DEVELOPMENT OF NEW GLASS-CERAMIC GLAZES THAT IMPROVE ANTI-SLIP PROPERTIES

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ABSTRACT

In view of the implementation of new regulations in regard to slipping for ceramic tiles used in areas with heavy pedestrian traffic, the ceramic market is faced with the need for products that improve the anti-slip properties of ceramic tiles.

As a continuation of the work that ESMALTES, S.A., has been conducting on glass-ceramic glazes adapted to porcelain tile bodies, materials have been developed that improve the tile coefficient of friction, without impairing the aesthetic qualities of the products, while concurrently improving product technical properties.

The materials developed generate crystallisations in the glassy phase and, with the addition of crystalline phases of high hardness to the composition of the material, they give rise to glass-ceramic materials in a single firing process.

For this, in the SiO_2-Al_2O_3-CaO phase stability diagrams we selected compatibility regions of the mullite and anorthite systems. In turn, frits were designed with a composition rich in SiO_2, Al_2O_3 and CaO.

Finally, we evaluated the quality parameters of all the developed glazes, adapted to the porcelain tile bodies.

1. INTRODUCTION

There is nowadays increasing interest in the ceramic tile production sector in obtaining new materials that display better technical performance features, thus enabling products to be fabricated of greater quality and, consequently, with higher added value.

One such technical feature demanded of late is the anti-slip effect of the materials, since new regulations[1,2] have just appeared on uses in heavily trafficked public floorings.

The so-called glass-ceramic glazes[3] address that need, since these represent a new generation of glaze compositions in which crystals form in the glassy phase, after the relevant composition has been subjected to the corresponding heat treatments.

In this sense, it is also possible to design and improve the technological performance of these materials by controlling the nucleation and crystallisation processes of the glassy compositions, as the desired technical performance is related to the nature, number and size of the crystals that form[4].

The firm Esmaltes, S.A., in collaboration with the research group of the Department of Inorganic and Organic Chemistry of Universitat Jaume I, has a long history of research into glass-ceramic systems, yielding ceramic glazes with new and improved properties[5,6,7]. And part of this research has focused on the SiO_2-Al_2O_3-CaO phase stability diagram (Figure 1).

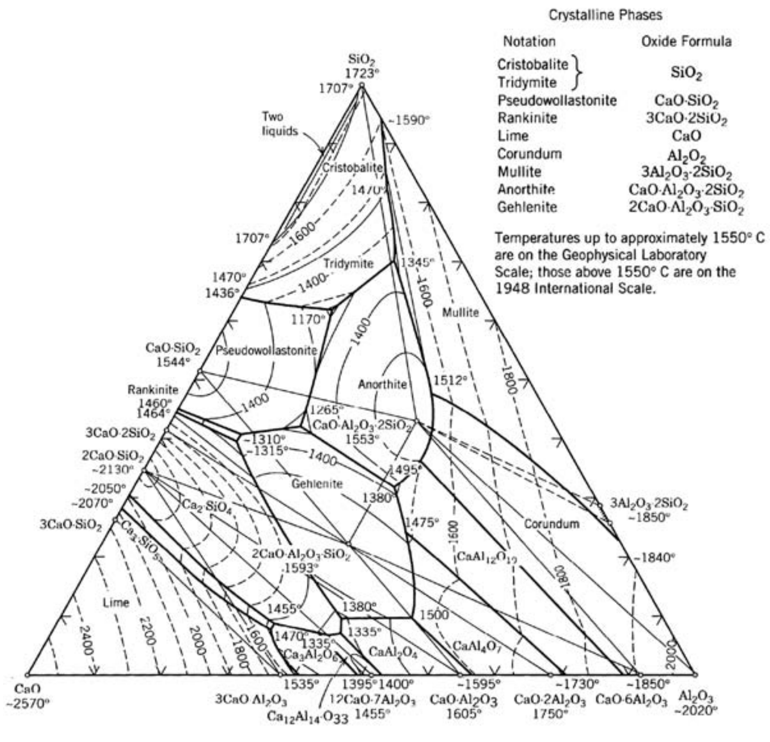

Figure 1. Phase diagram of the system CaO-Al_2O_3-SiO_2[8].

Based on the foregoing, the main objective of the present work has been the synthesis and characterisation of glass-ceramic glazes based on the system SiO_2-Al_2O_3-CaO, which improve the surface friction properties, yielding anti-slip glazes.

To attain this main objective, the work was programmed in terms of the following tasks:

- Study of the anorthite crystalline phase $CaO\cdot Al_2O_3\cdot 2SiO_2$ in the CaO-Al_2O_3-SiO_2 phase diagram
- Study and characterisation of frits with a composition rich in SiO_2, Al_2O_3, and CaO, which allow devitrification of the anorthite crystalline phase $CaO\cdot Al_2O_3\cdot 2SiO_2$.
- Development of glass-ceramic glazes from the frits obtained, and study and characterisation of these glass-ceramic materials
- Study of the possibility of adding these new glass-ceramic materials to other glazes to improve their properties.
- Application of the synthesised glazes onto porcelain tile bodies and characterisation of their physical and chemical properties, in addition to the quality parameters that allow their industrial use
- Characterisation of the anti-slip properties of the systems developed, in accordance with the standards

2. EXPERIMENTAL METHODOLOGY

2.1 MATERIALS AND METHODS

In order to develop glass-ceramic glazes that were able to devitrify anorthite, frits with the following composition were formulated (Table 1):

OXIDE	Al_2O_3	SiO_2	CaO	Others
% by weight	25-40	40-50	10-20	5-15

Table 1. Glass-ceramic glaze composition (% by weight)

The methodology used in developing the different glazes is summed up in the following diagram:

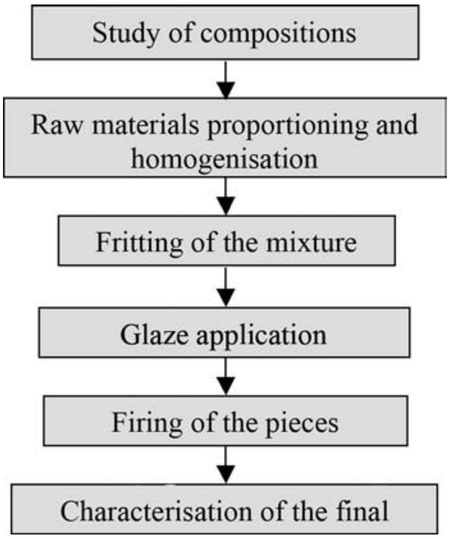

Figure 2. Flow chart followed in developing the glass-ceramic glazes

The anti-slip glass-ceramic glaze (AD) has been applied onto the following two types of glass-ceramic base glazes, obtained in previous research work by ESMALTES, S.A.:

- MT – Transparent matt base glaze for porcelain tile bodies.
- MO – Opaque matt base glaze for porcelain tile bodies.

Glaze AD was applied by disking onto materials MT and MO, and the optimum amount required to obtain the desired anti-slip effect was established, without impairing the desired pre-fixed technical or aesthetic qualities.

For this, applications of different amounts were made and after firing the pieces in the industrial kiln, we selected the optimum weight, which was found to be 7 g on 33x33 cm.

The firing cycle used to obtain the different end porcelain tile pieces is shown in Figure 3. The total cycle, with a peak temperature of 1200ºC, took 51 minutes.

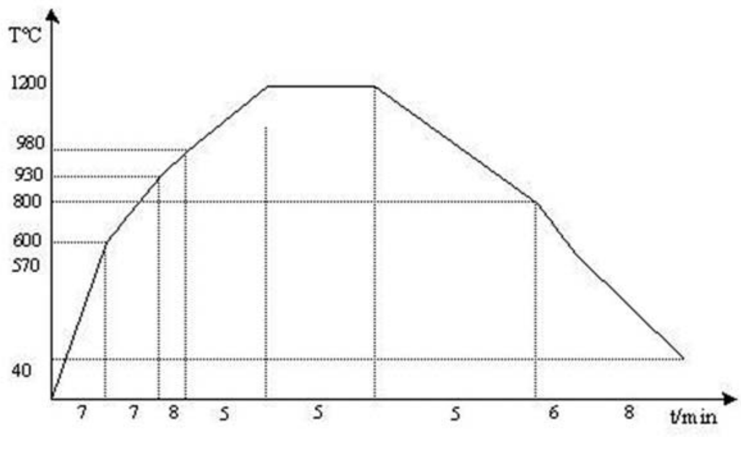

Figure 3. Firing cycle used in porcelain tile production.

2.2. CHARACTERISATION TECHNIQUES USED

For the appropriate characterisation of the materials developed in the present work, and for the measurement of their properties the following instrumental and analytical techniques were used:

- Scanning electron microscopy (SEM/EDX), with a LEO series 6300 instrument and an Oxford model ISIS energy-dispersive X-ray spectrometer, characterising the materials by secondary and backscattered electron imaging.

- SIEMENS model D5000 X-ray diffractometer, operating at 20 mA and 40 kV power, with Cu k_α cathode and Ni filter, fitted with a secondary graphite monochromator. Low-angle determinations were performed to determine the glassy halo displayed by the samples, as well as scanning between 20 and 70º (2θ) to analyse the crystalline phases present.

The following quality parameters of the developed materials were evaluated:

- Dynamic coefficient of friction or Tortus method and slip resistance by the pendulum method according to draft standard ISO 10545-17.[1]

- Resistance to surface abrasion of glazed tiles or PEI according to standard ISO 10545-7.[2]

- Chemical resistance according to standard ISO 10545-13.[2]

- Stain resistance according to standard ISO 10545-14.[2]

- Scratch hardness of surface (Mohs hardness) according to standard UNE 67101.[2]

- Measurement of toughness, through Vickers microhardness (Hv) according to standard UNE-EN ISO 6507-1. A Matsuzawa model MHT-1 instrument was used, performing the tests on the glazed pieces.

3. RESULTS AND DISCUSSION

The developed materials were structurally and microstructurally characterised, observing the formation of crystallisations in the glaze.

The X-ray diffraction spectra of the glass-ceramic glazes used can be observed in Figures 4-10, in which the crystalline phases present have been identified in each case.

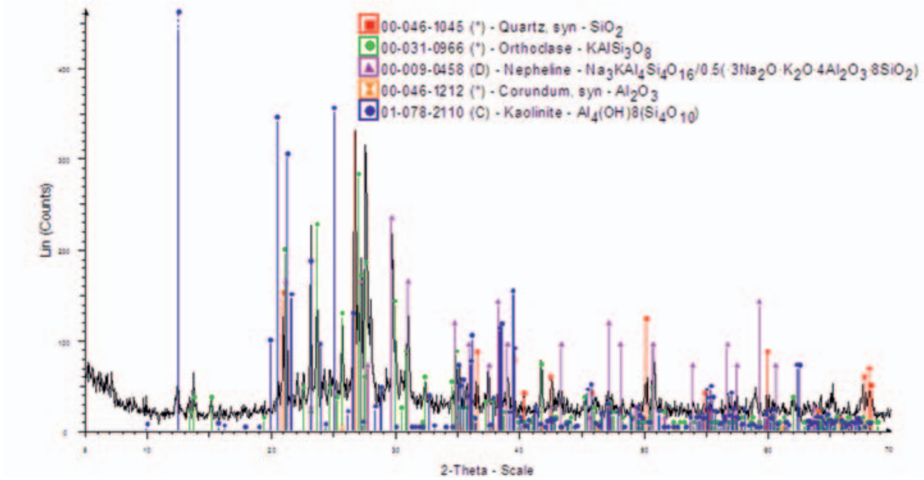

Figure 4. XRD spectrum of the unfired MT glaze.

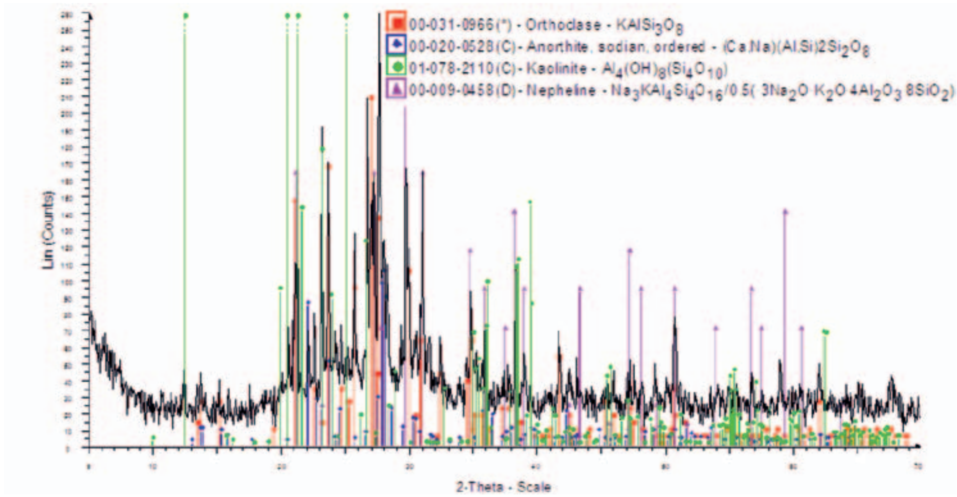

Figure 5. XRD spectrum of the unfired MO glaze.

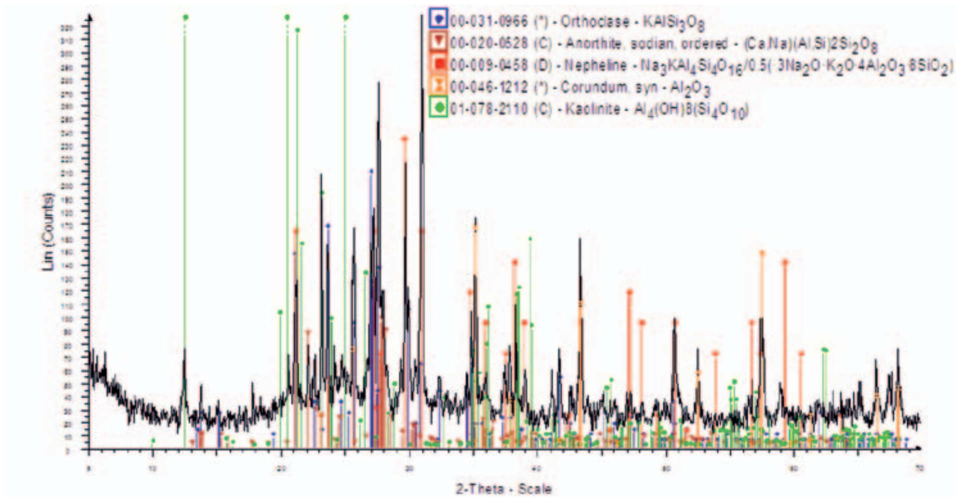

Figure 6. XRD spectrum of the unfired AD glaze.

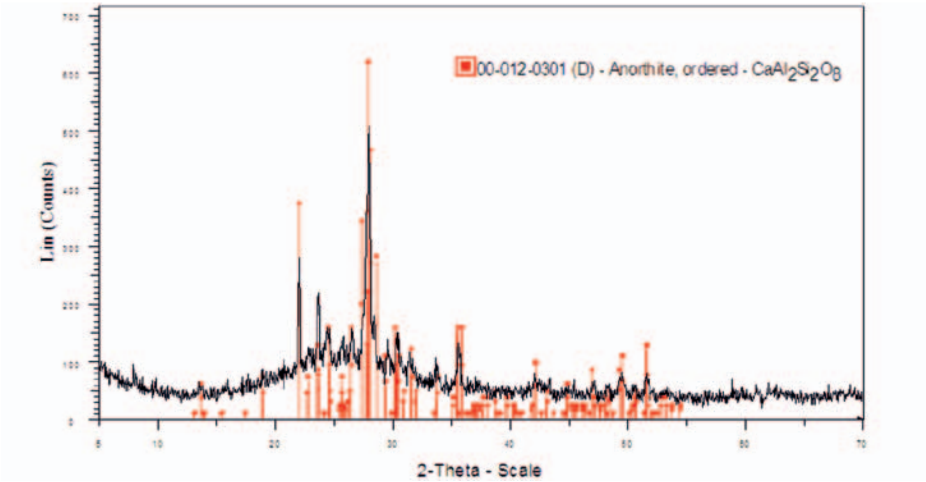

Figure 7. XRD spectrum of the fired MT glaze.

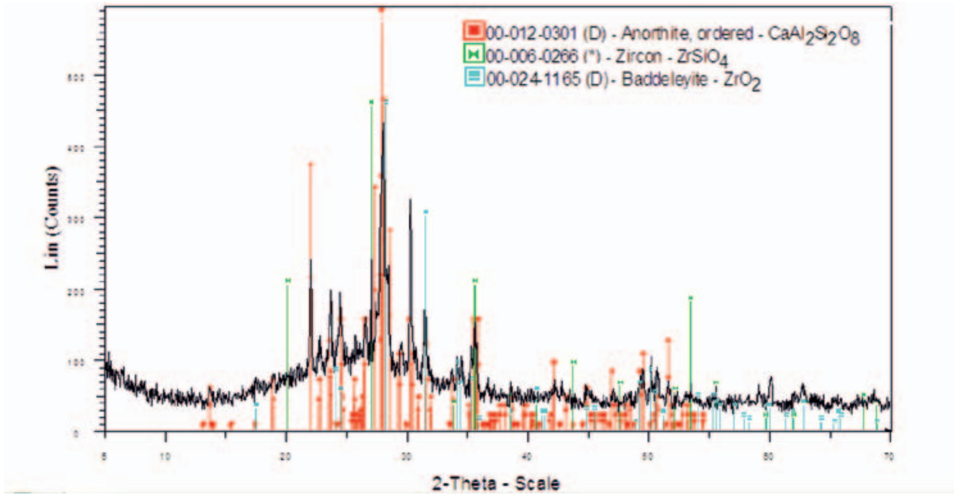

Figure 8. XRD spectrum of the fired MO glaze.

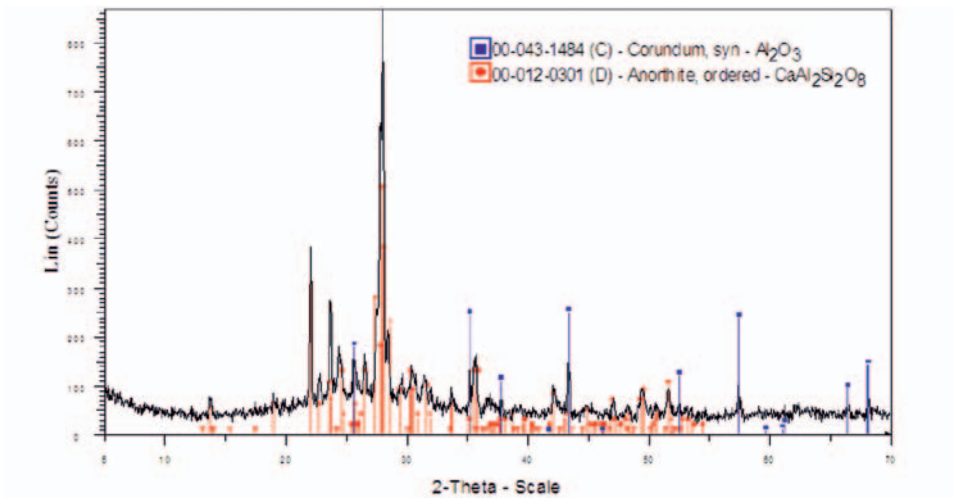

Figure 9. XRD spectrum of the fired MT+AD glaze.

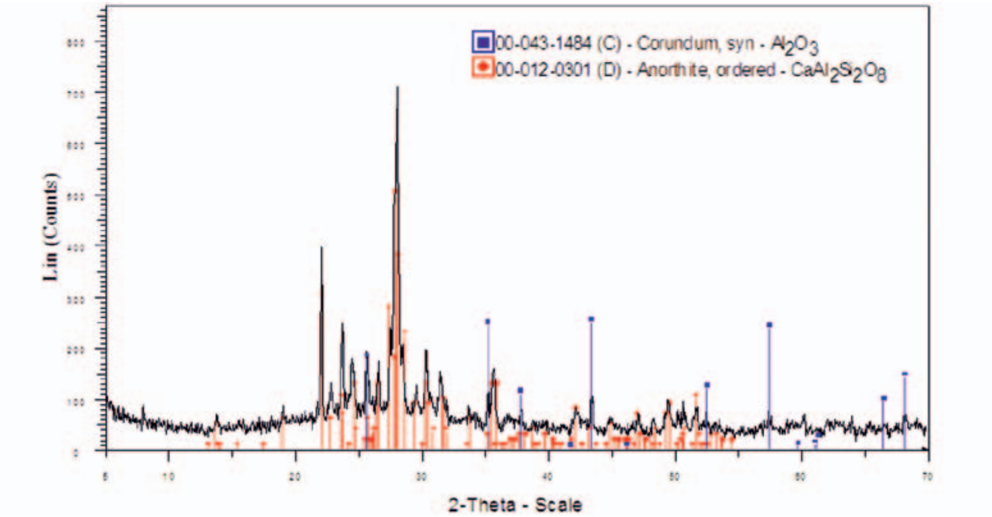

Figure 10. XRD spectrum of the fired MO+AD glaze.

It can be observed that in glaze MT and glaze MO, the phases existing in the unfired state disappear; anorthite develops in both glazes, while, in addition, baddeleyite and zircon appear in MO as this is an opaque glaze.

When the anti-slip material AD was applied onto these glazes and fired, the anorthite phase increased, and the presence of the corundum phase, introduced with glaze AD, was also observed.

The finished pieces were studied by scanning electron microscopy (SEM), taking several micrographs at different magnifications to observe the developed crystalline phases (Figures 11 and 12); the compositions of the crystals were determined by energy-dispersive X-ray microanalysis (EDX), shown in Figure 13.

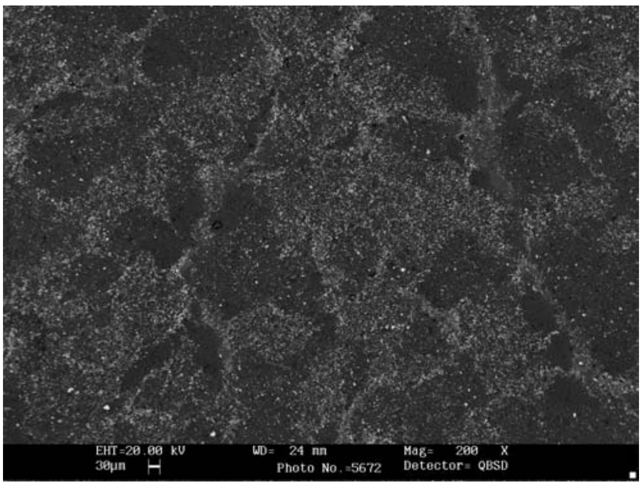

Figure 11. Micrograph (200x) of the tile surface coated with MO+AD.

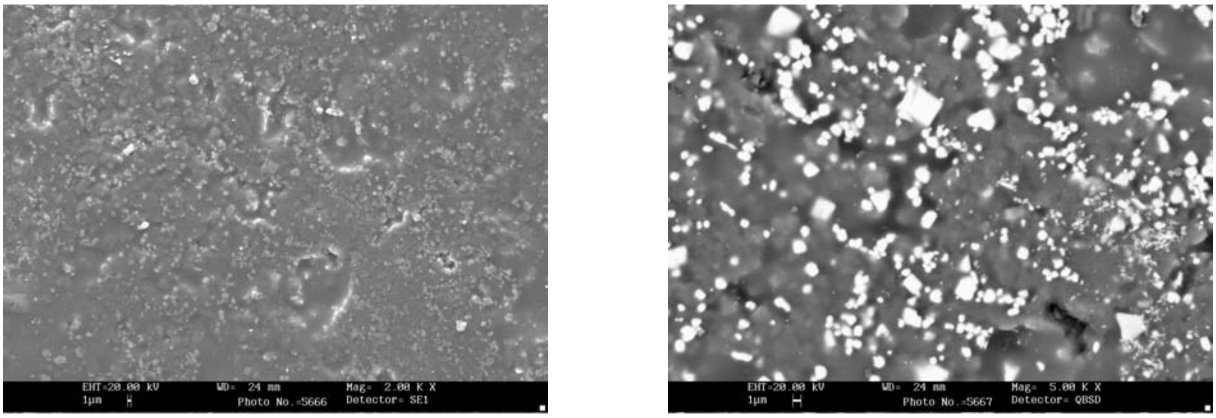

Figure 12. Micrograph (5000x) of the tile surface coated with MO+AD.

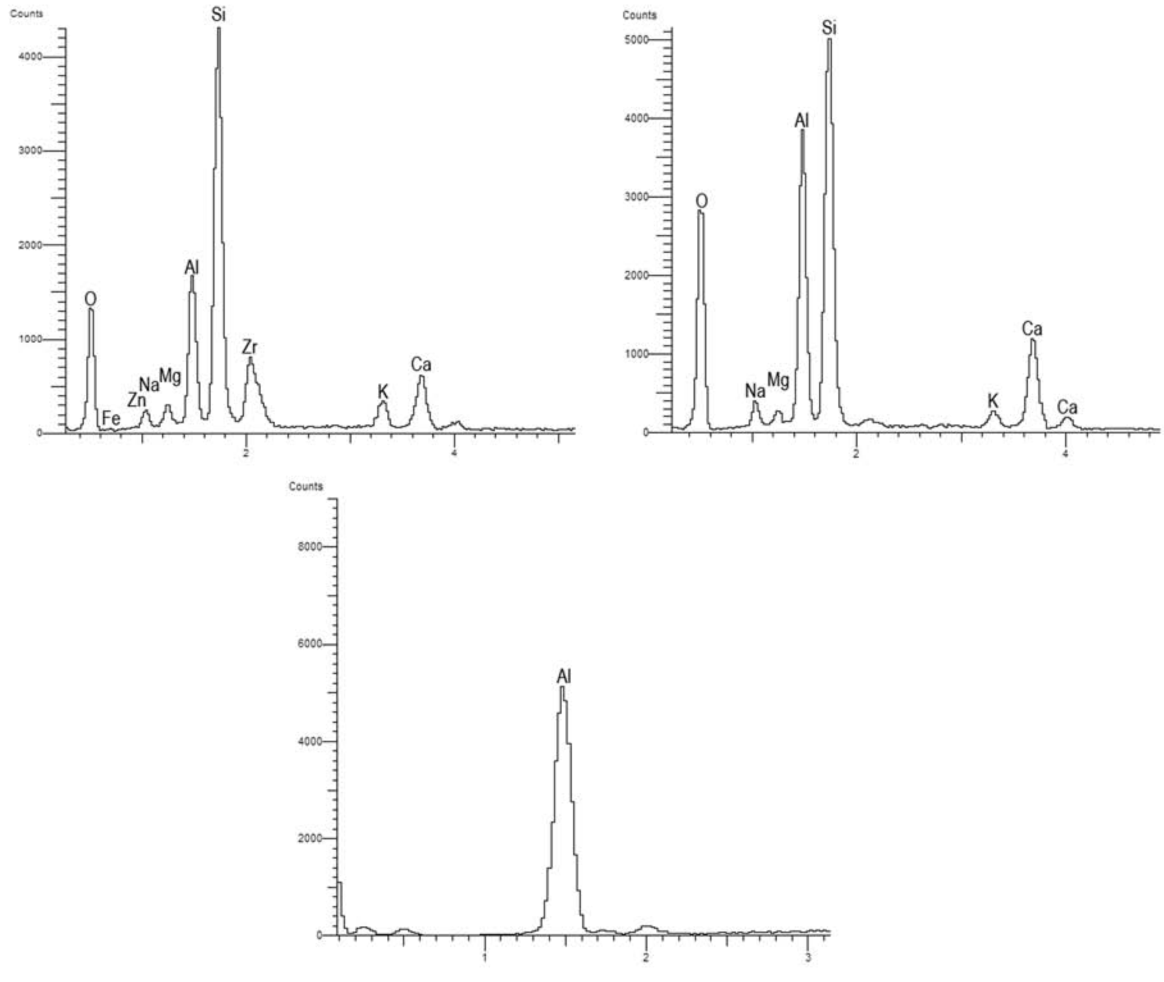

Figure 13. EDX microanalyses of the tile surface coated with MO+AD

Figure 11, at a magnification of 200x, shows a high concentration of crystals, homogenously distributed in the glaze. Figure 12, in the image on the left, at a magnification of 5000x, shows the micrographs of glaze MO+AD in secondary electron imaging (SE1) and, in the figure on the right, the same image is obtained, however, with backscattered electrons (QBSD). Particularly in this last image, lighter-coloured crystals can be observed through the different shades of greys, presumably corresponding to crystals of heavier elements. These are likely to correspond to the zircon crystals detected by XRD. The darker crystals presumably correspond to the crystallisations of anorthite and corundum observed by XRD.

Figure 13 shows the EDX microanalyses of the lighter-coloured regions (top left), which include Zr and confirm the presence of zirconium silicate crystals; and the dark-coloured regions (top right), which only show the lightest elements (Si, Al, Ca) in quantities close to that of the anorthite, corroborating their presence, already detected by XRD; and finally (below) the microanalysis with an aluminium peak that corresponds to the corundum crystals also detected by XRD.

Finally the quality parameters of the developed materials were evaluated. Table 2 shows that the PEI values are higher after the application of anti-slip glaze AD; the Mohs hardness values increase substantially, as do the Vickers microhardness values.

SAMPLE	PEI	MOHS	VICKERS
MT	IV	6	636
MT+AD	V	8	679
MO	IV	6	698
MO+AD	V	8	803

Table 2. Results of the measurement of abrasion resistance (PEI), scratch hardness (Mohs) and Vickers microhardness.

The results obtained in the stain test are set out in Table 3, which shows that it goes from class 5 to class 4 due to the slight roughness produced by the application of anti-slip glaze AD, but this just involves the elimination of stains with a weak cleaner instead of with water.

The chemical resistance to acids test (Table 3) displays no variation in the results after the application of anti-slip glaze AD.

SAMPLE	STAINS	ACIDS
MT	Class 5	GHA
MT+AD	Class 4	GHA
MO	Class 5	GHA
MO+AD	Class 4	GHA

Table 3. Results of the measurements of stain and acid resistance.

Finally, different tests were conducted to determine the anti-slip properties of the developed glazes, determining both the dynamic coefficient of friction and slip resistance (Table 4).

SAMPLE	TORTUS		PENDULUM	
	DRY	WET	DRY	WET
MT	0.48	0.42	45	40
MT+AD	**0.91**	**0.90**	63	58
MO	0.47	0.41	43	39
MO+AD	**0.90**	**0.89**	62	57

Table 4. Results of the dynamic coefficient of friction (Tortus) and slip resistance (Pendulum).

Note that the values recommended for the coefficient of friction by the TRANSPORT ROAD RESEARCH LABORATORY are as follows (Table 5):

MEAN VALUE (μ)	FLOOR RATING
Below 0.19	Dangerous
From 0.20 to 0.39	Marginal
From 0.40 to 0.74	Satisfactory
Above 0.75	***Excellent***

Table 5. Values recommended by the TRANSPORT ROAD RESEARCH LABORATORY

As Table 5 shows, the values obtained with the application of anti-slip glaze AD are far superior to the value of 0.75, which is rated excellent by the TRANSPORT ROAD RESEARCH LABORATORY.

Finally, the anti-slip glaze AD material was transformed into screen printing powder and applied as a final protective coating; this yielded results similar to the ones obtained with the material by disk application. A granulated glaze was also prepared, which was coloured in different hues for dry application, therefore displaying lower abrasion than the grits that are normally used; this material produces no static electricity and has a great flowability due to the treatment it undergoes in production, yielding enhanced definition in the applied designs.

4. CONCLUSIONS

- Glass-ceramic glazes based on the system SiO_2-Al_2O_3-CaO have been obtained by modulating the selected glaze composition.
- The developed glass-ceramic glazes substantially improve the anti-slip properties of the ceramic tiles used to date.
- Tile mechanical properties are held or improved appreciably, as is the case of the increased hardness and toughness of the pieces with the application of anti-slip glaze AD.
- In every case the aesthetic properties of the tiles on which glaze AD was applied were maintained.

- The developed glazes can be used as a final coating on any tile model in production; application is very versatile and can be performed by disk, screen printing and in granulate form.

- The study opens up a new generation of glazes of great interest in the field of the development of new functionalities for ceramic tiles, enhancing performance where high slip resistance is demanded.

5. ACKNOWLEDGEMENTS

The authors thank the Server Central d'Instrumentació Científica of Universitat Jaume I for their collaboration in the instrumental determinations and the Solid State Chemistry Research Group of the Dept. of Inorganic and Organic Chemistry for their collaboration in the present study.

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