GLASS-CERAMIC GLAZES WITH ALUMINATE AND ALUMINO-SILICATE CRYSTALLISATIONS, ADAPTED TO PORCELAIN TILE BODIES

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ABSTRACT

In the present study, ceramic glazes were developed from frits for porcelain tile bodies, compatible with the industrial production cycles used for this type of ceramic tile.

Frit compositions were modulated for this purpose in the quaternary system MgO-CaO-Al_2O_3-SiO_2, so that after being applied as glazes and undergoing porcelain tile firing cycles, they would devitrify, producing crystallisations of an anorthite and spinel nature in the glassy matrix from which they were generated.

Glazes of a glass-ceramic nature were thus produced which, after being applied to porcelain tile bodies and fired according to the corresponding firing schedule, exhibited good glaze-body fit, as well as good mechanical properties with regard to resistance to abrasive wear and scratch hardness, as well as good chemical resistance (resistance to chemical attack and stain resistance), making them suitable products for uses in internal and external environments. Finally, these materials satisfied modern aesthetic requirements in the field of ceramic design.

1. INTRODUCTION

Ceramic tile production has undergone spectacular growth in recent years, with product characteristics in Europe (mainly Italy and Spain) focusing particularly on the manufacture of new, more technological products with greater added value, as is the case of porcelain tile [1]. Porcelain tile characteristics involve practically zero porosity (<0.5%) and good mechanical properties, providing a broader range of uses, which include external areas.

A further requisite when it comes to developing new materials is that they need to allow decoration without impairing the attained product properties. It should be noted in this sense that a large percentage of porcelain tile production is currently subjected to polishing. This treatment yields products with excellent aesthetic characteristics, though it entails a series of drawbacks such as: reduction of mechanical strength and chemical resistance, which favour material wear with the impossibility of repolishing, thus also making the product more readily stainable, as a result of closed porosity becoming visible at the surface with lapping. A further disadvantage is a more expensive end product.

In view of the foregoing, a research line was started to develop ceramic glazes that would get around the disadvantages mentioned and hold or enhance ceramic tile surface properties [2-4].

In this sense, studies can be found in the literature which provide enough information on the processes that arise for designing glass-ceramics, yielding the keys to the development of glass-ceramic materials, namely nucleation control and crystal growth, as well as the nature of the starting glassy matrix [5,6].

The general objectives of the present study were thus to develop glazes of a glass-ceramic nature adapted to porcelain tiles, which held or enhanced the good surface properties of this type of ceramic body, eliminating the phenomenon of retained dirt, while also being slip resistant.

The concrete objectives materialised in the following workprogramme:

* Study of the crystalline phases that enable developing glass-ceramic glazes through glaze devitrification processes.

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[1] Biffi, G. *Il Gres Porcellanato,* Ed. Gruppo Editoriale Faenza Editrice s.p.a., Faenza (Italia), 1997..

[2] Leonelli, C.; Manfredini, T.; Paganelli M.; Pellacani G.C.; Amorós J.L.; Navarro J.E.E.; Orts M.J. Li_2O-SiO_2-Al_2O_2-Me_2O *glass-ceramic systems for tile glaze applications,* J.Am.Ceram.Soc 74,5,983-987 (1991)

[3] Ferrari, A.M.; Barbieri L.; Leonelli C.; Manfredini T.; Siligardi C.; Corradi A.B. *Feasibility of using cordierite glass-ceramics as tile glazes,* J.Am.Ceram.Soc. 80, 7, 1757-1766 (1997)

[4] Escardino, A. *Vidriados cerámicos de naturaleza vitrocristalina* , Ceram. Información 213, 17-35 (1997)

[5] Tichell, M. *Estudio y desarrollo de materiales vitrocerámicos con propiedades de interés,* Tesis doctoral. Dpto. Química Inorgánica y Orgánica, Univeristat Jaume I, Castellón (España) 1999

[6] Vogel, W; Höland, W. *Nucleation and Crystallization Kinetics of an* MgO-Al_2O_3-SiO_2 *base glass with various dopants,* Adv. Ceram. Vol.4 Nucleation and Crystallization in Glasses. Am. Ceram. Soc. (1982)

* Study and selection of frits rich in aluminium or their modulation for the targeted objectives.

* Development of glazes in which crystallisations of an alumino-silicate (anorthitic) and spinel nature originate, adapted for application onto porcelain tile bodies, and fired according to industrial production cycles.

* Study and control of finished product quality parameters.

2. EXPERIMENTAL DEVELOPMENT

2. 1.- CHARACTERISATION TECHNIQUES USED

The following instrumental and analytical techniques were used to characterise the materials developed in this study and measure their properties:

- Dilatometry, using a BÄHR, Model DIL801L, apparatus with a heating rate of 10°C/min.
- Mechanical measurements by Vickers measurements with a MATSUZAWA MHT-1, microhardness tester, up to 1 kg force.
- Microcharacterisation with an LEO, series 6300 scanning electron microscopy instrument and Oxford, ISIS, spectrometer, characterising the materials by images formed by back-scattered and secondary electrons.
- DTA curves obtained on a METTLER-TOLEDO 851^e instrument with a heating rate of 25°C/min.
- SIEMENS, Model D5000, X-ray diffractometer, running at 20 mA and 40 kV,b with a Cu k_α cathode and Ni filter, fitted with a graphite secondary monochromator. Determinations were performed at low angles to determine the glassy halo that the samples exhibited as well as scanning between 20 and 70° (2θ) to analyse the presence of crystalline phases.
- The bodies glazed with this frit were subjected to the industrial firing cycle used for porcelain tile. Finally, the mechanical properties were measured (Vickers microhardness, Mohs hardness (UNE 67-101) and abrasion resistance (UNE 67-154)), as were the chemical properties (stain and acid resistance (UNE 67-122/85)).

2. 2.- MATERIALS AND METHODS

The compositions studied are immersed in the anorthite and spinel primary crystallisation field, according to the following phase diagrams [7]:

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[7] Levin E.M.; Robbins, C.R.; McMurdie, H.F. *Phase Diagrams for Ceramists (Vol 1).* American Ceramic Society (1964)

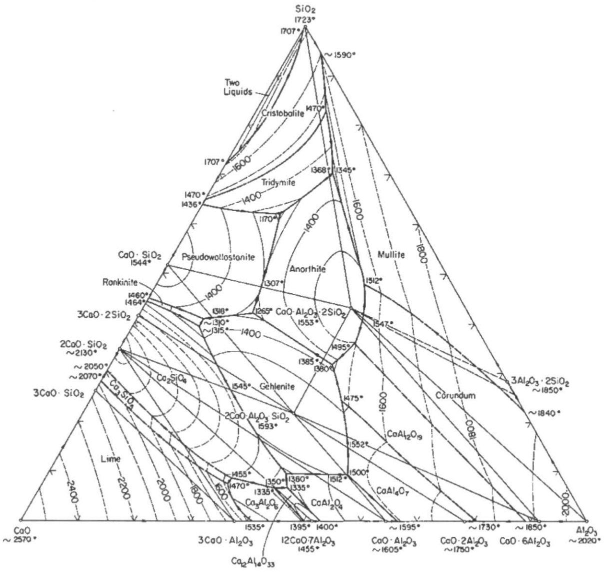

Figure 1. *Phase diagram of the system* $CaO\text{-}Al_2O_3\text{-}SiO_2$.

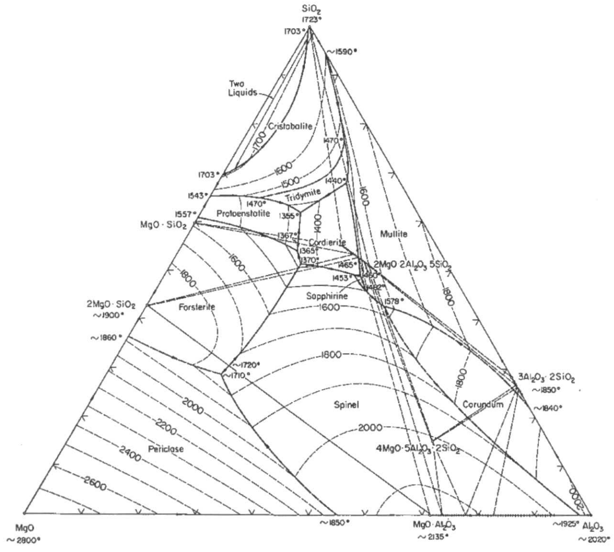

Figure 2. *Phase diagram of the system* $MgO\text{-}Al_2O_3\text{-}SiO_2$

The following qualitative glaze compositions were developed:

SiO_2	Al_2O_3	CaO	MgO	Others
40-60	10-20	15-25	0-10	5-15

Table 1. *Composition (wt%) of the anorthite glass-ceramic glaze (Glaze A)*

Al_2O_3	MgO	SiO_2	B_2O_3	BaO	CaO	Others*
30-40	12-18	15-28	2-4	3-8	4-10	5-15

(*) Fluxes of the Me_2O type.

Table 2. *Composition (wt%) of the spinel glass-ceramic glaze (Glaze B).*

The following diagram sets out the methodology used in developing the different glazes:

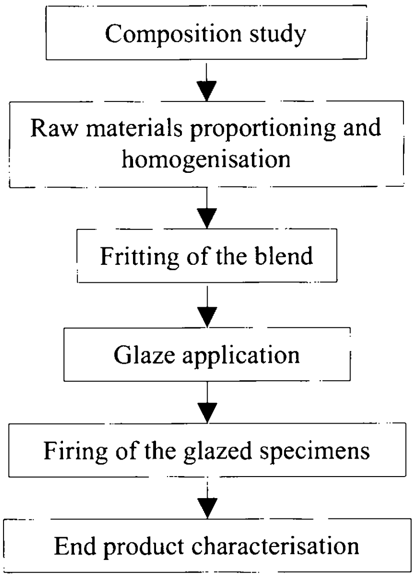

Figure 3. Flow chart of glass-ceramic glaze development.

2. 3.- RESULTS AND DISCUSSION

2.3.1.- Development of an anorthite glass-ceramic glaze

The development of the anorthite phase as major phase and the quartz crystallisations were examined in the glaze A-coated body by X-ray diffraction (XRD).

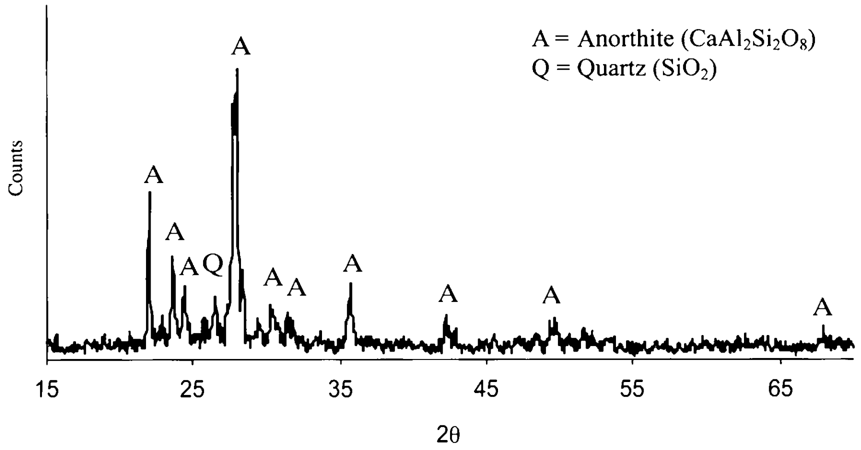

Figure 4. XRD diagram of the finished piece.

Differential thermal analysis (DTA) (Figure 5) shows that anorthite crystallisation occurred (925°C) after reaching the glass-transition temperature (750°C). The melting process of the material started at temperatures above 1150°C.

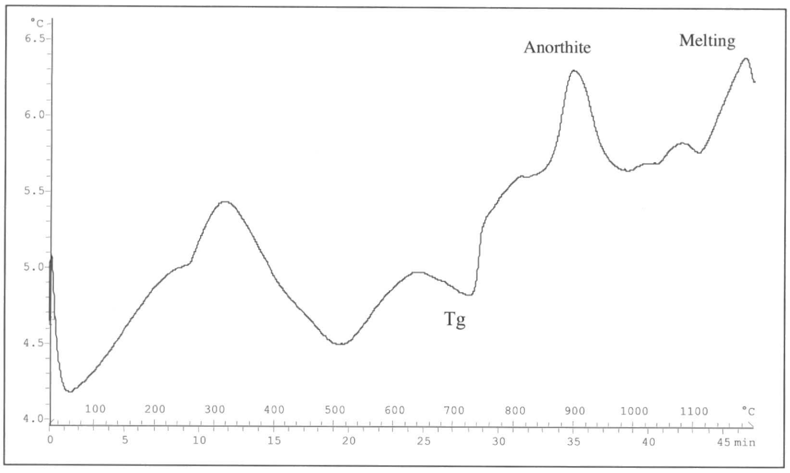

Figure 5. *Glaze A DTA diagram.*

The micrographs obtained by scanning electron microscopy (SEM) using a back-scattered electron detector and energy-dispersive X-ray analysis (EDXA) exhibit homogeneous anorthite crystal distribution at the glaze surface (Figures 6 and 7).

A glass-ceramic material is involved with a high volume percentage of crystals. As the figures show, the generation of molten phases with a similar composition to that of the arising crystals yielded a glassy matrix in which these crystals of an anorthitic nature were immersed.

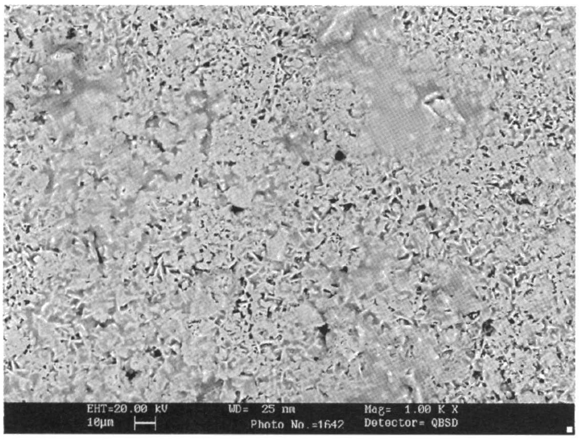

Figure 6. *Micrograph (1000x) of the glaze A surface, showing homogeneous anorthite crystal distribution.*

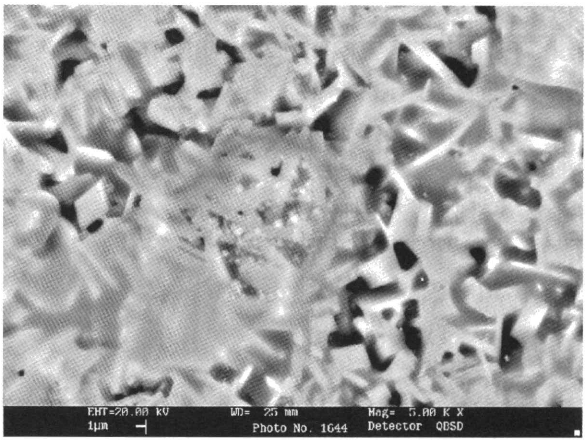

Figure 7. *Micrograph (5000x) of a detail of anorthite crystals and of the melting area.*

The mechanical properties of the body coated with glaze A are set out in the following table.

Vickers microhardness (Kg/mm^2)	854 ± 28
Mohs hardness (UNE 67-101)	6
Abrasion resistance (ISO 10.545-7)	PEI Class IV
Stain resistance (UNE 67-122/85)	Class 2
Acid resistance (ISO 1.0545-13)	Class AA

Table 3. *Glaze A mechanical properties.*

2. 3. 2.- *Development of a spinel glass-ceramic glaze*

The frit contains four types of components: i) Al_2O_3 and MgO to produce spinel crystals, ii) SiO_2 and Na_2O to generate the glassy matrix, iii) CaO and BaO as high-temperature fluxes, and iv) B_2O_3 and P_2O_5 as mineralisers. The studied frit therefore belongs to the system SiO_2-Al_2O_3-MgO-CaO-BaO-Na_2O-B_2O_3-P_2O_5.

Figure 8 presents the DTA curve up to 1200ºC of the frit made. Three features can be observed: i) Tg occurs at around 750ºC, ii) a small exothermic peak at 900ºC, attributed to spinel crystallisation, and iii) a large exothermic peak at 1050ºC corresponding to anorthite and celsian crystallisation.

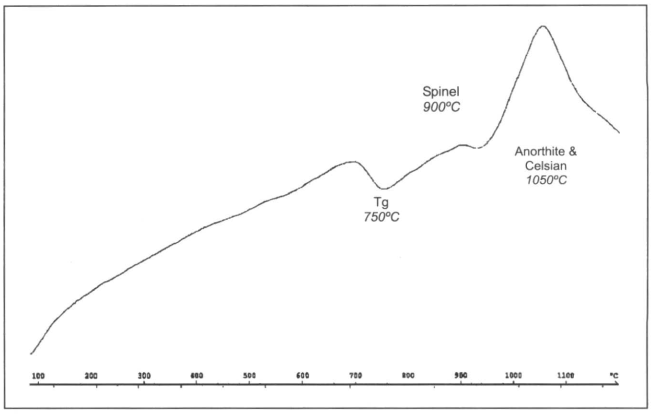

Figure 8. *Glaze B DTA curve with crystallisation temperatures.*

A liquid-phase separation process was observed after the glass transition temperature, which gave rise to the formation of a minor phase rich in Al_2O_3 and MgO in the form of spheres (circles in flat cross sections) in an SiO_2 rich matrix. This process had already been observed elsewhere in melts with a similar composition, Vögel et al. 1982 [6]. Spinel crystallised in both phases but with different characteristics (Figure 9), being much more abundant in the alumino-magnesian phase.

Isolated crystals appeared in the matrix with a cubic symmetry (euhedral habit), Figure 10, exhibiting characteristic spinel cubic morphology. These crystals were generated from a homogeneous nucleation process.

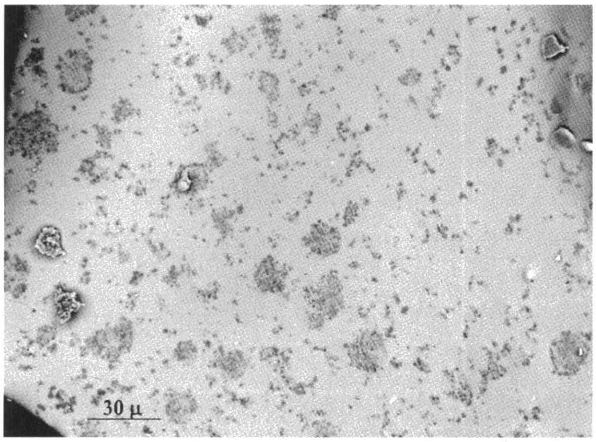

Figure 9. *Micrograph (500x) of frit B showing general spinel crystallisation.*

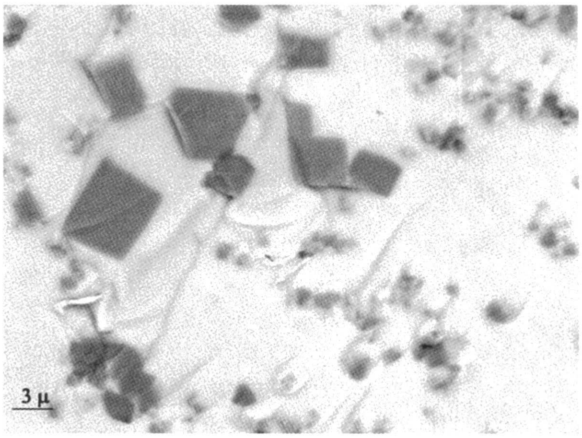

Figure 10. *Micrograph (5000x) showing spinel crystallisation in the glassy matrix.*

However, the crystallisation process in the minor phase (alumino-magnesian) was more complex. When the frit was heated at 900°C for short residence times, crystallisation was found to initiate at the interface with the matrix, initially bounding the shape of the spheres (Figure 11). At longer residence times, crystallisation was practically complete in the phase rich in Al_2O_3-MgO (Figure 12). Therefore, crystallisation starts with a heterogeneous nucleation process and sets forth with homogeneous nucleation in this phase.

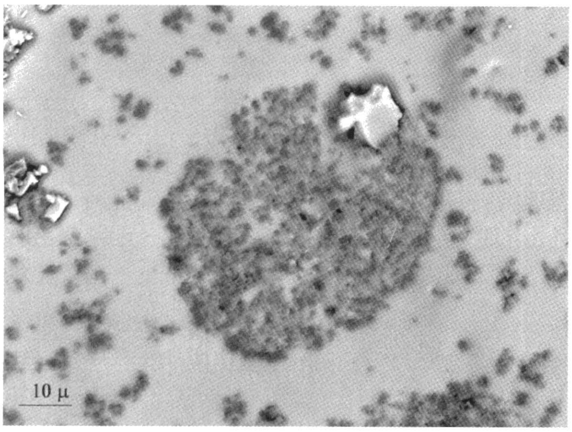

Figure 11. *Micrograph (2000x) of frit B showing spinel crystallisation in the minor phase at low residence times.*

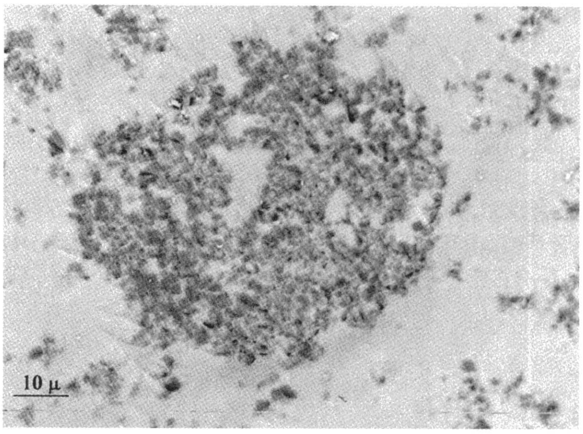

Figure 12. *Micrograph (2000x) of frit B showing spinel crystallisation in the minor phase at high residence times.*

On reaching 1050°C, the anorthite-celsian solid solution forms through a heterogeneous crystallisation mechanism from spinel nuclei (Figure 13), or from small surface cracks or imperfections (Figure 14).

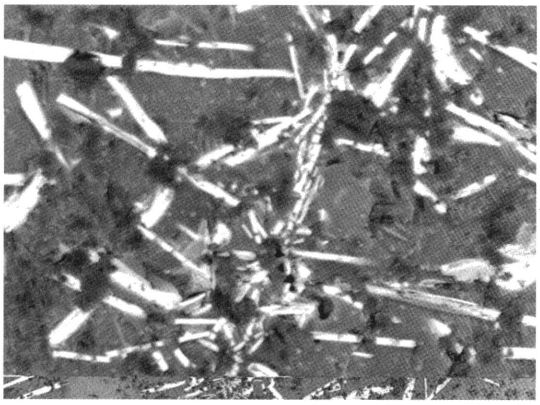

Figure 13. *Micrograph (5000x) of glaze B showing anorthite and celsian crystallisation from spinel nuclei.*

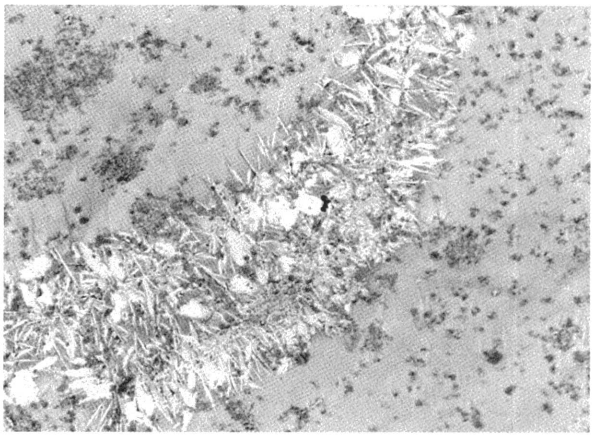

Figure 14. *Micrograph of frit B showing anorthite and celsian crystallisation from a crack in the frit surface.*

Finally, Figure 15 presents the XRD diffractogram of the glazed porcelain tile body, showing spinel to be the major phase appearing together with minor crystallisations of celsian and anorthite.

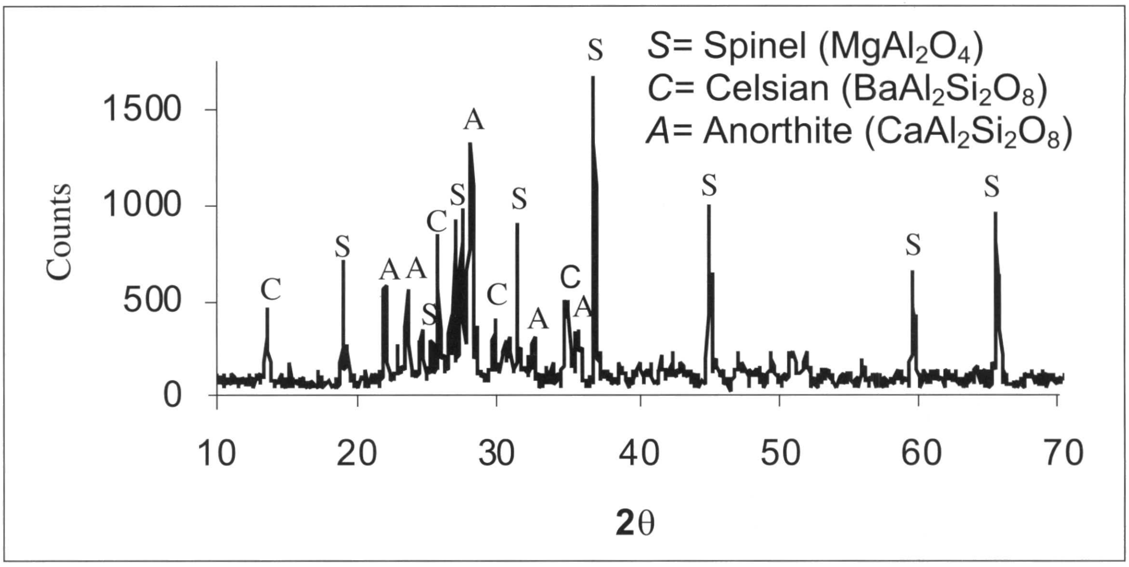

Figure 15. XRD diffractogram of the glazed porcelain tile body.

The mechanical properties of the glazed porcelain tile body are set out in the following table.

Vickers microhardness (Kg/mm^2)	1325 ± 42
Mohs hardness (UNE 67-101)	8
Abrasion resistance (ISO 10.545-7)	PEI Class V
Stain resistance (UNE 67-122/85)	Class 1
Acid resistance (ISO 1.0545-13)	Class AA

Table 4. *Measurement of the properties of the tile coated with glaze B.*

CONCLUSIONS

1. Glass-ceramic glazes were developed, adapted to the porcelain tile firing cycle: glaze A, of an anorthitic nature and glaze B of a spinel-anorthite-celsian nature.

2. These glazes noticeably improved the surface mechanical and chemical properties of the end product.

3. Products were obtained with which porcelain tile can be decorated without having to use polishing or body stains.