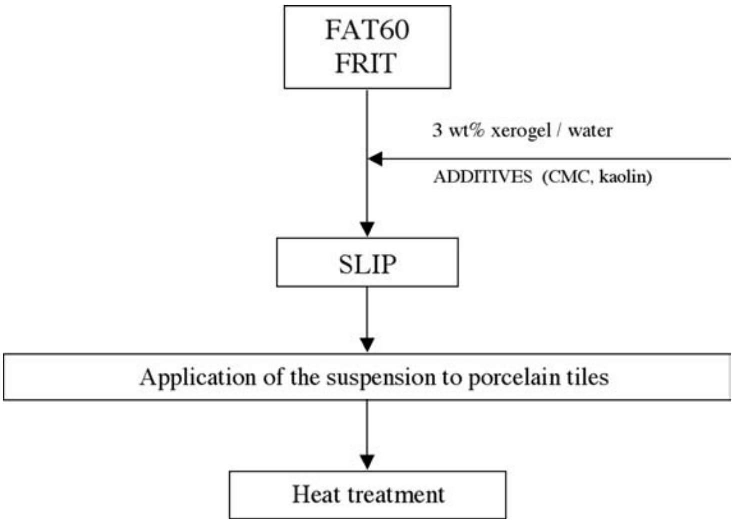


Figure 3. Methodology for obtaining glass-ceramic glazes.

2.3 HEAT TREATMENTS

2.3.1. Heat treatments conducted on the synthesised xerogels

The xerogels obtained have been subjected to a series of calcinations at different temperatures with a view to studying their capacity to generate the desired crystalline phases. For this, the following thermal cycle has been applied: heating in an electric kiln at a rate of 25º/min up to the maximum temperatures of 400º, 900º and 1200ºC, with a soak time at peak temperature of 2 hours, followed by free cooling.

2.3.2. Development of glass-ceramic glazes

The glazed ceramic pieces were subjected to industrial porcelain tile single firing cycles, i.e. with a peak temperature of 1200ºC, and duration of 60 minutes, as shown in figure 4.

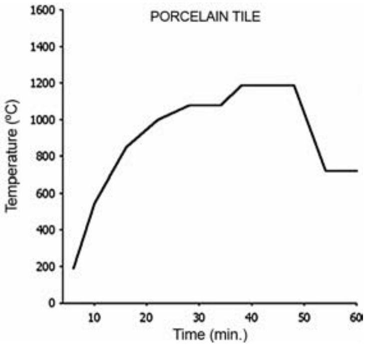


Figure 4. Heat treatment of the porcelain tile pieces.

2.4. CHARACTERISATION TECHNIQUES USED

In order to characterise fully the materials, the following instrumental techniques have been used:

- *X-ray diffraction (XRD):* a Siemens model D5000 diffractometer with copper anode was used. The measurements were performed at an intensity of 20 mA and a voltage of 40 kV, in a 2θ range from 5 to 70º. Count collection time was 3 seconds per step and goniometer speed was 0.050º 2θ /s. This technique was used to determine the crystalline phases present in the materials used.
- *Scanning electron microscopy (SEM) and energy-dispersive X-ray microanalysis (EDX).* A LEO model 440i scanning electron microscope was used, with an Oxford model Linx-ISIS energy-dispersive X-ray microanalysis instrument with backscattered and secondary electron detector. The conditions used for obtaining the different microanalyses have been an alteration voltage of 20.000 kV and a current intensity in the filament of 2000 pA.
- *Differential thermal and thermogravimetric analysis (DTA/TG).* For the study of the thermal evolution of glazes prepared with the xerogels, a Mettler-Toledo, model simultaneous TGA/STDA851e was used, connected to a Balzers ThermoStar molecular mass spectrometer, for reaction gas analysis. The working conditions used were: heating rate of 25º/min in a range of temperatures from 25º to 1500ºC.

- *Scratch hardness of surface according to the Mohs scale.* The Mohs hardness test was performed on the fired glazed pieces according to standard UNITES 67-101.
- *Vickers Microhardness.* Vickers microhardness was measured according to standard UNE-EN ISO 6507-1. A Matsuzawa model Mht-1 instrument was used, conducting the tests on the glazed pieces.

3. RESULTS AND DISCUSSION

3.1. CHARACTERISATION OF THE SYNTHESISED XEROGELS

3.1.1. Differential thermal and thermogravimetric analysis. (DTA/TG)

Differential thermal and thermogravimetric analyses allowed monitoring the endothermic and exothermic processes that the gels underwent in the thermal cycle. For this a heating rate was applied of 25ºC/min from 25 to 1500ºC, followed by free cooling.

Figure 5 shows the DTA/TG figures of the different tested systems. The black curve represents the thermogravimetric analysis, the blue curve the differential thermal analysis, and the red one the first derivative of the differential thermal analysis, in which the exothermic peaks are represented upwards and the endothermic ones downwards.

The curve corresponding to thermogravimetric analysis (TG, black line in the diagrams) shows that all the systems have around 50% mass loss; associated with the elimination of water and organic matter originating from the solvent and the precursors used.

Differential thermal analysis (DTA, red line) shows the presence in all the systems of an endothermic peak at 100ºC corresponding to water loss and an exothermic peak at 375ºC corresponding to organic matter burnout. The crystallisation temperatures for each xerogel system are detailed in table 3, indicating the exothermic DTA peaks; no variations in mass occurred in the TG analysis.

	T(ºC)	ASSOCIATED EFFECT ACCORDING TO THE LITERATURE
	850º, 1375º exothermic peaks	Peak at 850ºC corresponds to the spodumene phase.[11]
MAS	900º exothermic peak	Crystallisation of cordierite[7]
CMAS-1	1125º and 1375º exothermic peaks	Peak at 1125ºC, crystallisation of diopside[9]
CMAS-2	1125º, 1250º and 1375º exothermic peaks	Crystallisation of α-cristobalite at 1125ºC[1]

Table 3. Characteristic crystallisation temperatures of the green and dry xerogels, detected by DTA/TG analysis and assigned according to the literature.

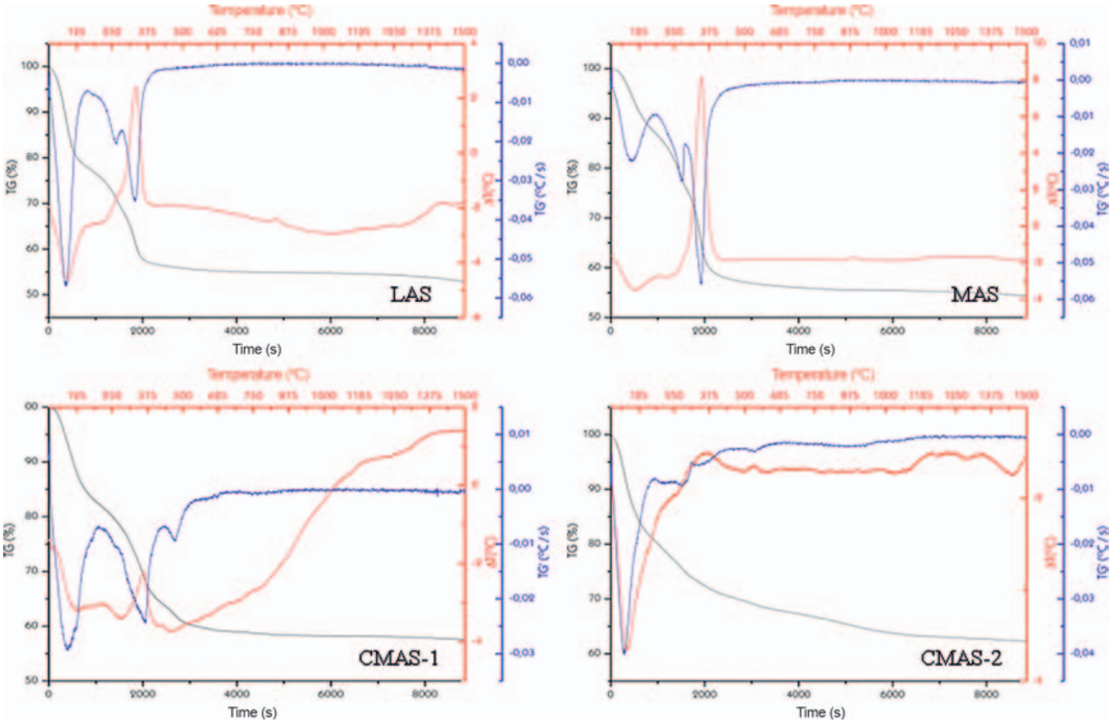


Figure 5. DTA/TG diagrams of the different synthesised xerogels.

1.2. STRUCTURAL AND MICROSTRUCTURAL STUDY OF THE PREPARED XEROGELS

In order to study the capacity of the prepared xerogels to generate the desired crystalline phases from the nominal initial composition, the xerogels have been treated at different temperatures after drying. The thermal cycle indicated previously has been used (treatments of 400°, 900° and 1200°C).

The crystalline phases generated in the calcined samples and the dry non-calcined xerogels were identified by ray-X diffraction (figure 6).

The diffractograms of the different systems show that in the case of the dry xerogels, before calcination, they are totally amorphous. This tests the homogeneity of the prepared samples on a molecular scale.

In the LAS system, amorphous diffractograms appear up to 400°C. Beyond 900°C, diffraction peaks are identified corresponding to the β-spodumene phase; these peaks become more intense at 1200°C, but they are accompanied by other, less intense peaks corresponding to collateral phases.

In the MAS system, amorphous diffractograms appear up to 400°C. At 900°C, diffraction peaks appear of sapphirine and cerianite phases. At 1200°C diffraction peaks are identified corresponding to the α-cordierite phase. However, in this case minor peaks also continue to appear of the secondary phases.

In the CMAS-1 system, small calcite crystallisations appear in the diffractograms at 400°C, as a result of the precursors used. At 900°C crystallisations appear corresponding to cerium oxide, cerianite. Small peaks corresponding to the desired diopside phase are also identified. At 1200ºC diffraction peaks are identified of the diopside phase and also peaks of α-cristobalite.

In the CMAS-2 system, the corresponding diffractograms are amorphous up to 900ºC. At 1200ºC, α-cristobalite develops as sole phase. This system, together with the LAS system, is the one that displays a greater crystallinity of the crystalline phases of interest.

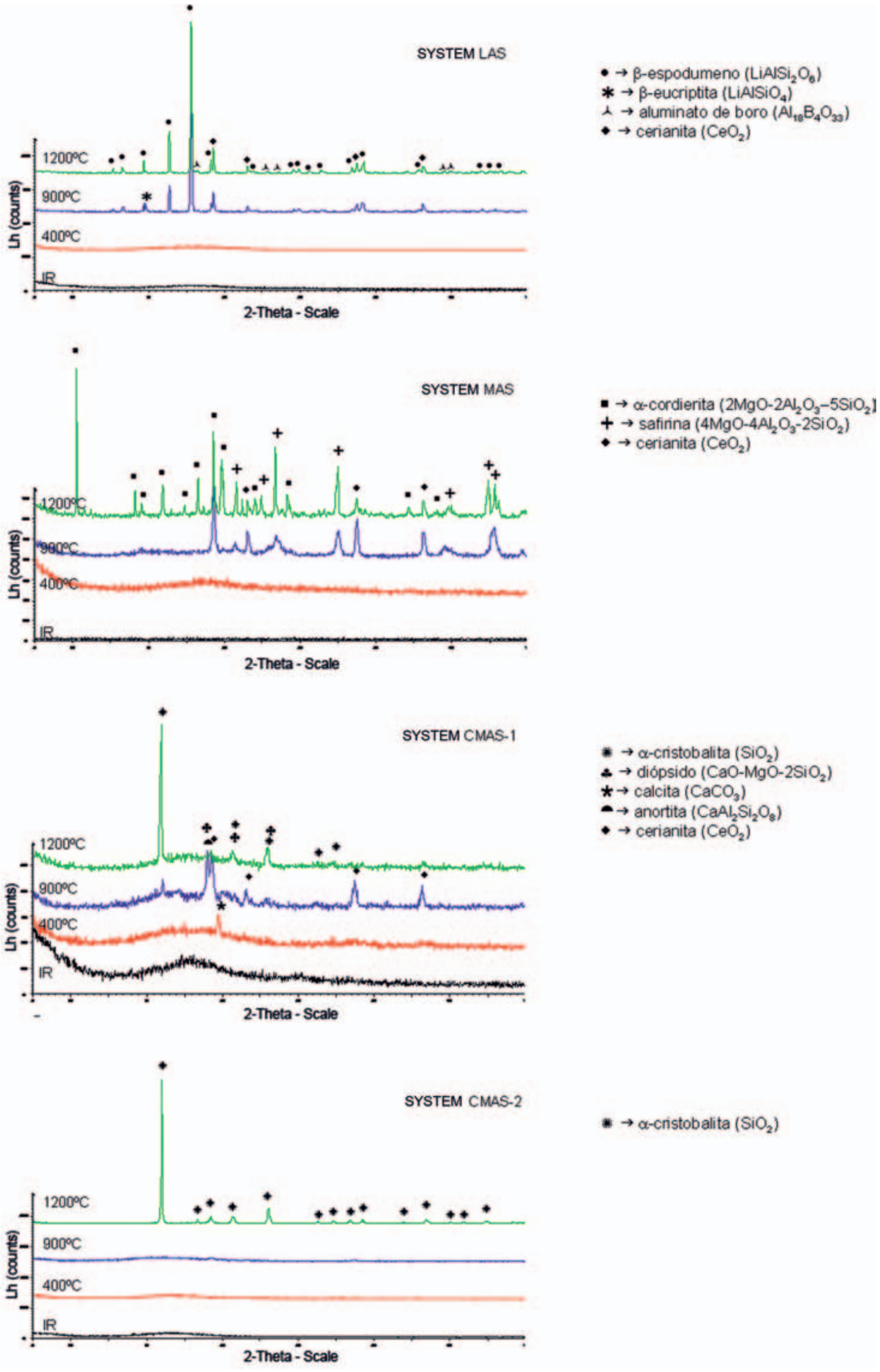


Figure 6. Diffractograms of the gels calcined at different temperatures.

3.3. STRUCTURAL AND MICROSTRUCTURAL STUDY OF THE GLASS-CERAMIC GLAZES DEVELOPED

In the first place, a morphologic characterisation has been carried out of the glazed surface of pieces of already fired porcelain tile. The SEM micrographs show crystallisations distributed regularly throughout the observed area of the glassy matrix in all the prepared compositions. By way of example, the micrograph in figure 7 shows the case of the sample in which the composition of the LAS system has been introduced as seeding.

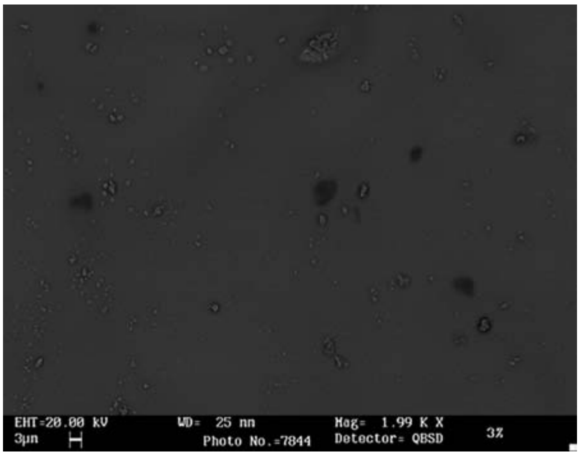


Figure 7. Micrograph of the glass-ceramic glaze in which the composition of the LAS system has been introduced as seeding, obtained at a magnification of 2000x with the backscattered electron detector.

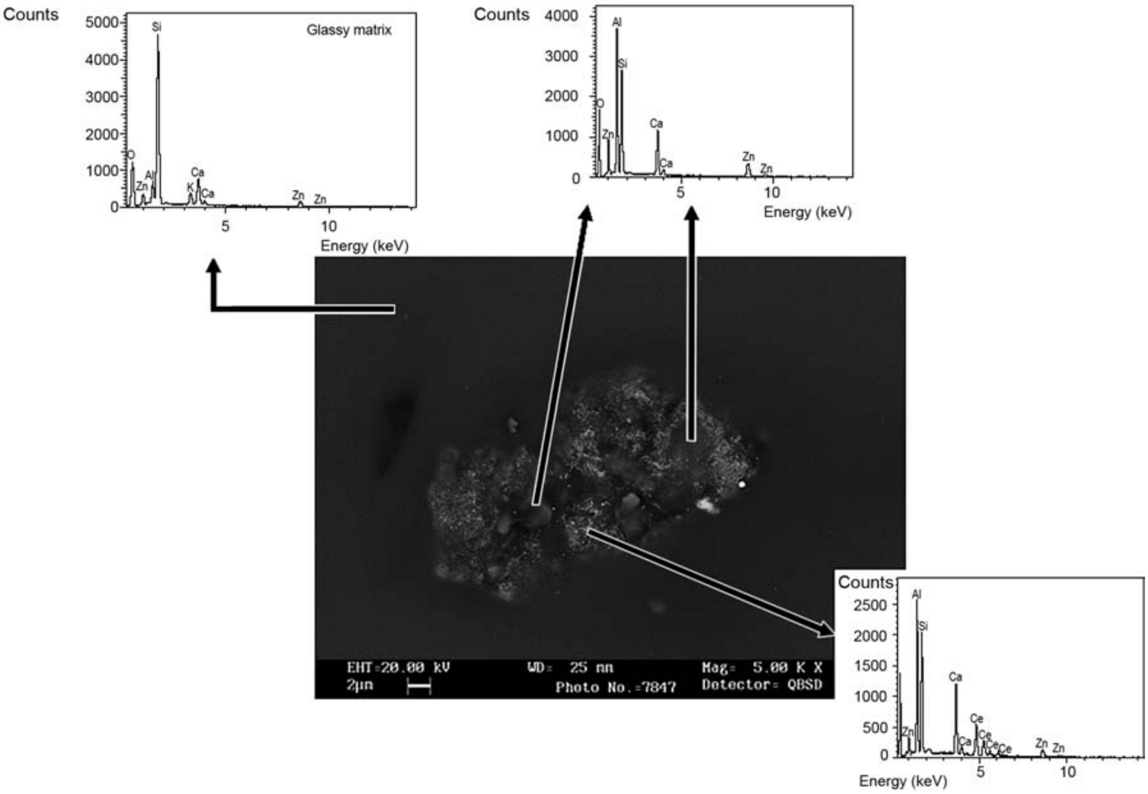


Figure 8. Micrograph obtained at a magnification of 5000x by a backscattered electron detector of a crystal agglomerate in the glaze, introduced as seeding into the LAS composition, together with the EDX microanalyses of different crystals.

The seeding crystals introduced in the glassy matrix of the glaze were identified compositionally by EDX microanalysis. As the micrograph in figure 8 shows, in which an agglomerate of seeding crystals of the same composition is identified at a greater magnification, in this image it is possible to distinguish the formation of crystals of different composition. EDX microanalysis shows there is a compositional variety, in which the glossiest crystals contain cerium, which is consistent with the presence of crystals containing cerianite detected by XRD, and which are approximately 100 nm in size; these crystals have grown on other crystals rich in silicon, aluminium and calcium, corresponding to the different aluminosilicate crystallisations, also observed by XRD.

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

The surface properties of porcelain tiles glazed with the glaze compositions developed by the seeding system have been determined. These glaze compositions display good adaptability to the industrial porcelain tile production process, with good stretching and absence of surface defects, yielding transparent and glossy glazed surfaces.

The mechanical properties and toughness in the glazed surface have also been characterised, obtaining Vickers microhardness values around 5.5 GPa and a Mohs scratch hardness of 6.

4. CONCLUSIONS

- Xerogels have been prepared from the oxide systems LiO_2–Al_2O_3–SiO_2 (LAS), nominal composition of β-spodumene, CaO-MgO–Al_2O_3– SiO_2 (CMAS), nominal composition of cristobalite and diopside, and MgO–Al_2O_3–SiO_2 (MAS), nominal composition of cordierite.
- The dry xerogels and the xerogels calcined at 1200ºC have developed seeding particles of the crystalline phases β-spodumene ($LiAl_2Si_2O_6$), in the system LAS, α-cordierita (2MgO-2Al_2O_3–5SiO_2), in the system MAS, diopside (CaO-MgO–2SiO_2), in the system CMAS-1, and α-cristobalita (SiO_2), in the system CMAS-2. A single phase only appears in this last system.
- Glass-ceramic glazes have been developed by means of seeding a transparent glossy glaze for porcelain tile, introduced as 3% by weight of the dry green xerogel in the glaze, when the glaze is applied onto the porcelain tile body.
- In these glazes, crystal agglomerates have been identified originating from the seeding, which all displayed a regular distribution throughout the glassy matrix of the glaze.
- The glass-ceramic glazes exhibit good adaptability to the industrial porcelain tile production process and, after single firing, they yield transparent glossy glazes, without any defects being detected in the surface and displaying good mechanical properties.
- This work opens up new perspective in the design and formulation of glass-ceramic glazes, in which the composition and degree of crystallinity can be modulated *a priori*, as a function of the desired final characteristics.

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