DEVELOPMENT OF HYBRID GLAZES FROM FRITS AND GELS, ADAPTED TO SINGLE-FIRE STONEWARE AND PORCELAIN TILE CYCLES

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ABSTRACT

As a result of the co-operation between Colorobbia España, S.A. and the Dept. of Inorganic and Organic Chemistry of Universitat Jaume I de Castellón, two glass-ceramic materials have been developed, one with mullite crystallisation and the other with corundum crystallisation, as major phases. The raw material is of a hybrid type, as it consists of a frit (with a great crystallisability) and a gel (as a nucleating agent, whose particles act as seeds in the crystallisation process). Gels were chosen instead of minerals, owing to the greater surface area/weight ratio of the submicron gel particles. The mullite gel crystallises instantly at 990°C and corundum starts crystallising at around 950°C, i.e., in both cases, the material contains regularly distributed crystals before the frits become a melt, capable of producing atomic diffusion phenomena. When the frit reaches sufficiently high temperatures, the microcrystals grow owing to frit cation diffusion, achieving maximum recrystallisation during the peak firing temperature stage. These materials can be applied to ceramic floor tiles in different ways, e.g., as glaze, granulars, by screen printing, etc. Owing to the presence of refractory crystals, the resulting materials provide much higher surface mechanical properties and resistance to chemical attack than conventional glazes.

I. INTRODUCTION

With a view to innovating in the field of ceramic materials, Colorobbia España, S.A. co-operated with the Dept. of Inorganic and Organic Chemistry of Universitat Jaume I de Castellón in the development of new ceramic materials with good surface strength and chemical resistance, suitable for direct introduction into the ceramic market. In this collaborative undertaking, the company developed the frits and the University Department the gel, in teamwork, the applied aspects being directed by the company and the pure science aspects being led by the University Department.

Traditional unfired glazes usually consist of a fritted part and a polymineral part, yielding a basically glassy end product after firing, which contains some residual crystalline phases and the partial crystallisation of other new phases. This type of glaze cannot be considered a glass-ceramic, as the crystallisation process is normally restricted to quite a minor crystalline-phase proportion, which is much smaller than the glassy phase (see the reviews of Shaw, 1971 [1]; Parmelle, 1973 [2]; Taylor y Bull, 1986 [3]).

Research has been undertaken in recent years on the so-called glass-ceramic glazes [4, 5, 6, 7 and 8], conceptually different in many ways from traditional glazes (see the reviews on the basic concepts of glass-ceramics in McMillan 1974, [9]; Beall, 1986 [10]; Strnad, 1986 [11]). In the first place, the unfired glaze consists of a crystal-free glassy frit produced by melting a polymineral mixture that is subsequently quenched in water. Secondly, after applying and firing the glaze, the resulting coating consists of a major crystalline phase in the glassy matrix in which crystallisation has arisen during the firing of the glazed tile. In this case, crystallisation is encouraged by nucleating agents, which are oxides (usually TiO_2, ZrO_2 and P_2O_5) designed to promote crystalline-phase formation by heterogeneous nucleation.

This study presents the micro-textural and technical characteristics of glass-ceramic materials with refractory crystalline phases (mullite and corundum), for use as floor tile coatings. It is important to note that although transparent glass-ceramics have been developed before [12], no studies have been found in the literature on their use in ceramic floor tiles. Similarly, there are references in the literature on glass-ceramics containing corundum as a secondary phase, but not as a single phase, nor of its use in traditional

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[1] SHAW, K. (1971) *Ceramic glazes. Applied Science.* Elsevier Publishing, Londres.

[2] PARMELLE, C.W. (1973) *Ceramic glazes* Cahners Publishing. Pennsylvania.

[3] TAYLOR, J.R. Y BULL, A.C. (1986) *Ceramic glaze technology. Pergamon Press,* Oxford.

[4] ESCARDINO, A. (1997) *Vidriados cerámicos de naturaleza vitrocristalina.* Cerámica Información 231, 17-35.

[5]·LEONELLI, C.; MANFREDINI, T.; PAGANELLI, M.; PELLACANI, G.C.; AMORÓS, J.L.; ENRIQUE, J.E.; ORTS, M.J.; BRUNI, S.; CARIATI, F. (1991) *Li_2O-SiO_2-Al_2O_3-MeIIO glass-ceramic systems for tile glaze applications.* J. Am. Ceram. Soc. 74, 5, 983-987.

[6] FERRARI, A.M.; BARBIERI, L.; LEONELLI, C.; MANFREDINI, T.; SILIGARDI, CORRADI, A.B. (1997) *Feasibility of using cordierite glass-ceramic as tile glazes.* J. Am. Ceram. Soc. 80, 7, 1757-1766.

[7] BARBIERI, L.; LEONELLI, C.; MANFREDINI, T. (1996) *Technological and product requirements for fast firing glass-ceramic glazes.* Ceram. Eng. Sci. Proc. 17, 1, 11-22.

[8] GENERALI, E.; BALDI, G.; FERRARI, A.M.; LEONELLI, C.; MANFREDINI, T.; SILIGARDI, C.; PELLACANI, G.C. (1996) *Studio di sistemi vitroceramici appartenenti al sistema M_2O-CaO-ZrO_2-SiO_2 come componenti di smalti per piastrelle.* Ceramica Informazione 358, 16-18.

[9] MCMILLAN, P.W. (1977) *Glass-ceramics.* New York, London, Academic Press.

[10] BEALL, G.H. (1986) *Glass ceramics.* Commercial Glasses, Boyd, D.C. y MacDowell, J.F. (eds). Adv. Ceramics 18, 157-173.

[11] STRNAD, Z. (1986) *Glass-ceramic materials,* Amsterdam, Elsevier.

[12] BEALL, G.H. Y DUKE, D.A. (1969) *Transparent glass-ceramics.* J. Mater. Sci. 4, 340-352.

ceramics. To obtain these glass-ceramic materials, frits (with a very particular composition) and gels have been developed in this study, having compatible compositions with a view to using the gels as nucleating agents, in the form of "seeds", to foster frit crystallisation. Furthermore, the effect was compared of using gels with the same addition in weight as the addition of industrial minerals, finding better results with the gel addition. However, from an industrial point of view, the use of industrial minerals can also be feasible as seeds if these have a sufficiently small grain size to provide homogenous distribution in the frit.

Having developed these hybrid materials mainly composed of frit and a minor proportion of gel, their practical use was investigated as a ceramic floor tile glaze (specifically for porcelain tile), adapting their composition and thermal evolution to obtain enhanced surface mechanical properties and chemical resistance compared to traditional glazes and polished porcelain tile.

On the other hand, it is to be highlighted that the present collaborative research does not only have a scientific justification (regarding the use of gels as seeds), but it also serves to acquaint the ceramic sector with interesting new materials for the market, owing to the beneficial properties found and therefore the possibility of industrial production.

Finally, the specific objectives of the present study were as follows:

i. Obtaining frits with a high SiO_2 and Al_2O_3 content at the usual fritting temperatures used in industry, therefore being accessible from an industrial standpoint.

ii. Developing sol-gel routes that yield crystalline phases (mullite and corundum) at the lowest possible temperatures (in any case below 1000°C) in submicron-size grains.

iii. Developing hybrid materials with good surface properties and chemical resistance, for use as glass-ceramics by adding small proportions of gels to the glassy frits and therefore providing multiple uses in the ceramic branch (glazes, granulars, screen prints, etc.).

Fig. 1 presents the logical flow chart and work method for achieving the set objectives.

II. MATERIALS AND EXPERIMENTAL METHODS

A) MATERIALS

Four types of materials were used (frits, gels, glazes and ceramic bodies), which are described below:

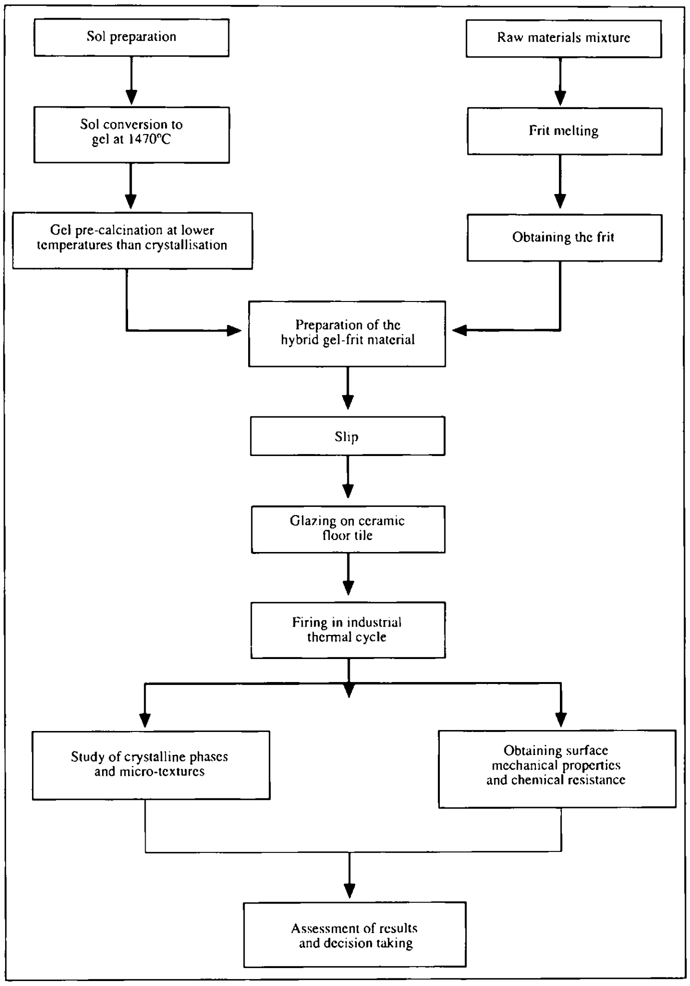

Figure 1. *Logical flow chart of the various work stages for achieving the main objectives and producing glass-ceramic glazes with advanced properties compared to conventional glazes.*

i. *Frits.* Two frits were developed in the system SiO_2-Al_2O_3-B_2O_3-P_2O_5-CaO-Na_2O-K_2O-MgO-BaO using common industrial minerals from the raw materials branch to formulate the frits. The frit yielding mullite crystallisation (frit A) had a greater silica content than the other frit. The frit with the corundum crystallisation potential (frit B) had a higher alumina content than the mullite-producing frit.

ii. *Gels.* Two sol-gel routes were developed to produce gels (silicon and aluminium oxides in submicron particles, with a local amorphous structure but with a well-developed degree of short-range order). The mullite gel was produced using the sol-gel polymer route from organic precursors (TEOS) and inorganic precursors (aluminium chloride). The Pechini route was used for the corundum gel, requiring a blend of organic compounds (ethylene glycol EG and citric acid CA in an EG/CA molar ratio of 5/1) and non-hydrated aluminium nitrate.

iii. *Glazes.* These materials were produced from a mixture of frits and gels, together with organic additives involving a binder (CMC) and deflocculant (HMF) and inorganic suspending additives (kaolin).

iv. *Ceramic bodies.* Slips were prepared with the glazes and applied to ceramic floor tile bodies, basically red stoneware and porcelain tile bodies, i.e. using peak firing temperatures in the 1140 to 1200°C range.

B) MATERIALS PREPARATION TECHNIQUES

The following briefly sets out the laboratory preparation methods of the foregoing materials, except for the ceramic bodies, which came from industrial suppliers.

i. *Frits.* The raw materials mixture was homogenised and charged in a ceramic crucible with a 3-litre volume. The crucible was then placed in a laboratory melting kiln, heating at 1450°C for two hours. The molten mass was quenched in water to produce the actual frit.

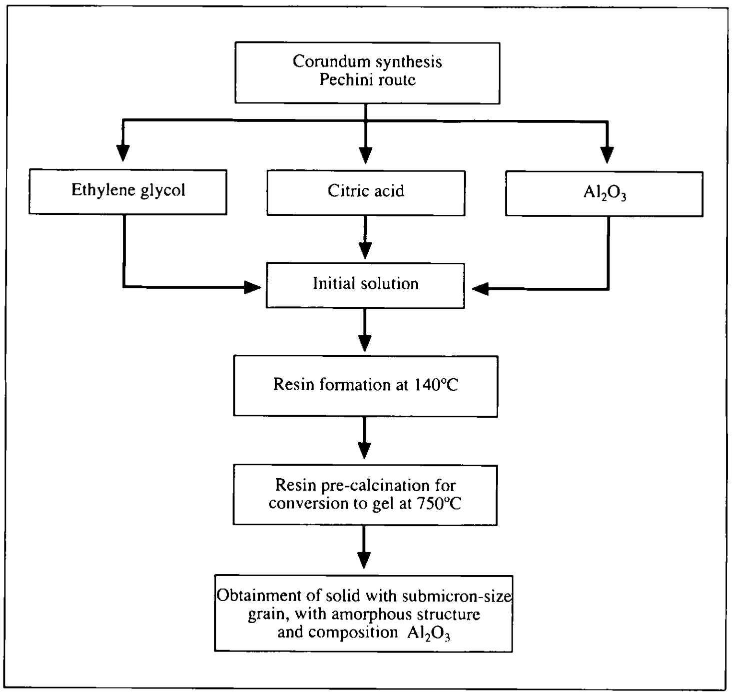

Figure 2. *Schematic illustration of corundum gel processing by the Pechini method.*

ii. *Corundum gel.* The Pechini route basically involves preparing a resin from an aqueous solution of EG and CA. The CA acts as a complexing agent of the Al^{3+} cations previously dissolved in EG. The solution needs to be heated at 140°C to prepare the resin. The resin-to-gel and the gel-to-crystal transformation temperatures depend on solution formation starting conditions and on solution transformation to resin. The basic variables of the Pechini process were therefore studied to produce corundum from the gel at the lowest possible temperatures. This led to the optimisation of the EG/CA ratio, CA/Al^{3+} ratio, quantity of water in the solution and possible aluminium cation precursors in the starting solutions. In the optimum mixture, corundum crystallisation initiated at 950°C. The gels added to the frit were therefore pre-calcined at 800°C for an hour, producing a very fine white powder with a fluffy appearance when observed by scanning electron microscopy (SEM), indicating a high surface area/volume ratio. As a summary, Fig. 2 presents the flow chart of corundum gel preparation by the Pechini route.

iii. *Mullite gel.* It is well known that the mullite structure can accommodate a very wide compositional range with values of x from 0.1 to 0.59 in the formula

$Al_2(Al_{2+2x}Si_{2-2x})O_{10-x}$. For this study, the mullite known as 3:2, i.e., having the formula $3Al_2O_3$-$2SiO_2$ or $Al_6Si_2O_{13}$, was synthesised. The chosen route was the so-called polymer sol-gel route, which starts with organic precursors of the alkoxide type (TEOS) for Si cations and inorganic precursors (aluminium chloride) for the Al cations. Mixing the precursors yields a sol that converts to a gel by heating at 650 °C. The gel is composed of an intimate mixture of both oxides on a molecular scale, but with an amorphous structure and white colour, which is used as a frit addition. Fig. 3 presents the work flow chart of mullite gel preparation.

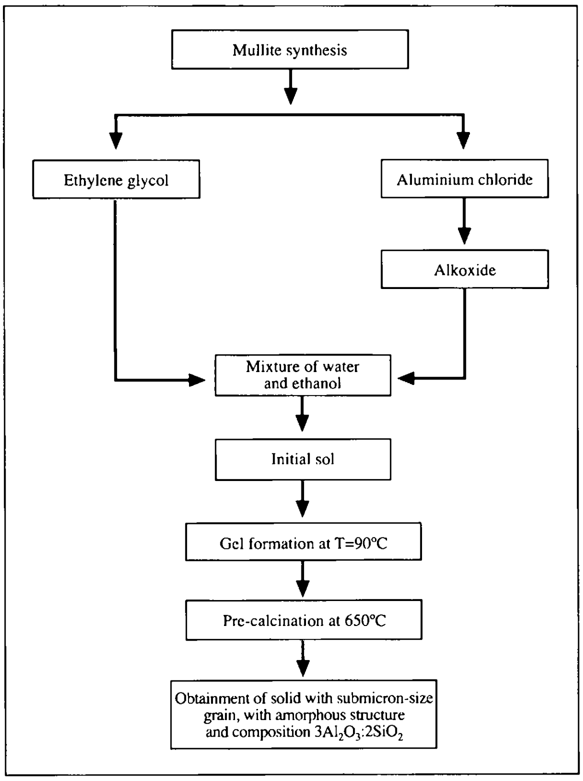

Figure 3. Schematic illustration of the mullite gel processing stages by the polymer sol-gel method.

iv. *Hybrid materials.* These were prepared from mixtures of frit and gel (mullite and corundum) in a variable weight proportions from 98:2 to 70:30 respectively. Slips were made up with these mixtures and applied to ceramic bodies with a laboratory applicator to produce 400-µm-thick layers. After drying, the coated bodies were put through different firing cycles depending on the body used.

C) MATERIALS CHARACTERISATION TECHNIQUES

i. *Characterisation of the green materials.* To study the thermal behaviour of the developed hybrid materials, and therefore of their adaptability to the bodies, a hot-stage microscope was used to study the sintering curves. Their coefficient of thermal expansion was found by the usual dilatometric techniques. On the other hand, the conversion of sol to gel and gel to crystals was studied by differential thermal and thermogravimetric analysis (DTA-TG). The frit-gel mixtures were also studied by

DTA to verify the presence of the crystallisation phenomena at the required temperatures.

ii. *Structural and micro-textural characterisation of the fired specimens.* After firing the specimens according to the industrial firing cycles in laboratory kilns, X-ray diffraction (XRD) scans were run to identify the arising crystalline phases, and chips were taken from the glaze coat to study the micro-texture by SEM.

D) METHODS USED TO STUDY THE MECHANICAL, CHEMICAL RESISTANCE AND OPTICAL PROPERTIES

i. *Microhardness.* This test was performed with a Vickers microhardness tester, comprising an optical microscope connected to a diamond-tipped indenter, measuring microhardness by the extent of the resulting mark.

ii. *Mohs hardness.* The tests were performed according to standard UNE 67 101.

iii. *Abrasion resistance.* The tests were performed according to standard UNE- EN ISO 10545-7, the results being expressed in terms of weight loss.

iv. *Chemical resistance.* The tests were performed according to standard UNE 67 122.

v. *Chromatic coordinates.* The tests were conducted by colorimetry with a Minolta CR200 instrument.

vi. *Gloss.* The gloss measurements were obtained on a Statistical Novoglass Rhopoint instrument.

III. GEL CHARACTERISATION

A) MULLITE GEL CRYSTALLISATION

Fig. 4 presents a diagram of sol evolution with temperature after conversion to gel at low temperature, showing the weight losses by the TG analysis curve. The gel stopped losing mass at around 675°C, converting to a mixture with an amorphous structure made up of SiO_2 and Al_2O_3 oxides. Similarly, in the DTA curve, a broad endothermic band is first observed, corresponding to gel decomposition and a very narrow intense exothermic peak corresponding to the temperature at which the mullite crystallisation process initiates, around 990°C. This synthesis temperature is comparable to the one found by other authors [13,14]. To prepare the hybrid materials, the gel was therefore pre-calcined at temperatures below its crystallisation temperature and above the temperature at which mass loss ended, thus producing an amorphous white powder.

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[13] SACKS, M.D.; LEE, H.; PASK, A. (1986) *A review of powder preparation methods and densification procedures for fabricating high density mullite.* J. Am. Ceram. Soc. 69, 6, 167-207.

[14] YOLDAS, B.E. (1992) *Effect of ultrastructure on crystallization of mullite.* J. Mat. Sci. 27, 6667-6672.

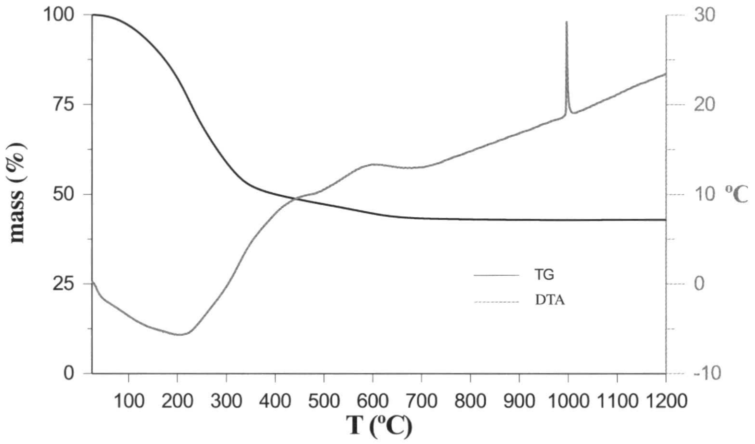

Figure 4. DTA and TG curves of the mullite gel obtained on heating at 25°C/min, showing the basic transformations with the heating process.

Fig. 5 presents the XRD diagram of the gel sample subjected to a calcining cycle similar to that of porcelain tile, i.e., heat treating at 1200ºC for 15 minutes. The figure shows that the mullite phase was the only phase that formed as a result of the heat treatment involved. The great crystallinity of the material with such a limited thermal cycle is to be noted.

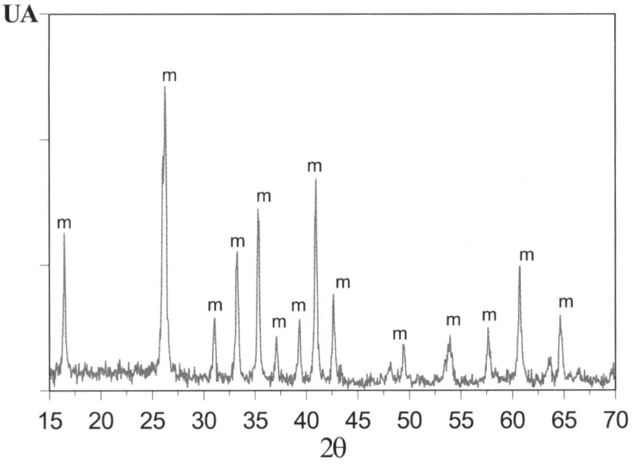

Figure 5. Difractogram of the mullite gel heated according to the porcelain tile industrial cycle (1200°C/15 min), developing the mullite of crystalline phase as sole species.

B) CORUNDUM GEL CRYSTALLISATION

Fig. 6 presents the DTA and TG diagrams of the resin made from the solution obtained by the Pechini method. The curve plotting weight loss (TG) has two slopes. The first between 250 and 375ºC corresponds to the greatest weight loss with water loss and breakdown of organic matter with CO_2 emissions. After this treatment, the material was a black colour, owing to the presence of a carbon residue in the form of graphite fibres, as found by SEM. The second mass loss was much less pronounced and corresponded to the combination of residual carbon with air atmosphere and the formation of CO_2. Mass loss ended at around 750ºC. The DTA curve exhibited two thin exothermic peaks corresponding to the first weight loss and a broad exothermic peak corresponding to the second loss. However, unlike the mullite gel, no crystallisation peak was observed. To verify gel crystallisation starting temperature, prolonged heat treatments were run at different temperatures, and crystallisation was found to start at 950 °C. The resins were therefore calcined at 750 °C to eliminate all the organic matter and carbon rests, and enable this amorphous gel to be used in the hybrid materials

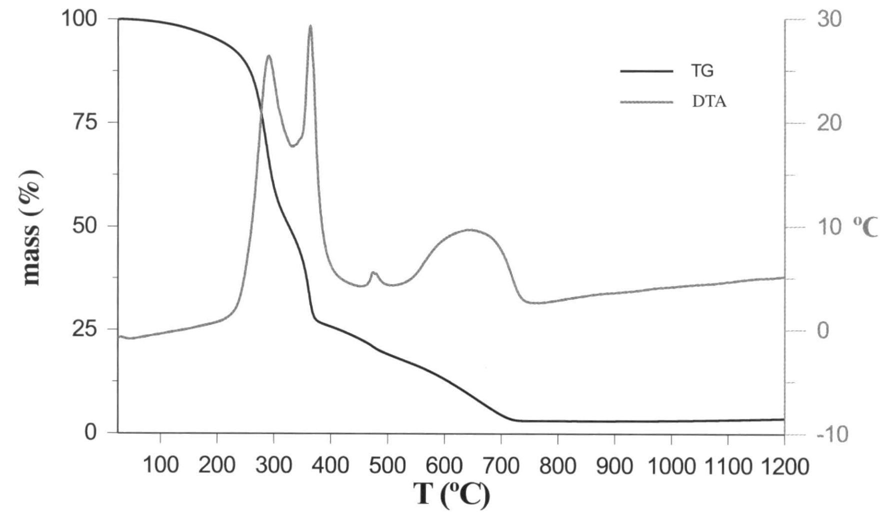

Figure 6. DTA and TG curves of the Pechini resin for corundum synthesis, presenting the most important transformations with temperature.

To confirm the crystallisability of the pre-calcined gel, it was subjected to the same heat treatment as the mullite gel, i.e., heat treatment at 1200°C for 15 minutes. Fig. 7 presents the XRD diagram of the powder sample, showing that corundum was the only phase to crystallise.

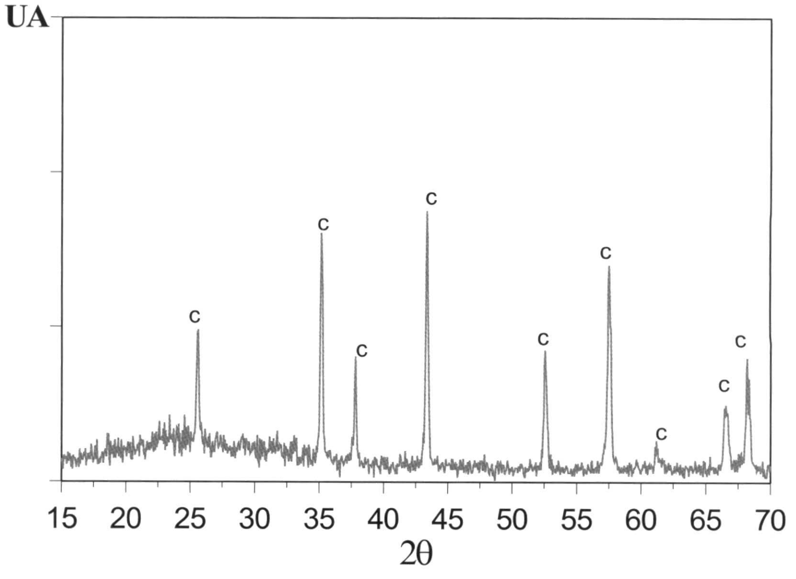

***Figure 7.** Diffractogram of the corundum gel heated according to the porcelain tile industrial cycle (1200°C/15 min) developing a corundum crystalline phase as sole species.*

IV. CHARACTERISATION OF THE HYBRID MATERIALS

A) CRYSTALLISATION OF THE FRIT A - MULLITE GEL MATERIAL

To prepare the hybrid materials, mixtures with different proportions of frit-gel were prepared. Fig. 8 presents the DTA curve of a hybrid with 5% gel, exhibiting a T_g around 700ºC and an exothermic crystallisation peak at around 1000ºC. As an example, Fig. 9 shows the XRD diagram of a porcelain tile glazed with the hybrid material containing 5 wt% gel, revealing the presence of mullite (m), as well as the appearance of two other phases, corundum (c) and a very minor form of anorthite (a). The figure also exhibits a broad band corresponding to the glassy matrix that contained the crystals.

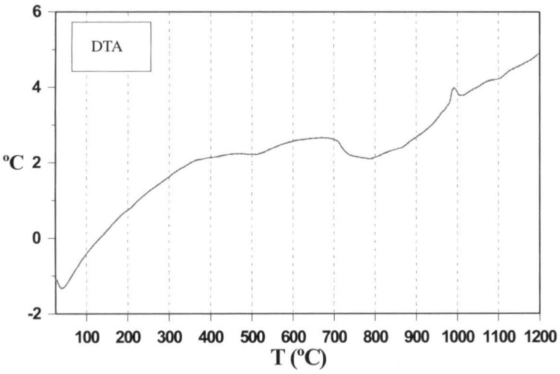

Figure 8 DTA curve of the frit A-mullite gel hybrid material, showing the T_g region and crystallisation exothermic peak.

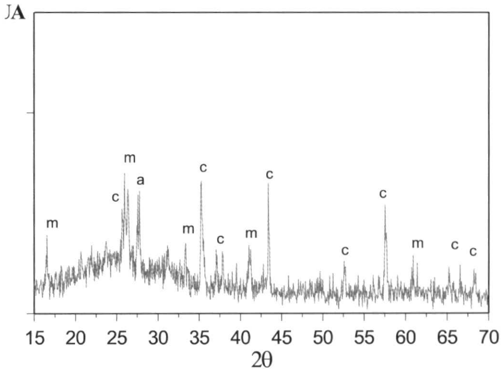

***Figure 9.** Diffractogram of the specimen glazed and fired with the hybrid material, showing the mullite phase (m), together with corundum (c) and a very minor anorthite (a) phase.*

Fig. 10 shows an example of the attainable type of micro-texture in the glass-ceramic glazes developed. The example corresponds to a porcelain tile glaze with 5% gel in the starting mixture. Clusters of crystals can be observed in the figure, whose rounded morphologies correspond to liquid-phase immiscibility phenomena, in which mullite and corundum crystallisations occur. The anorthite crystals are dispersed throughout the glaze.

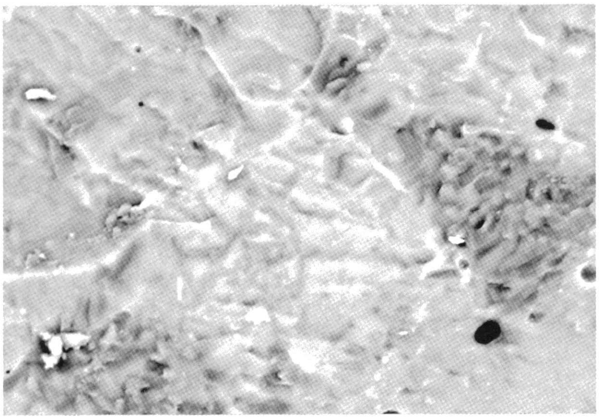

***Figure 10.** SEM image obtained using a back-scattered electron detector, showing oval regions with a darker colour, which correspond to mullite and corundum crystallisation, and a centre region exhibiting tabular anorthite crystals.*

B) CRYSTALLISATION OF THE FRIT B - CORUNDUM GEL MATERIAL

Fig. 11 presents the DTA diagram of a material consisting of 5% gel, exhibiting a T_g at around 675 °C and an exothermic crystallisation peak at about 975°C. Fig. 12 depicts the diffractogram of a red stoneware body glazed with the hybrid material mentioned, exhibiting the sole presence of corundum, without any other crystalline phases appearing. A broad band can also be observed corresponding to the glass of the glass-ceramic glaze.

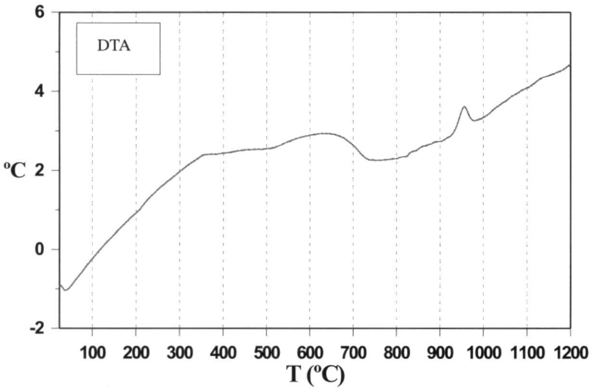

Figure 11. DTA curve of the frit B-corundum gel hybrid material, showing the T_g region and crystallisation exothermic peak.

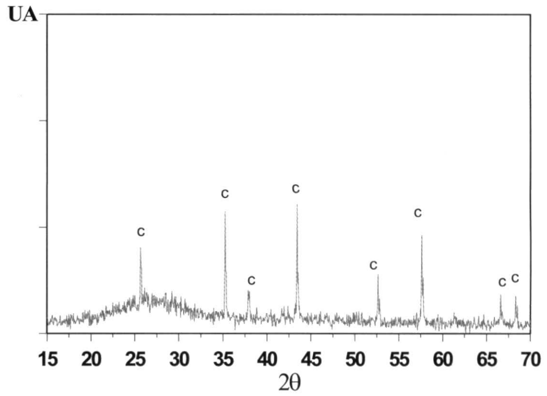

Figure 12. Diffractogram of the specimen glazed and fired with the hybrid material, showing the corundum phase to be the sole crystallising species.

Fig. 13 presents an example of the attainable type of micro-texture in corundum glass-ceramic glazes. The example corresponds to a red stoneware body coated with a glaze containing a 5% gel in the starting mixture. Dispersed corundum crystals can be observed with fibrous and tabular morphologies without a direct relationship with liquid-phase immiscibility phenomena.

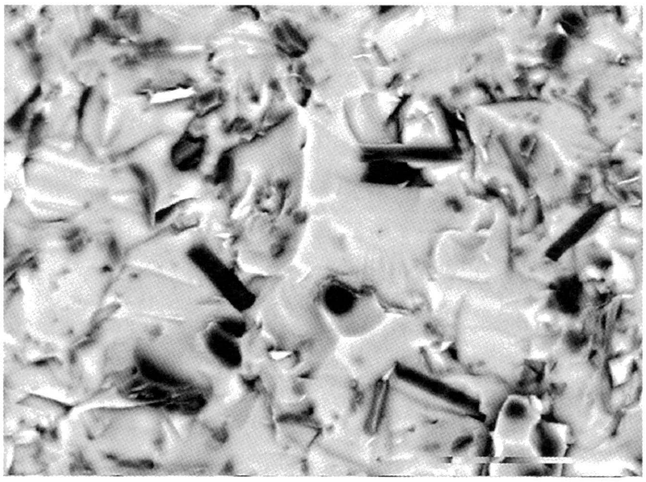

Figure 13. SEM image obtained using a back-scattered electron detector showing dark-coloured corundum crystals with tabular and fibrous shapes and a crystal-size distribution ranging from 1 to 3 µm.

C) THERMAL AND DILATOMETRIC PROPERTIES OF THE HYBRID MATERIALS

Figures 14 and 15 plot the sintering curves obtained on the hot-stage microscope of the two examples of hybrid materials developed, corresponding respectively to the corundum and mullite glass-ceramic glaze. Sintering can be observed to cease once the crystallisation process has initiated at around 1000°C.

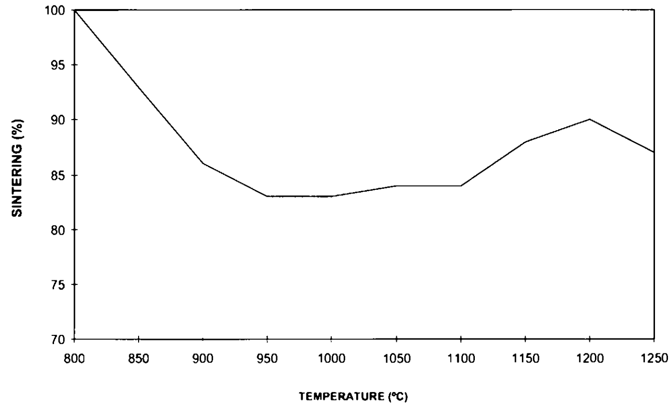

Figure 14. *Sintering curve of the corundum glass-ceramic material, plotting sintering percentage versus temperature.*

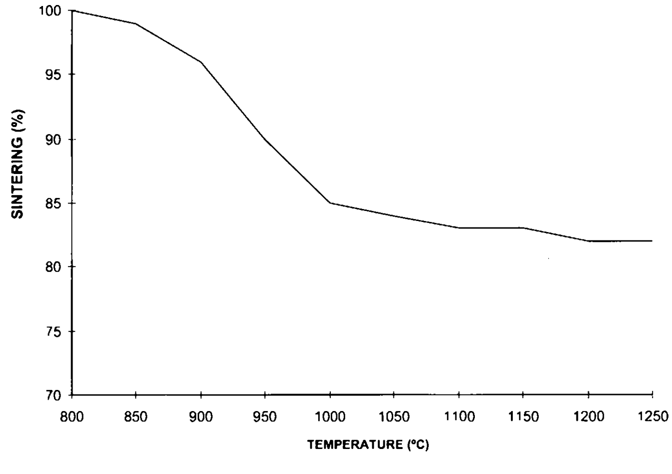

Figure 15. *Sintering curve of the mullite glass-ceramic material, plotting sintering percentage versus temperature.*

A dilatometric study was also performed of the glass-ceramic glazes, which yielded coefficient of linear expansion values in the range $55\text{-}70 \cdot 10^{-7}$ K^{-1}.

VI. MECHANICAL STRENGTH AND CHEMICAL RESISTANCE

The following table sets out the data obtained on surface mechanical strength and resistance to chemical attack of the glass-ceramic glazes developed:

For comparative purposes, weight loss on abrading was measured on polished porcelain tile bodies, yielding values of 200 mg, which highlights the good results found with the hybrid glazes developed.

	SURFACE PROPERTIES			CHEMICAL ATTACK		OPTICAL PROPERTIES			
	Vickers	Mohs	Weight loss Abrasion (mg)	Acid	Base	Gloss (60º)	L*	a*	b*
MULLITE GLAZE	1050	7-8	60	NO	NO	10	86,5	0,4	2,4
CORUNDUM GLAZE	950	6-7	65	NO	NO	7	90,8	-0,2	0,3

Tabla 1

VII. CONCLUSIONS

The main conclusions drawn from the present study were as follows:

1. Frits were developed with high SiO_2 and Al_2O_3 contents from industrial raw materials, which yielded a melt at temperatures around 1450ºC, with a potential crystallisability if they are subsequently treated in an industrial thermal cycle of the type used for ceramic floor tile.

2. Gels were developed by the sol-gel process capable of respectively crystallising mullite and corundum at temperatures below 1000ºC from the polymer sol-gel route and the Pechini route.

3. Hybrid materials were prepared, which consisted of two components: frit and pre-calcined gel, which can be used as glass-ceramic glazes for coating ceramic floor tile bodies. These glazes have much higher mechanical properties and chemical resistance than traditional glazes.