"DEVELOPMENT OF NEW GLASS-CERAMIC GLAZES WITH SELF-COLOURING PROPERTIES"

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ABSTRACT

At present with the development of porcelain tile more technological ceramic products are being obtained, although production cycles are more extreme.

The production of the Spanish ceramic tile sector is directed toward the manufacture of glazed porcelain tile that is capable of maintaining its technical characteristics, while enhancing its decorative and aesthetic qualities.

With this objective, the present work has addressed the development of glazes for porcelain tile bodies, which can generate crystallisations in the glassy phase, enabling these during their genesis to encapsulate the chromophore agents, thus producing glazes with glass-ceramic characteristics, while these crystals act as ceramic pigments themselves, all in just one single-fire process.

With this objective, compatibility regions of the mullite, anorthite and zircon systems were selected in the stability phase diagrams of SiO_2-Al_2O_3-CaO and SiO_2-Al_2O_3-ZrO_2. At the same time, frit compositions rich in SiO_2 and Al_2O_3 were designed, introducing different chromophore agents in the same fritting process, which were all elements of the first transition series.

In this way a variety of glazes with different chromatic ranges were prepared, all presenting good colour homogeneity, as well as appropriate technical characteristics in the glass-ceramic coating itself.

The study characterised the formation of crystallisations in the glaze structurally and microstructurally evidencing the encapsulation of the different chromophore elements in the arising crystalline structure.

*The different colorations that developed were also parameterised through the CIE-L*a*b* co-ordinates.*

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

The study lays the groundwork for a new generation of self-colouring glazes of great interest in the field of ceramic design.

KEY WORDS: Pigments, glass-ceramic glazes, porcelain tile, colour.

1. INTRODUCTION

1.2 GLASS-CERAMIC GLAZES

Currently there is growing interest in the ceramic production sector in developing new materials that provide better technical performance, enabling products to be made of greater quality and thus with greater added value[1].

The so-called glass-ceramic glazes meet this need, since they constitute a new generation of glazes in which crystals form in the glassy phase itself, after undergoing the corresponding thermal treatments.

In this sense, it is possible to design and improve the technological performance[2] of these materials, by controlling the nucleation and crystallisation processes of the glassy compositions, relating technical performance to the nature, number and size of the arising crystals.

1.2. COLOUR PRODUCTION MECHANISM IN GLAZES

Generally speaking, two fundamental mechanisms are involved in colouring a glaze:

a) Development of the colour in the silicate network itself, as an integral part of the network, as part of the fundamental silicate network[3] or not. This mechanism can be divided into two other groups, whose behaviour differs:

   -soluble ions that generate colorations and form part of the fundamental silica structure.

   -colloidal suspensions distributed in the glazes.

b) Inclusion or mix of individual particles of calcined pigments in the glaze structure.

The origin of the colour depends on the oxidation state[4] and coordination number of the metallic ion. In the molten state they attain equilibrium surrounding themselves with a certain number of oxygens, belonging to the silicate, while this depends on whether they are occupying glass former or modifier positions. The equilibrium state is influenced by the composition of the glass (competition of silicon and other cations for the oxygen, oxygen pressure), combustion atmosphere, cooling rate, etc., amongst other factors.

The objective of the present work was to develop new glazes of a glass-ceramic nature that contain different chromophore agents in the crystalline structure of the glaze, thus generating "self-colouring" glazes for porcelain tile bodies, in just one single-fire process (glaze and ceramic body).

This enables producing glazes with enhanced technical performance and in turn, a range of stable colours through these glazes.

2. EXPERIMENTAL

2.1. MATERIALS AND METHODS

A number of compositions have been designed for the development of frits within the primary fields of anorthite, diopside and zircon crystallisation, according to the corresponding phase diagrams (Figures 1 and 2).

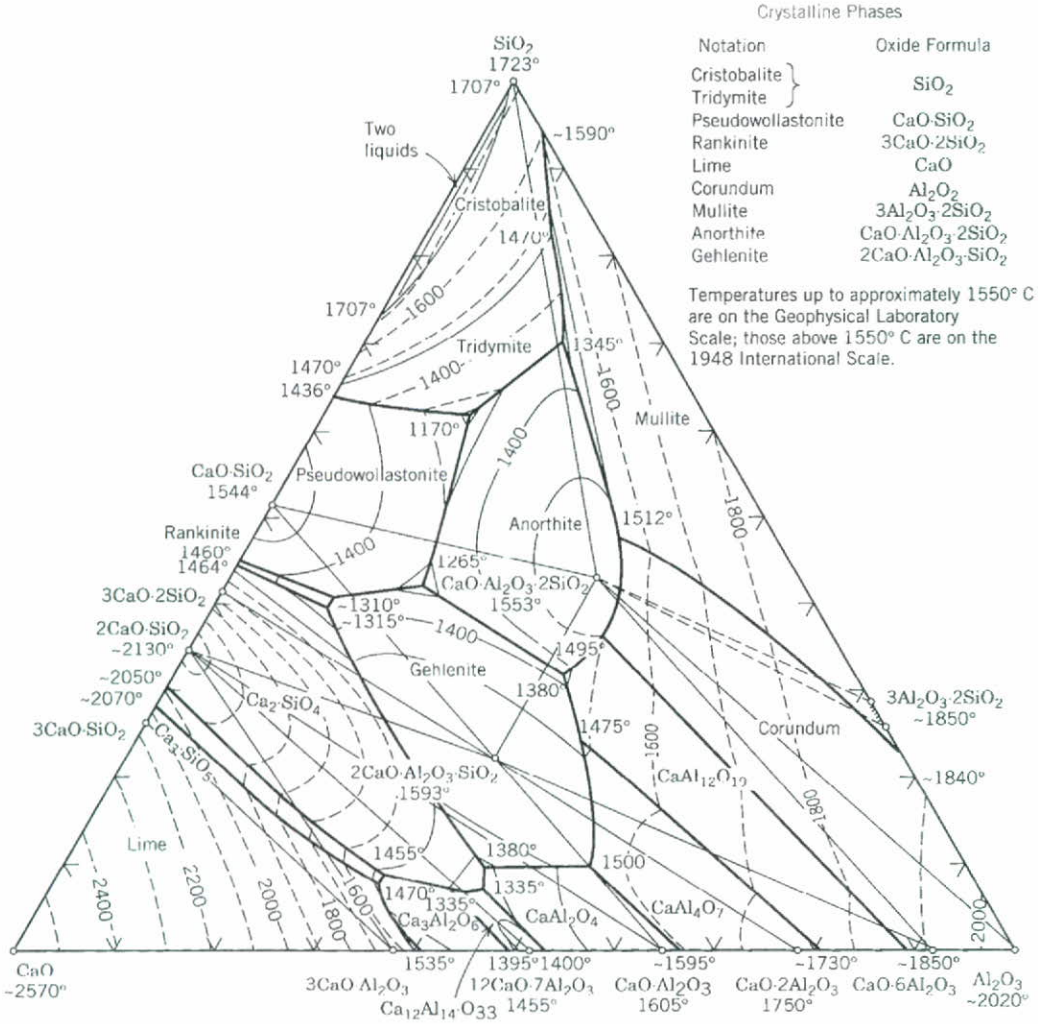

Figure 1. Phase diagram[5] of the system $CaO-Al_2O_3-SiO_2$.

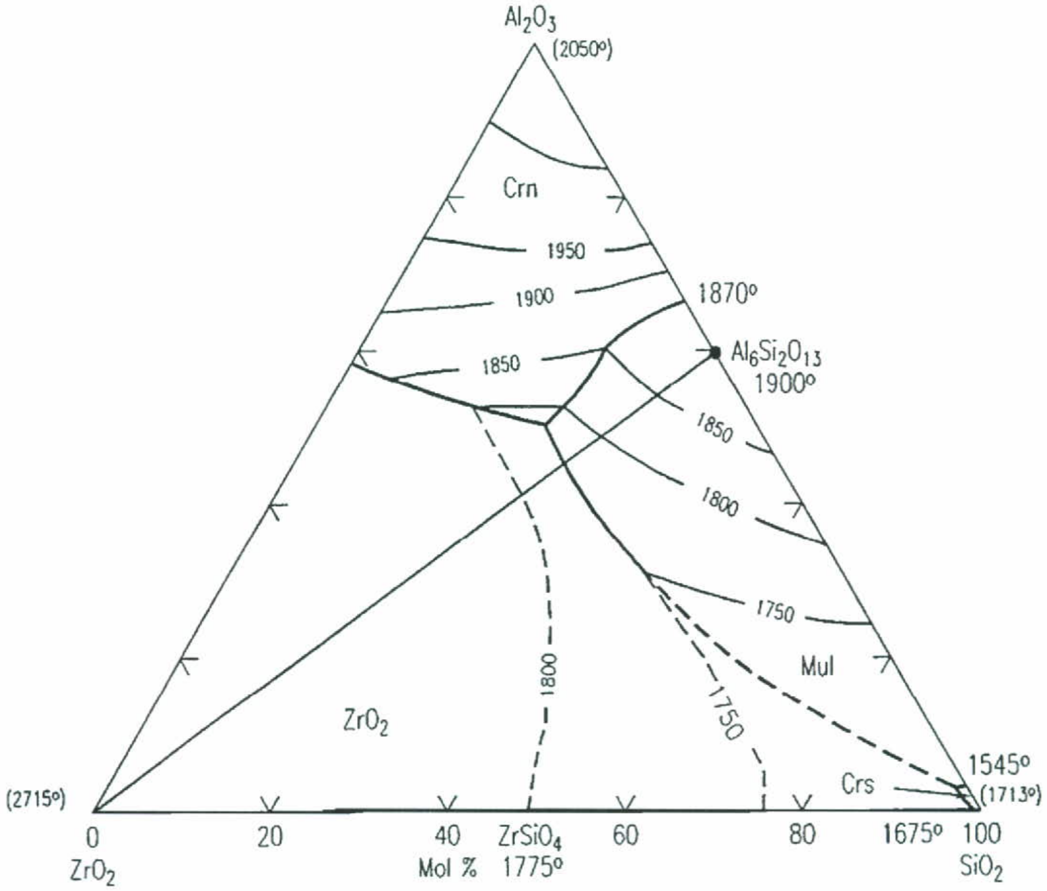

Figure 2. Phase diagram[6] of ZrO_2-$Al2O_3$-SiO_2.

The frit formulations were completed, designing two base mixtures for this purpose, whose different qualitative compositions are presented in Tables I and II.

Composition	**Potass. feld.**	**Kaolin**	**Quartz**	**$CaCO_3$**	**$BaCO_3$**	**ZnO**	**Hydrated Alumina**

Table I. Qualitative composition of base mixture A.

Composition	**Potass. feld.**	**Quartz**	**$CaCO_3$**	**ZnO**	**Hydrated Alumina**	**$ZrSiO_4$**	**Dolomite**	**Colemanite**
wt%	**1-10**	**25-35**	**10-20**	**0-5**	**15-25**	**10-20**	**25-35**	**1-10**

Table II. Qualitative composition of base mixture B.

Different chromophore oxides were added to these base mixtures with a view to producing frits in which a pigmenting structure develops. The ions of the precursor oxides with the base mixtures used, together with their references are given in Table III.

Base mixture	Chromophore ions	Reference
A	Fe	A1
A + mineraliser 1	Fe	A2
A + mineraliser 2	Fe	A3
A	Fe, Ni, Cr	A4
A	Co	A5
A	2Fe, Ni, Cr, 1Co	A6
A	1Fe, Ni, Cr, 2Co	A7
A + mineraliser 2	Fe, Ni, Cr, Co	A8
A	1Cr	A9
A	1.4Cr	A10
A	3Cr	A11
A + alumina	3Cr	A12
A + alumina	1Cr	A13
A	5Cr	A14
A + mineraliser 3	Cr	A15
A + mineraliser 2	Cr	A16
A + mineraliser 2 y 4	Cr	A17
A + mineraliser 1	3Fe, 1Cr	A18
A + mineraliser 1↑	3Fe, 1Cr	A19
A + mineraliser 1	5Fe, 0.5Cr	A20
A + mineraliser 1	Fe, Cr, Sn	A21
A	Cr, Mn	A22
A	0.5Cr, Mn, Nd	A23
A + alumina	Cr, Mn	A24
A + alumina↑	Cr, Mn	A25
A + alumina↑ + mineraliser 5	Cr, Mn	A26
A + alumina	Cr, Sn	A27
A + alumina	Mn	A28
A + alumina	Sn, V	A29
A + alumina	Cr, Y	A30
A + alumina	0.1Cr, Y	A31
A + alumina	Sn, Sb, V	A32
B	V	B33
B	Fe	B34

Table III. Base mixtures used with chromophore ions together with their references.

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

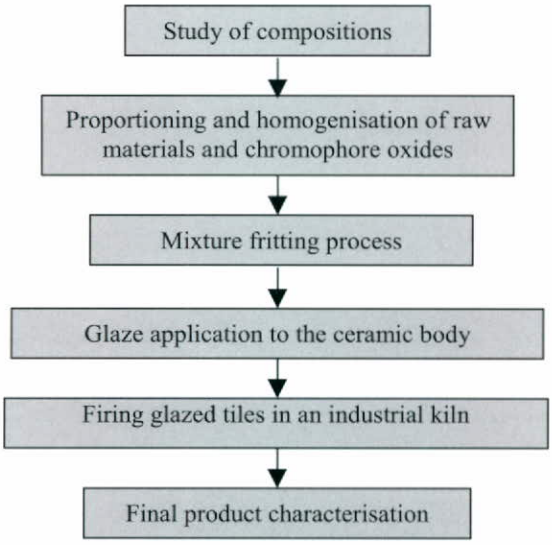

Figure 3. Flow diagram of coloured glass-ceramic glaze development.

The frits made, together with the oxide chromophore added to their composition, were applied as glazes to porcelain tile bodies and subjected to thermal treatment equivalent to that used in industrial porcelain tile production. The cycle is presented in Figure 4.

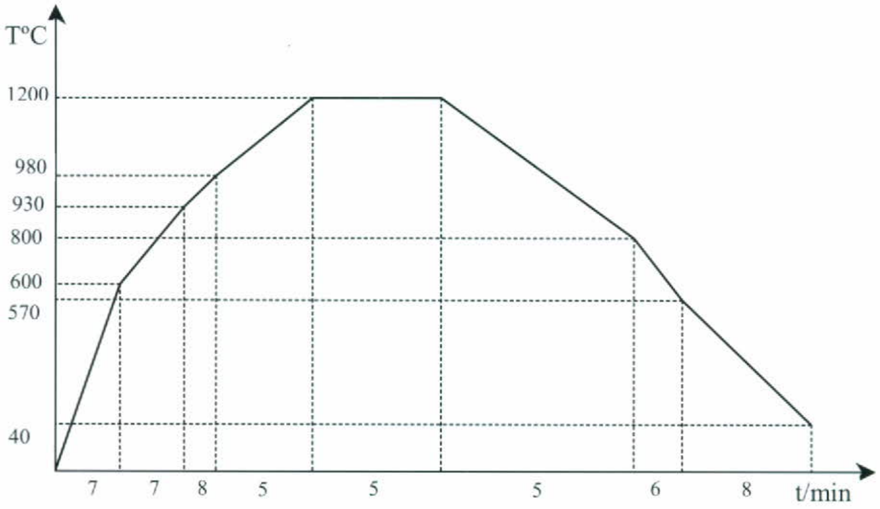

Figure 4. Firing cycle to 1200°C followed in porcelain tile production.

3. CHARACTERISATION TECHNIQUES

All the starting materials were analysed and the resulting products were characterised. The structural characterisation was carried out by X-ray diffraction (XRD), with a Siemens D5000 diffractometer, fitted with a copper cathode. Measurements were performed at a voltage of 40kV and 20mA, in the range 2θ from 15 to 70°.

Microstructural and analytical characterisation were done by scanning electron microscopy (SEM) with a Leica, model READS 440 instrument, fitted with an energy-dispersive X-ray analysis spectrometer (EDX).

The mechanical properties of the glazes were determined by Vickers microhardness measurements, with a MATSUZAWA, model MHT-1, microhardness tester up to 1 kg force. Mohs hardness measurements were also performed (according to standard UNE 67-101).

Finally, the developed colours were analysed and the colour parameterised through the CIE-L*a*b* chromatic co-ordinates by means of a MINOLTA CM-508i, spectrophotometer, with SpectraMagic software for Windows.

4. RESULTS AND DISCUSSION

4.1. STRUCTURAL CHARACTERISATION

XRD analysis of the fired glazed pieces shows the development of the anorthite phase as major phase in all the samples (Table IV).

Reference	*Phase developed*
A1	**anorthite**
A2	**anorthite**
A3	**anorthite**
A4	**anorthite**
A5	**anorthite**
A6	**anorthite**
A7	**anorthite**
A8	**anorthite**
A9	**anorthite**
A10	**anorthite, $ZnAl_2O_4.Al_2O_3$**
A11	**anorthite, $ZnAl_2O_4.Al_2O_3$**
A12	**anorthite, $ZnAl_2O_4.Al_2O_3$**
A13	**anorthite**
A14	**anorthite, $ZnAl_2O_4.Al_2O_3$**
A15	**anorthite**
A16	**anorthite**
A17	**anorthite**
A18	**anorthite**
A19	**anorthite**
A20	**anorthite**
A21	**anorthite**
A22	**anorthite**
A23	**anorthite**
A24	**anorthite**
A25	**anorthite**
A26	**anorthite**
A27	**anorthite**
A28	**anorthite**
A29	**anorthite**
A30	**anorthite**
A31	**anorthite**
A32	**anorthite**
B33	**anorthite, $Ca(MgAl)(SiAl)_2O_6$, $ZrSiO_4$**
B34	**anorthite, $Ca(MgAl)(SiAl)_2O_6$, $ZrSiO_4$**

Table IV. Phases developed in the glazed pieces together with their references.

As Table IV indicates, some samples develop gahnite crystalline phases $ZnAl_2O_4.Al_2O_3$ in the glazes whose frits were enriched with alumina, while the samples coated with glaze compositions containing frits enriched with zirconium show the presence of zircon, together with the diopside phase. As an example some diffractograms are shown in Figure 5, in which the crystalline phases present are indicated.

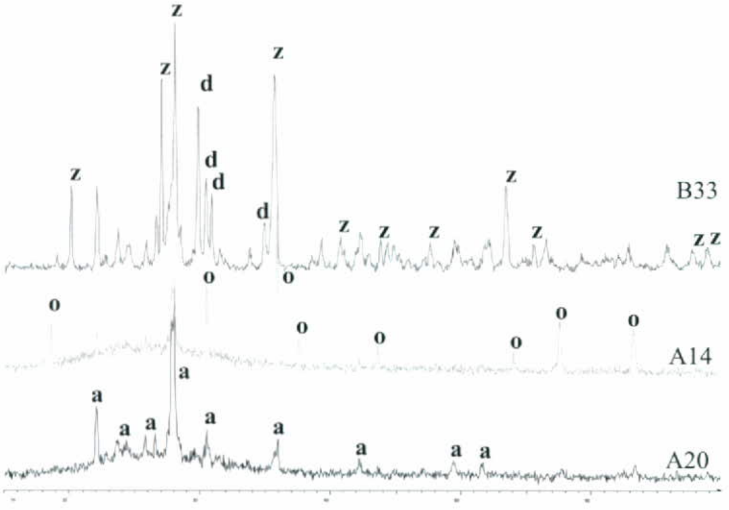

Figure 5. XRD analysis of samples A20, A14 and B33. a: anorthite phase; o: gahnite phase $ZnAl_2O_4.Al_2O_3$; d: diopside phase; z: zircon phase.

4.2. MICROSTRUCTURAL AND ANALYTICAL CHARACTERISATION

All the samples produced were microstructurally characterised by SEM and EDX. The images were obtained with a backscattering electron detector, in which the sample constituents can be distinguished by the atomic weights of the elements through light colours (greater atomic weight) and dark colours (lighter elements, with smaller atomic weight). The glazed samples shown in the X-ray diffractograms were chosen as representative examples, including the sample with reference A7. Figure 6 shows the SEM micrograph of sample A7.

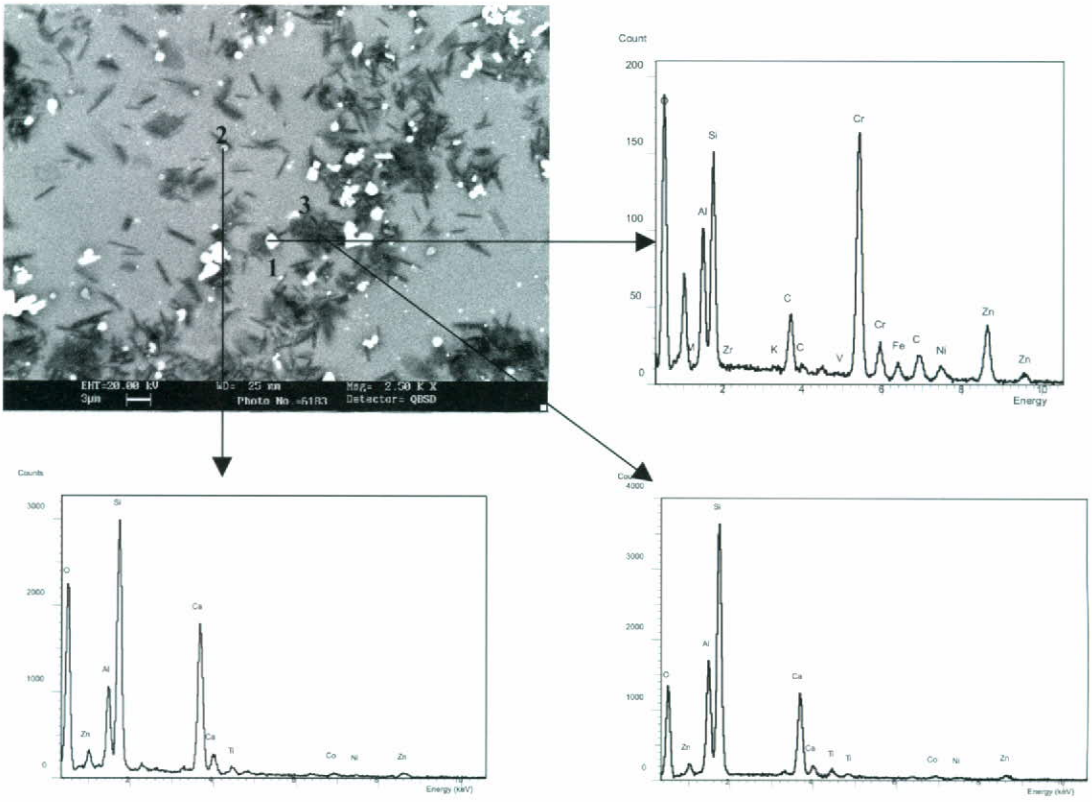

Figure 6. Micrograph of sample A7 x 2500 magnifications and EDAX microanalysis.

As the micrograph shows, two crystal morphologies appear. Some crystals are of an acicular type, which according to the corresponding spot analysis (spot 2 and 3) on each crystal would belong to the anorthite phase recorded via the XRD diffractograms (Table V).

A7	Al_2O_3	SiO_2	CaO	TiO_2	Cr_2O_3	Fe_2O_3	CoO	NiO	ZnO
spot 1	13.15	20.59	3.96	0.63	31.44	2.83	4.52	2.78	20.08
spot 2	14.10	50.38	27.57	1.80	-	-	1.37	0.92	3.86
spot 3	24.26	52.44	16.31	1.22	-	1.33	0.86	-	3.58

Table V. Semi-quantitative values of spot chemical analyses of sample A.

Another type of crystals, much less abundant, which appear in the image as more brilliant agglomerates and whose spot analysis (spot 1 in Table V) evidences ZnO and

Cr_2O_3 enrichment, are possibly gahnite crystals, not recorded by XRD owing to their minor presence.

Figure 7 shows the micrograph of sample A14.

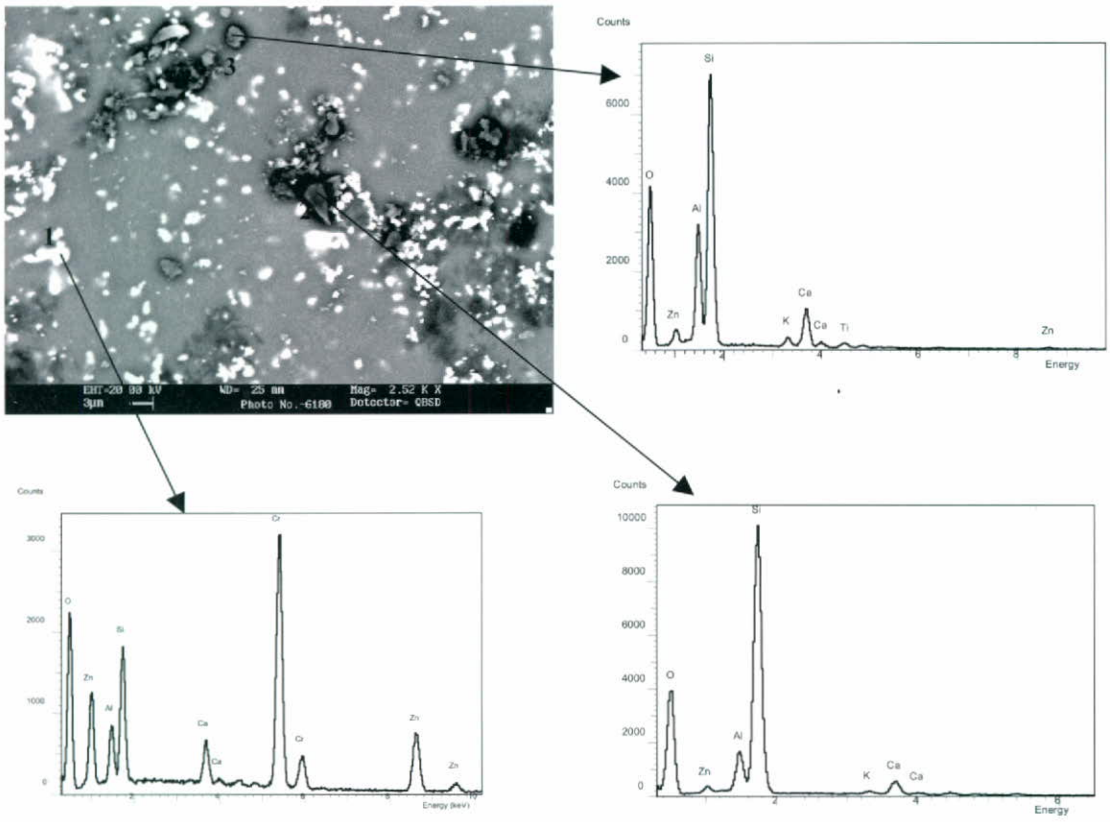

Figure 7. Micrograph of sample A14 x 2500 magnifications and EDAX microanalysis.

Also in this case, several types of crystallisations can be observed, whose semi-quantitative spot chemical analysis data are set out in Table VI.

A14	**Al_2O_3**	**SiO_2**	**CaO**	**K_2O**	**Cr_2O_3**	**ZnO**
spot 1	7.45	17.44	3.75	-	43.01	28.36
spot 2	10.49	83.72	4.39	0.63	-	0.77
spot 3	22.59	65.84	8.35	1.52	-	1.70

Table VI. Semi-quantitative values of spot chemical analyses of sample A14.

More brilliant, rounded grains appear, whose spot analysis is given in Table VI as spot 1. By their ZnO content they could be assigned to gahnite crystals, indicated in Table IV. The darkest crystallisations (spot 2 and 3 in Table VI) by their make-up, evidence the presence of anorthite phase (Table VI).

Figure 8 shows the micrograph of sample A20, together with the corresponding microanalysis.

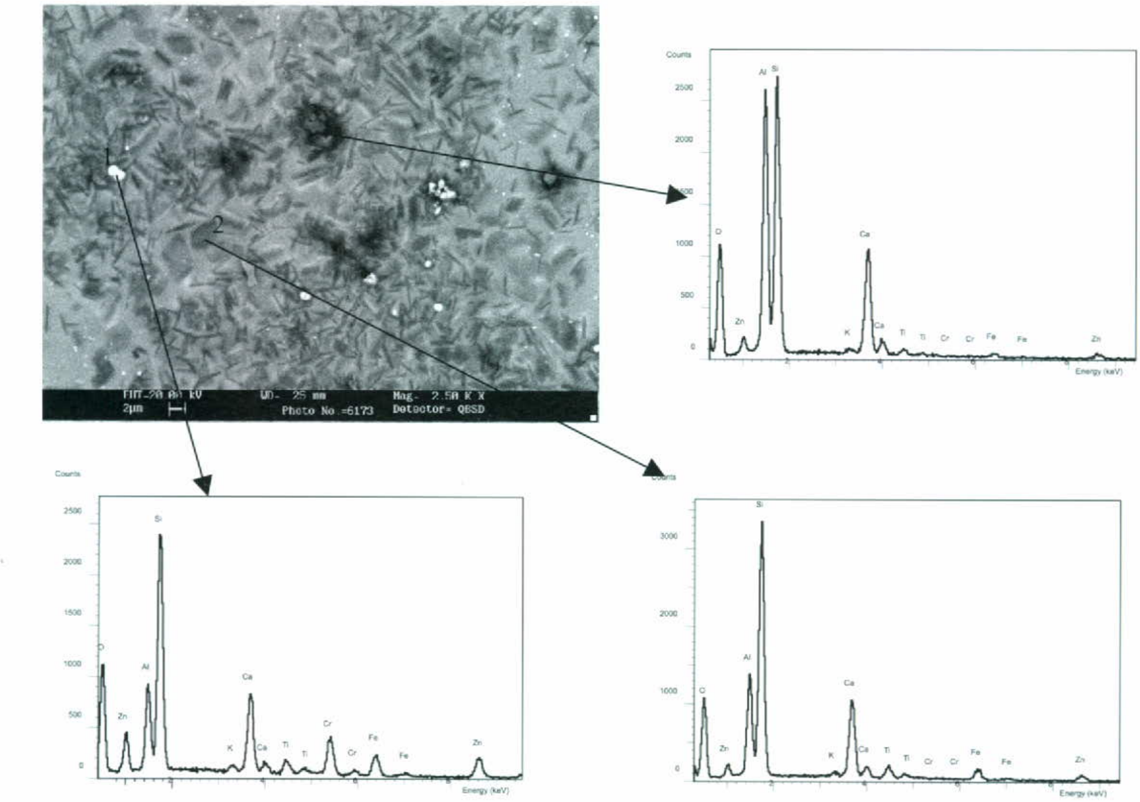

Figure 8. Micrograph of sample A20 x 2500 magnifications and EDAX microanalysis.

Just as with sample A7 (Figure 6), the same crystallisation morphologies appear, with acicular crystals assigned by microanalysis (spot 2 and 3 Table VII) to the anorthite phase.

A20	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Cr_2O_3	$Fe2O_3$	ZnO
spot 1	13.50	41.35	0.75	10.94	2.53	9.62	7.39	13.91
spot 2	17.79	53.34	0.63	15.01	3.38	-	4.86	5.25
spot 3	33.34	45.78	0.45	15.09	1.02	-	1.27	2.97

Tabla VII. Semi-quantitative values of spot chemical analyses of sample A20.

The most brilliant, rounded crystals would be assigned by microanalysis (spot 1 in Table VII) to the gahnite phase (Table IV), which were not recorded by XRD owing to their scarce concentration.

Figure 9 shows the micrograph of sample B33. Compared to the foregoing samples, the degree of crystallinity reached is much larger.

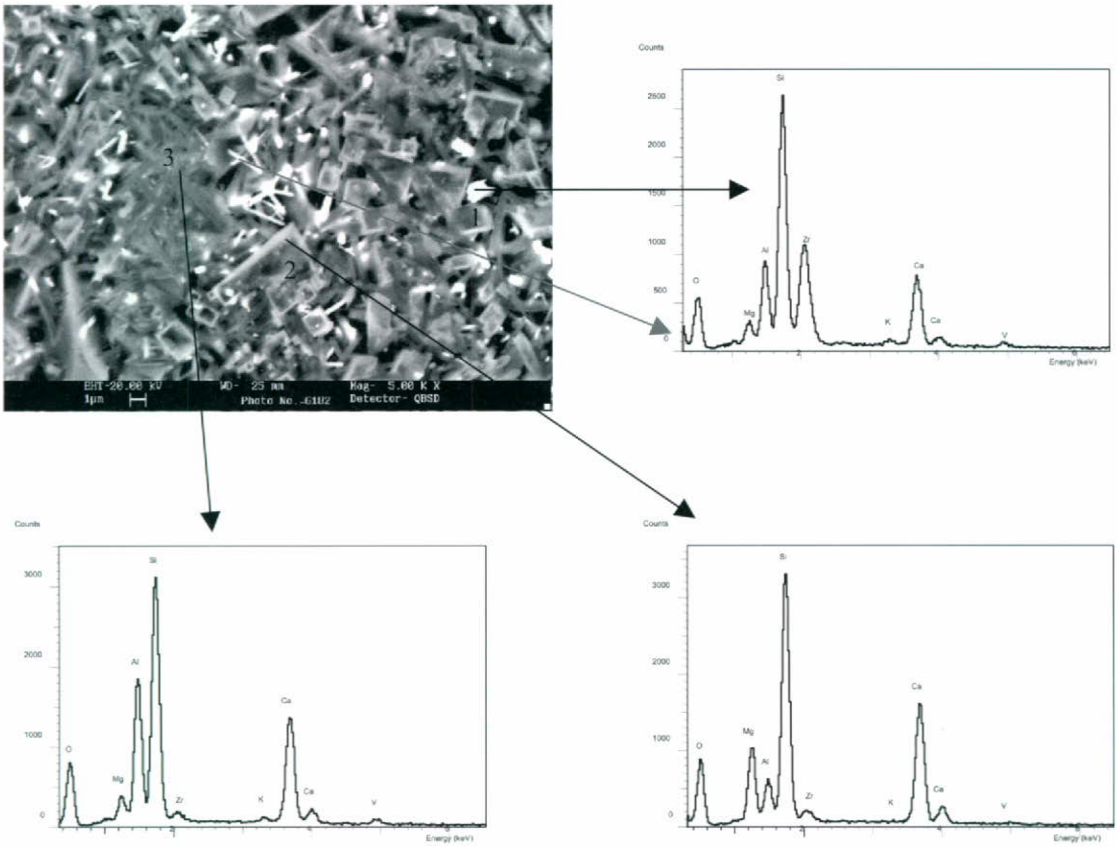

Figure 9. Micrograph of sample B33 x 5000 magnifications and EDAX microanalysis.

Table VIII sets out the spot chemical analysis data on each type of crystal appearing in sample B33.

B33	Al_2O_3	SiO_2	MgO	K_2O	CaO	V_2O_5	ZrO_2
spot 1	11.68	41.00	3.09	0.63	11.55	2.51	29.54
spot 2	7.59	50.81	13.45	-	23.58	-	4.47
spot 3	23.21	48.56	3.61	-	19.59	1.76	3.26

Table VIII. Semi-quantitative values of spot chemical analyses of sample B33.

As can be observed in Table VIII, zirconium and silicon are concentrated in spot 1, evidencing the formation of crystals assignable to zircon. The presence of vanadium oxide could be explained by the possible formation of zircon crystals with vanadium ions trapped inside the structure. Several spot analyses were also run on the brilliant crystals in which, in all the cases, the presence of zirconium and vanadium was detected. Spot 2 highlights the development of phases that can be assigned to diopside by their content. Finally in spot 3 an area of glassy concentration appears, in which crystals are detected that would belong to the anorthite phase by their make-up.

4.3. MECHANICAL PROPERTIES MEASUREMENTS

Hardness is not a simply defined property and is generally associated with bond strength values of the oxides making up the glass network[7]. Hardness is defined as the resistance that a body presents to penetration by another. On the basis of this general definition, several types of hardness can be distinguished. In the present work scratch hardness and resistance to indentation have been measured. In the former the hardness of the sample is compared with the standard hardness of the Mohs scale. In the latter, a load is applied to a single point on a glaze. The measurement expressed by the Vickers method (diamond tip) represents the relation load/contact surface of an estimated degree of reticular cohesion (rigidity) of the glassy structure and is related to its composition, temperature and type of cooling.

The results obtained through this method and for each reference sample are indicated in Figure 10.

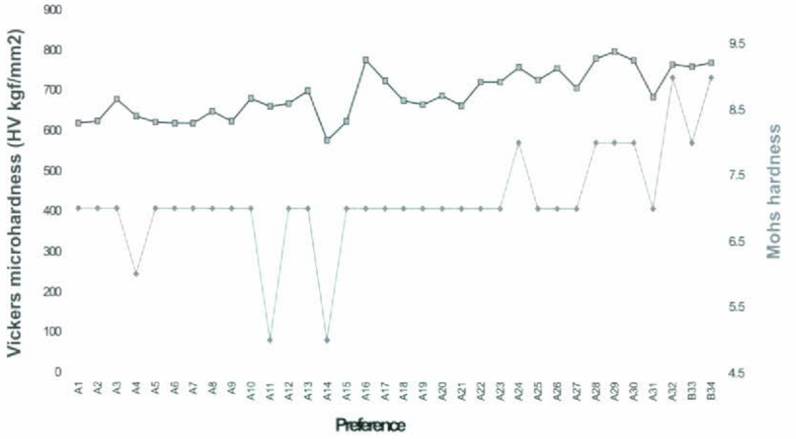

Figure 10. Values found with the Vickers microhardness and Mohs hardness tests.

As a reference, the ceramic glazes used in ceramic floor and wall tile manufacture usually have Mohs hardness ranging from 4 to 7. The values reached in the glazes developed all exceed these values, which establish good scratch hardness characteristics. The values achieved with Vickers microhardness also establish good toughness characteristics of these materials.

4.4. COLOUR MEASUREMENT AND PARAMETERISATION

All the colours developed in the glazes have been analysed using the CIE-L*a*b* system[8]. In this system the chromatic diagrams are represented by three rectangular axes with a linear scale (Figure 11).

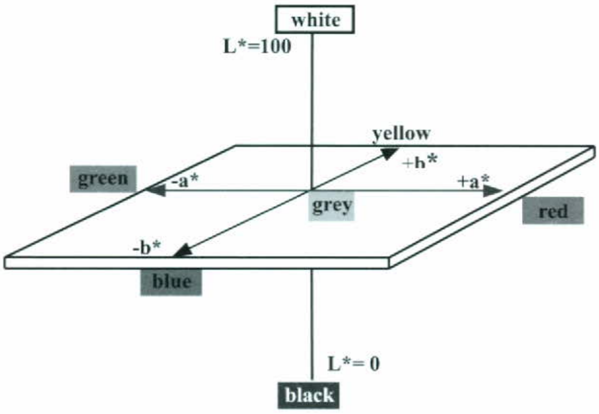

*Figure 11. Chromatic co-ordinates in the CIE-L*a*b* system.*

The abscissa is known as the red-green axis (red+green), the ordinate as the yellow-blue axis (yellow+blue) and the vertical axis represents brightness L* (value of greater or lesser brightness), which can range from 0 to 100.

Table IX lists the colour measurements of all the developed glazes.

REFERENCE	CHROMATIC CO-ORDINATES			COLOUR
	L*	a*	b*	
A1	66.34	0.24	28.71	green
A2	62.97	2.84	33.55	green
A3	64.02	1.04	32.31	green
A4	34.82	7.11	10.08	brown
A5	27.07	12.95	-22.36	blue
A6	30.39	0.79	3.51	black
A7	29.87	-1.1	-0.45	black
A8	30.32	0.54	3.11	black
A9	60.82	0.25	17.59	green
A10	56.38	-3.75	17.01	green
A11	55.7	0.43	12.41	green
A12	52.12	1.41	12.61	green
A13	64.39	2.85	17.77	green-dun
A14	56.99	-0.58	11.92	green
A15	59.22	-0.65	17.28	green
A16	62.97	-0.84	16.15	green
A17	64.27	3.41	17.16	green
A18	48.96	17.32	25.19	leather
A19	45.09	13.41	20.84	leather
A20	43	10.59	18.7	leather
A21	47.64	15.03	23.3	leather
A22	56.09	5.43	15.41	dun
A23	59.08	6.57	15.81	brown
A24	56.38	5.43	14.74	brown
A25	57.74	8.6	16.2	reddish-brown
A26	53.62	5.11	12.7	brown
A27	64	2.26	17.44	green
A28	85.21	0.28	9.65	pink
A29	72.99	2.27	15.94	beige
A30	79.47	-1.38	16.31	green
A31	85.26	5.25	10.41	light green
A32	82.74	-1.48	8.54	light green
B33	79.68	-6.21	-2.27	turquoise
B34	80.3	-1.39	27.33	yellow

Table IX. Chromatic co-ordinates found in the developed glazes.

As can be observed in samples A1, A2 and A3 a green colour develops, probably due to the ferric oxide which largely depends on the glass composition in which it is dissolved: alkaline glasses can generate a green colour, especially if zinc is present. The blue colour in sample A5 due to the cobalt oxide that develops blue colours, may be one of the oldest oxides used for decorative purposes in glazes. The cobalt ion usually presents two different co-ordinations, 4 and 6. In the first case, the ion behaves as a network former and the resulting colour is blue; in the second case it behaves as a network modifier and acquires a pink coloration. The black colour found with the specimens referenced A6, A7 and A8 could be based on the possible formation of a nickel, iron and chromium spinel, according to the DCMA[9] ceramic pigments structural classification. The samples that exhibit green colours contain Cr, which has very low solubility in glazes.

The colour depends on the equilibrium between the Cr^{+3} and Cr^{+6} ions present in the glaze. The trivalent form, the most abundant one, has a very small, active ion; in the glassy network it occupies the position of a structure modifier and produces a green colour. The brown colour that develops in the glazes referenced A23, A24, A25 and A26 can perhaps be attributed to a zinc, chromium and magnesium spinel, in which the zinc is part of the frit components. The pink colour that develops in sample A28 could be assigned to the manganese, corundum and aluminium structure. The turquoise blue obtained in the sample with vanadium could be explained by the presence of the zircon vanadium structure detected by XRD and SEM as a crystalline phase in sample B33. The samples with references A18, A19, A20 and A21 exhibit a leather coloration, which could be due to the possible formation of a brown iron-chromium spinel. Figure 12 plots the chromatic co-ordinates a* and b* of all the colours found

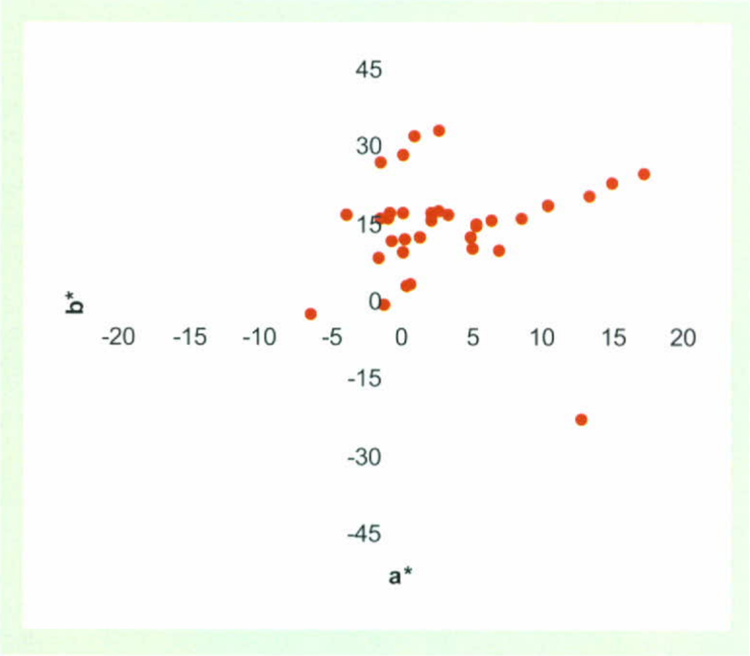

*Figure 12 Plot of the chromatic co-ordinates found in the CIE-L*a*b* system.*

5. CONCLUSIONS

The results obtained enable drawing the following conclusions:

1. Coloured frits have been produced capable of developing glazes of a glass-ceramic nature adapted for porcelain tile bodies.
2. The crystalline phases detected in the glazes have been anorthite phase as major phase, beside gahnite, diopside and zircon phases.
3. The presence of a chromophore agent has been evidenced in all the cases, incorporated next to the crystalline phases.
4. Self-colouring glass-ceramic glazes have thus been produced in the same single-fire process adapted to porcelain tile cycles.
5. The glass-ceramic glazes developed exhibit good mechanical resistance properties with regard to scratch hardness and Vickers microhardness.

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