DEVELOPMENT OF THERMOGLAZES, GLAZES WITH ELECTRIC AND THERMAL CONDUCTION PROPERTIES, FOR USE AS THERMAL CERAMIC TILES

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ABSTRACT

In the research lines currently being implemented in the Spanish ceramic manufacturing sector, the term innovation, core of R+D+I (Research+Development+Innovation), is acquiring ever greater importance. Through innovation new materials can be designed, better adapted to their function, opening up new market prospects for the ceramic products developed in the sector.

The objective set in the present study, fruit of the collaboration between Universitat Jaume I and the firm Colorobbia España S.A., was the development of new glazes with certain electric conductivity properties (ionic and/or electronic), which on being deposited on the ceramic tiles and subjected to a potential difference, would also present certain thermal properties, to generate the feeling of a warmer atmosphere on the surface of these tiles, when used in cold environments, as occurs with wooden panelling, parquet, etc.

For this, the glazed surface has been idealised as a resistive-type electric circuit, such that on applying a voltage, electric conductivity develops, and by the Joule effect, there is a loss of energy in the form of heat across the whole glazed surface. The following objectives were thus established for developing the glaze:

- *Allow appropriate electric conductivity (ionic and/or electronic) when an electric potential difference is applied at the ends of the glazed surface of the ceramic tile.*

- *On the basis of the developed electric conductivity, generate heat across the whole glazed surface.*

- *The developed glaze should meet the quality requirements, set out in the standards, for use as floor tiling.*

On the other hand, the role of the ceramic body would be that of heat accumulator, requiring for this purpose a good body-glaze or body-engobe-glaze fit. To be able to apply the developed products, several types of frits were selected in the present work, which are all used in industry.

To modulate the required conduction property for the glaze, different types of crystalline structures were synthesised that have a conducting or semiconducting character, adding these after synthesising to the frit to produce the conducting glaze of a glass-ceramic nature. This glaze composition was applied onto different ceramic surfaces (stoneware and porcelain tile) and fired, respectively using single-fire cycles of 1150° C and 1200° C. The physical parameters of electric conductivity in the glaze were evaluated, distinguishing between ionic conductivity and/or electronic conductivity, after applying a potential difference to the same ceramic tiles, while also evaluating heat generation. The role of thermal accumulator was also studied in the different selected ceramic bodies.

Key words: glazes, electric conductivity, thermal conductivity, ceramics

1. INTRODUCTION

Due to the points involved in the present work, it is important to highlight the interrelation between the electric current and heat generation, through the Joule effect.

Electric energy, just as all forms of energy, can be transformed into another type of energy, depending on the conditions of the circuit through which the current passes. It generally becomes heat, due to mobile electrons continuously hitting the conductor, producing a kinetic energy exchange between the two[1], which leads to a rise in conductor temperature (Joule effect), as indicated in equation [1].

$$Q = Pt = VIt = RI^2t = \frac{V^2}{R}t \qquad [1]$$

where Q is heat (J), P electric power (W), t time (s), I electric current (A), V potential difference (V) and R electric resistance(Ω).

Ohm's Law relates the potential difference (V) applied with the current that flows (I) and resistance (R), according to equation [2].

$$V = IR \qquad [2]$$

where I: Electric current (A), V: Potential difference (V) and R: Electric resistance (Ω).

The electric resistance, R, depends on the dimensions of the sample analysed, while electric resistivity does not depend on the dimensions; both are related by equation [3].

$$\rho = R\frac{S}{L} \qquad [3]$$

where ρ: Electric resistivity (Ω.·m), S: Area of the cross section perpendicular to the direction of the electric current (m^2), L: Distance between the points at which the voltage, sample length is measured (m).

The electric conductivity, σ, is defined as the inverse of resistivity, according to equation [4].

$$\sigma = \frac{1}{\rho} \qquad [4]$$

where σ: Electric conductivity, $(\Omega \cdot m)^{-1} = S \cdot m^{-1}$ and ρ: Electric resistivity, $(\Omega \cdot m)$

Although ceramic materials are commonly considered electric insulators, the range of conductivities that they can end up reaching covers 25 orders of magnitude[2], from the most insulating materials to the most conductive. Figure 1 shows the range of conductivities for common ceramic insulators and conductors[3].

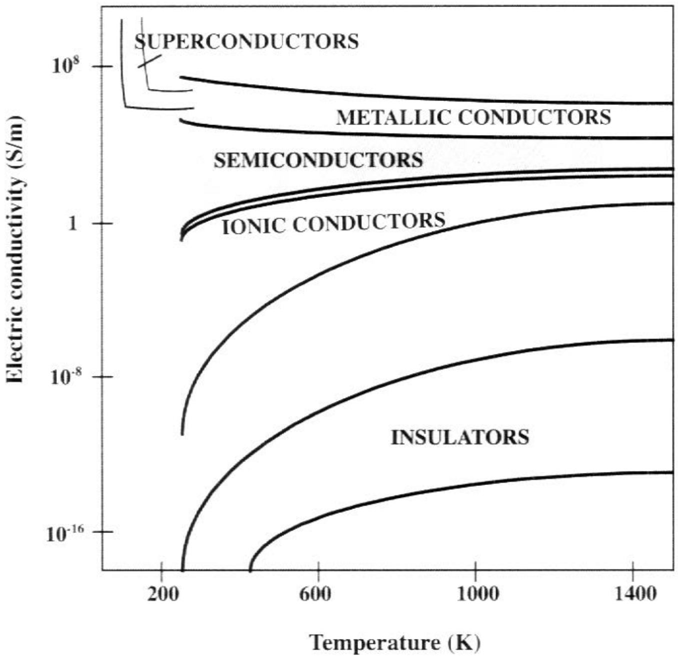

Fig. 1. Different electric behaviour of materials.

In ceramic solids the electric properties depend on the typology of the charge carriers (electrons or ions). If the charge carriers are electrons, it is called electronic conductivity; when the charge carriers are ions, it is referred to as ionic conductivity[4].

Ionic conductivity takes place in materials known as solid electrolytes, superionic conductors or rapid ion conductors[5]. These materials are characterised by rigid structures between which a group of ions forms a mobile subcell. The structural requirements for high ionic conductivity are the availability of holes into which the mobile ions can jump and, on the other hand, that the energy barriers to be overcome by these ions, in order to jump from one hole to another, are small.

Electronic conductivity develops to different extents and through different mechanisms, in a great variety of materials. It is responsible for the electric properties of metals, superconductors and semiconductors.

Semiconductivity lies midway between metallic conductivity and insulators. The number of electrons involved in the process depends on the temperature and level of impurities, in contrast to metallic conductivity. When the electric characteristics of the semiconductor are determined by atoms of impurities (dopant), the material is said to be an extrinsic semiconductor[6]. The ability to dope semiconductors and modify their properties gives rise to many applications and is the basis of the microelectronics industry, amongst others.

Another of the important characteristics in the frame of the present work is heat transmission. In the first place, it is to be noted that the different heat transmission processes are divided into conduction, convection and radiation[7].

Heat conduction is the term given to the exchange mechanism of internal energy from one body to another, or from one part of this body to another. This energy or heat flow goes from higher energy to lower energy molecules, i.e., from the region with the higher to that with the lower temperature[8]. The main characteristic of conduction is that it takes place within the limits of the body or through the line separating two touching bodies, without producing appreciable displacement of the matter of which they are made. In a simplified form, conduction is given by equation [5]:

$$Q = \frac{c_t S \Delta T t}{L} \qquad [5]$$

where the quantity of heat transmitted by conduction, Q (J), is proportional to the surface cross section, S (m^2), at the difference in temperature, $(T_1-T_2)=\Delta T$ (K), in the period of time, t (s), and inversely proportional to the distance between the two cross sections considered, L (m), where c_t is thermal conductivity ($J/(K\cdot m\cdot s)$).

Convection is the mechanism of heat transmission in a fluid when mixing a part of this with another, due to the movement of the fluid mass. However the real process of energy transmission from one particle or molecule of the fluid to another continues to be conduction; it is considered to be convection because the energy can be transported from one point of the space to other points by the very displacement of the fluid. As in the case of conduction, convection is given, in a simplified form by equation [6].

$$Q = h_c S \Delta T t \qquad [6]$$

where Q is heat gained or lost (J), S surface area (m^2), $T_1-T_2 = \Delta T$ (K) difference in temperature between the surface and the fluid, t time (s) and h_c convection coefficient ($J/(K\cdot m^2\cdot s)$).

Finally, thermal radiation is the electromagnetic radiation emitted thermally by the surface of an excited body. It is emitted in all directions, and when it strikes another body, part of it can be reflected, another transmitted and yet another absorbed. If the incident radiation is thermal, i.e., if it is of appropriate wavelength, the absorbed radiation will be present in the body absorbing it in the form of heat, according to equation [7]. Therefore, heat can pass from one body to another without needing a medium to transport it between the two. A separation can exist, such as air, which is unaffected by this passage of energy.

$$Q = e\sigma ST^4 t \qquad [7]$$

where σ is the Stefan constant (σ=5.67·10^{-8} J·s^{-1}·m^{-2}·K^{-4}), e is called emissivity, whose value ranges between 0 and 1 and depends on the material, S is the energy radiating surface, T its temperature (K) and t time (s).

It is necessary to indicate that though ceramic materials have low thermal conductivity, they are not sufficiently thermally insulating. For this reason ceramic tiles used for flooring do not produce the feeling of warmth that other types of materials do, such as wood, parquet, etc. Thus, in order to compositionally modulate the glazes, a new type of ceramic materials could be developed, of a semiconducting nature, which by causing a small flow of electric current, generates heat release by the Joule effect, giving the feeling of heat that these types of materials do not otherwise provide.

For these reasons, to tackle the present work, it was aimed to develop a new family of glazes capable of generating heat, based on the application of an electric current by the so-called "Joule effect", producing an increase in temperature at the surface of the glazed ceramic tile, while at the same time having the body act as a thermal insulator and enable producing "warm" ceramics, which can be used as floor tiling in cold environments.

For this, the following concrete objectives were set:

1. Production of an electric "semiconductor" glaze.
2. Heat release in the glazed surface after applying a potential difference, which is sufficiently low for safety reasons.
3. The developed glazes should fit the ceramic bodies well and be suited for industrial firing cycles.
4. These glazes should have good physical and chemical properties, as well as meeting standard requirements for use.

2. EXPERIMENTAL

2.1. MATERIALS AND METHODS

First, different types of industrially feasible frits were designed, which enable incorporating the electric conductivity promoting elements and, consequently, the generation of heat, since the purpose of this frit is not only to act as the main glaze constituent, but also to serve as the matrix in which the semiconductor agent particles are dispersed, allowing the following requirements to be met for industrial adaptability:

1. Possess appropriate melt viscosity, as well as suitable coefficients of expansion for its bonding to the body as a glaze.
2. Be suitable for industrial stoneware and porcelain tile single-fire cycles.
3. Have compositional flexibility, since they must allow the variation of constituent contents and admit the oxides and compounds that are to be added for thermal and electric response as a glaze.

Table I details the representative qualitative analysis of a frit of the family of frits developed[9].

Oxides	SiO_2	Al_2O_3	B_2O_3	ZnO	CaO	MgO	Na_2O	K_2O	Sb_2O_3
wt%	58	5	5	10	10	3	1	5	3

Table I. Qualitative analysis of a representative frit of the frits used in the study.

For this the following raw materials were used, all of industrial quality (Table II)

Raw materials	***Content in oxides (wt%)***
Boric acid, H_3BO_3	56% B_2O_3
Borax, $Na_2B_4O_7 \cdot 10H_2O$	49.3% B_2O_3 and 21.9% Na_2O
Quartz, α-SiO_2	98-99% SiO_2
Alumina, α- Al_2O_3	99.3% Al_2O_3
Sodium carbonate, Na_2CO_3	58% Na_2O
Potassium nitrate, KNO_3	46.2% K_2O
Zinc oxide, ZnO	99.5% ZnO
Calcium carbonate, $CaCO_3$	55.8% CaO
Antimony oxide (III), Sb_2O_3	99% Sb_2O_3
Kaolin, $2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$	39% Al_2O_3 and 47% SiO_2

Table II. Composition of the various raw materials used to prepare the frits.

As a semiconductor system the tin oxide system doped with antimony (V) was chosen. For this, SnO_2 (99.9%) was used as well as Sb_2O_3 which is part of the frit formulation[10].

The general methodology used to obtain the semiconductor glazes was based on the frit melting process itself, followed by the addition of SnO_2 in glaze preparation, schematically illustrated in Figure 2.

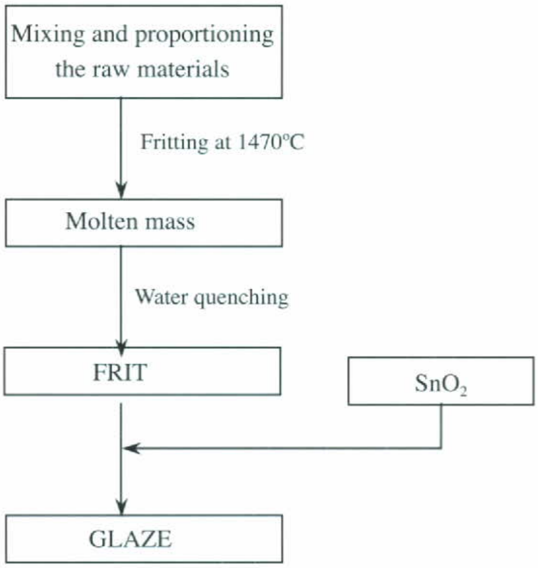

Fig. 2. Methodology of semiconductor glaze synthesis.

Two types of ceramic bodies were selected: red stoneware bodies and porcelain tile bodies.

2.2. HEAT TREATMENTS

The stoneware and porcelain tile specimens glazed with the semiconductor glaze were subjected to single fire industrial thermal cycles at 1150° C for the stoneware body and 1200° C for the porcelain tile body, using identical cycles to those used in industrial production. Figure 3 shows the firing cycles of the glazed stoneware and porcelain tile specimens.

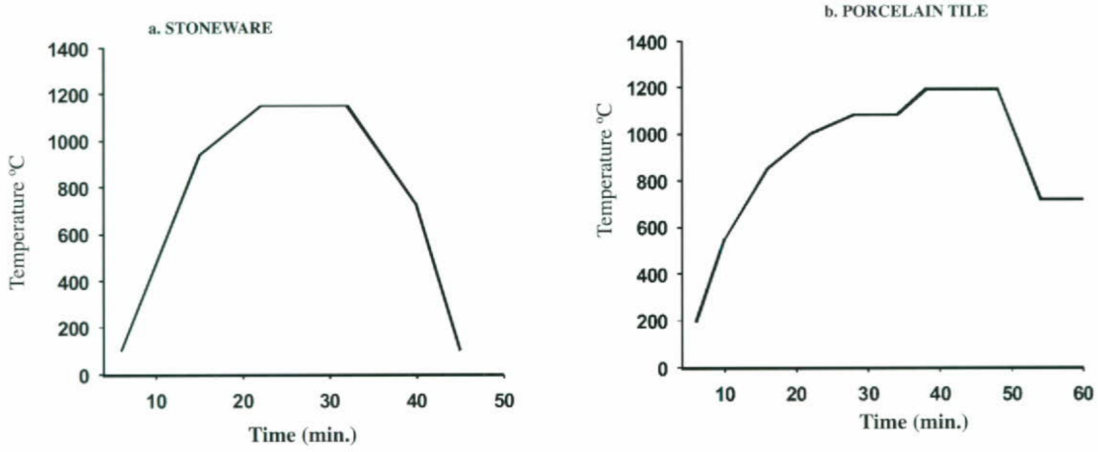

Fig. 3. Thermal treatment for the stoneware (a) and porcelain tile (b) specimens.

This treatment was conducted in a gas-fuelled, single-deck roller kiln for trials at the firm Colorobbia España, S.A.

2.3. CHARACTERISATION TECHNIQUES USED

a) Materials characterisation:

X-ray diffraction. (XRD): The instrument used was a Siemens, model D5000, diffractometer with copper anode. The measurements were performed at an intensity of 20 mA and voltage of 40 kV, in a 2θ range from 10 to 80°. Count step time was 10 seconds and goniometer velocity was 0.050° 2θ/s. This technique was used for the determination of the crystalline phases present in the studied materials.

Scanning electron microscopy (SEM) and microanalysis (EDX): A Leica Mod. LEO440i scanning electron microscope was used with an energy-dispersive X-ray microanalysis instrument, OXFORD, EDX Link-ISIS, with a secondary and backscattering electron detector. Wavelength dispersive X-ray analysis (WDX) was also performed with the CASEMAX, Microprobe Sx50, fitted to an OXFORD scanning electron microscope.

Dilatometry. The measurements were made on a BAHR DIL 803L dilatometer with a heating rate of 5°/min. This was used in frit characterisation.

Hot stage microscopy. A MISURA hot stage microscope was used with a heating rate of 40°/min. This technique enabled determining the characteristic temperatures of each frit.

b) Measurement of electric and thermal properties

Measurement of electric transport properties. By means of a HP, model 4192A, impedanciometer, which measures in the range 100 Hz to 1 MHz.

Measurement of temperature increase. To measure the temperature increase in the glazed surface of the ceramic tile, a device was used similar to the one schematically illustrated in Figure 4. The ceramic tile glaze was connected to an alternate current source, using metal plates to favour contact. Temperature was determined at the surface of the ceramic piece with a thermometer, at different times.

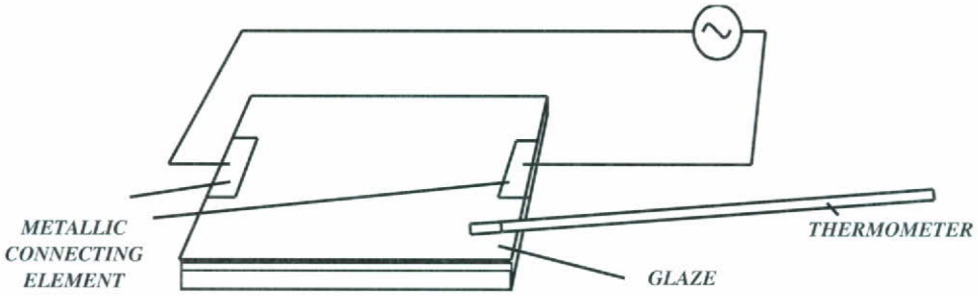

Fig. 4. Scheme used for measuring the increase in temperature at the glazed tile surface.

c) Determination of ceramic tile quality parameters.

The following quality tests were run on the finished products:

Resistance to surface abrasion. The glazed pieces were subjected to abrasion resistance tests according to standard UNE 67-154-92 EN-154.

Chemical resistance. Chemical resistance tests were conducted on the glazed pieces according to standard UNE-EN ISO 10545-13.

Stain resistance. Stain resistance tests were conducted on the glazed pieces according to standard UNE-EN ISO 10545-14.

Scratch hardness of surface according to Mohs. Scratch hardness tests were conducted on the glazed pieces according to standard UNE 67-101.

Vickers microhardness. The Vickers microhardness measurement was carried out according to standard UNE-EN ISO 6507-1. A Matsuzawa, model MHT-1, tester was used, running the tests on the glazed pieces.

Gloss measurement. A Rhopoint Statistical Novoglass instrument was used (Promotest) and the measurements were taken at an angle of incidence of 60° on the glazed tiles.

*Measurement of the chromatic co-ordinates CIE-L*a*b*.* A Minolta CR200 colorimeter was used to measure the chromatic co-ordinates CIE-L*a*b* of the glazed pieces.

3. RESULTS AND DISCUSSION

3.1. STRUCTURAL AND MICROSTRUCTURAL STUDY OF THE SAMPLES

The frit used for the conductive glaze possesses physico-chemical characteristics that make it compatible for industrial use. Figure 5 shows the base frit characteristic temperatures found by hot stage microscopy.

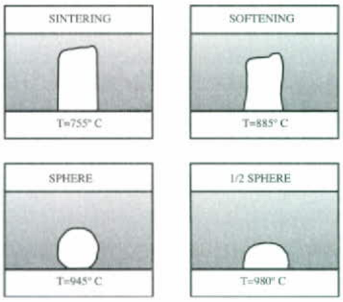

Fig. 5. Characteristic temperatures of the base frit found by hot stage microscopy.

The dilatometric study of the frit (Figure 6) enabled determining transformation temperature ($T_G = 650^\circ$ C), softening temperature ($T_R = 695^\circ$ C), and the coefficient of linear expansion (α) between 50 and 400° C, which was $65 \cdot 10^{-7}$ K^{-1}.

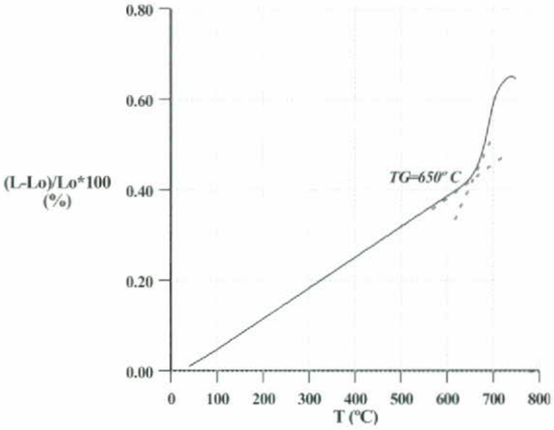

Fig. 6. Dilatometric curve of the base frit.

In the XRD analysis, the conductive glaze is observed to have high crystallinity (Figure 7), due to the addition of crystalline phase SnO_2 after the fritting process and its stability with regard to the frit. To be noted is the absence of other crystalline phases above the XRD instrument detection limit.

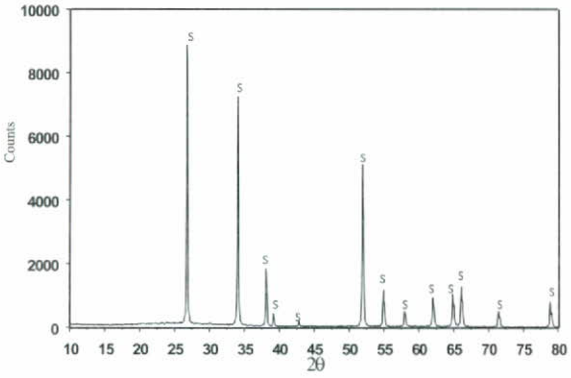

Fig. 7. X-ray diffractogram of the surface of the glaze used (s=SnO_2, cassiterite, ASTM 41-1445).

SEM shows the SnO_2 crystals (Figure 8), already detected by XRD, while Sb cannot be distinguished from Sn by EDX, since they possess similar emission lines (Sn L_α=3.44 and Sb L_α= 3.60) and signal overlapping occurs. For this reason the microprobe with spectrometry analysis by wavelength dispersion (EDL) was used, which enabled discerning between both elements (Figure 9).

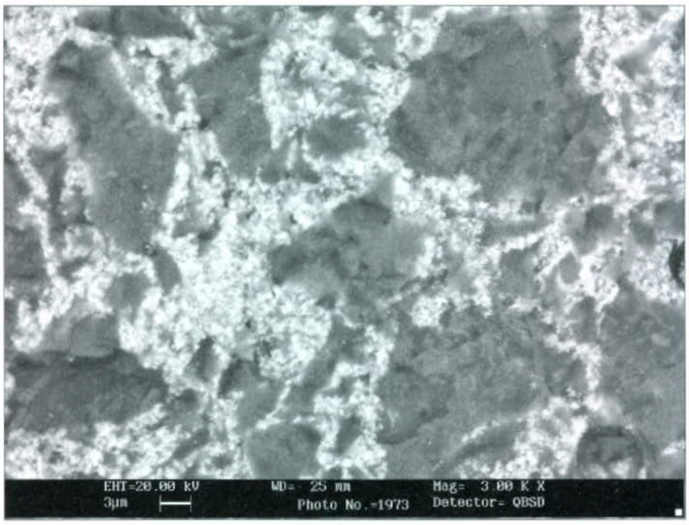

Fig. 8. Micrograph of the semiconductor glaze surface (magnification 3000 x).

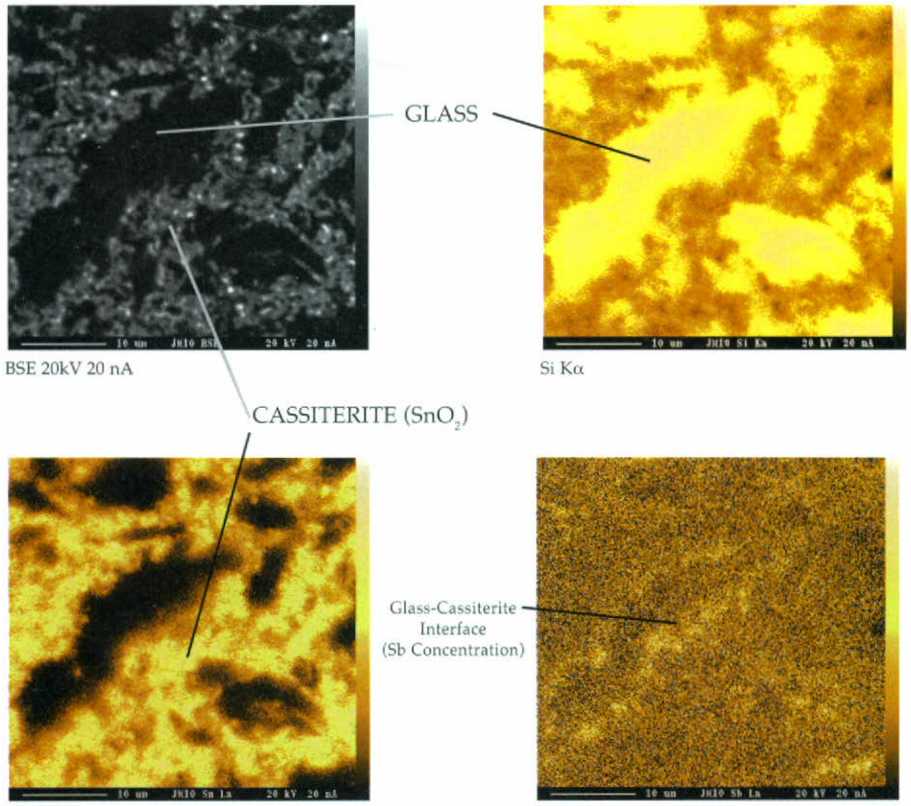

Fig .9. Analysis of element density (mapping) in the semiconductor glaze surface by the microprobe fitted with a wavelength dispersion detector (EDL).

It can thus be observed how the antimony has diffused from the glass toward the glass-cassiterite interface, where the antimony is located next to the SnO_2 grain boundaries. The distribution of antimony around SnO_2 and its introduction in the network generates areas in the cassiterite particle surface in which the electric conductivity will be high, and far more than that of the glass or the cassiterite particles themselves.

To explain this conductivity, a microstructural model is proposed in which the antimony acts as a dopant, but does so in the surface layer of the SnO_2 particles, generating a network of contacts that are schematically presented in Figure 10.

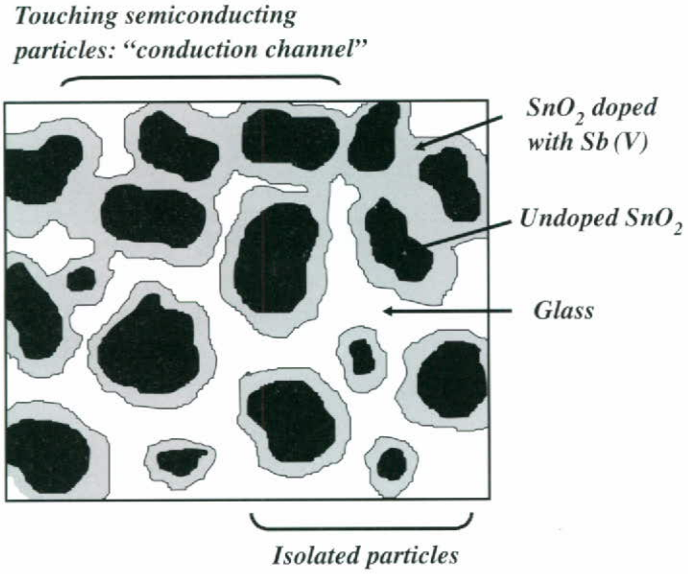

Fig. 10. Microstructural model of a glaze that incorporates the SnO_2 semiconductor doped with Sb(V).

3.2. STUDY OF THE QUALITY PROPERTIES OF THE RESULTING GLAZED PIECES

Table III details the most significant results found on carrying out the different quality tests according to the standards for the ceramic tiles glazed with the semiconductor glaze.

TEST	APPLIED STANDARD	CLASSIFICATION	TEST SOLUTIONS	EFFECTS
Determination of abrasion resistance	UNE 67-154-92 EN-154	CLASS IV		
Determination of chemical resistance	UNE-EN-ISO 10545-13	GA	Ammonium chloride and sodium hypochlorite	No visible effects
		GLA	Acids and alkalis in low concentration	No visible effects
		GHA	Acids and alkalis in high concentration	No visible effects
Determination of stain resistance	UNE-EN-ISO 10545-14	5	Chromium oxide in light oil	Stain removed
		5	Iodine/alcohol solution	Stain removed
		5	Olive oil	Stain removed

Table III. Most significant results of the quality tests performed.

3.3. THERMAL STUDY OF THE SAMPLES

The glazed ceramic tiles were set in a resistive circuit, such as the one shown in Figure 11.

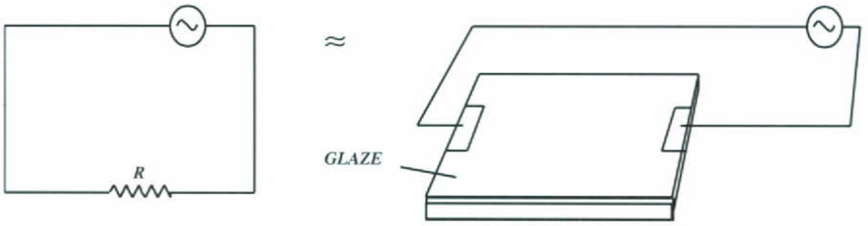

Fig. 11. Scheme of the ceramic tile set in a resistive circuit in AC.

When these tiles were subjected to different voltages, the following ΔT values were found for the different times (Table IV).

	220 V		110 V		60 V	
T (min)	**T (°C)**	**ΔT (°C)**	**T (°C)**	**ΔT (°C)**	**T (°C)**	**ΔT (°C)**
0	25	*0*	25	*0*	25	*0*
5	38	*13*	29	*4*	28	*3*
10	47	*22*	32	*7*	29	*4*
15	51	*26*	34	*9*	30	*5*
20	54	*29*	34	*9*	30	*5*
25	56	*31*	35	*10*	31	*6*
30	57	*32*	35	*10*	31	*6*
35	58	*33*	35	*10*	31	*6*
40	58	*33*	35	*10*	31	*6*
45	59	*34*	36	*11*	31	*6*
50	60	*35*	36	*11*	31	*6*
55	60	*35*	36	*11*	31	*6*
60	61	*36*	36	*11*	31	*6*
65	61	*36*	36	*11*	31	*6*
70	61	*36*	36	*11*	31	*6*
75	61	*36*	36	*11*	31	*6*
80	61	*36*	36	*11*	31	*6*

Table IV. Temperatures and temperature increases of the glazed tile surface as a function of time at different voltages.

The values of ΔT versus time are plotted in Figure 12.

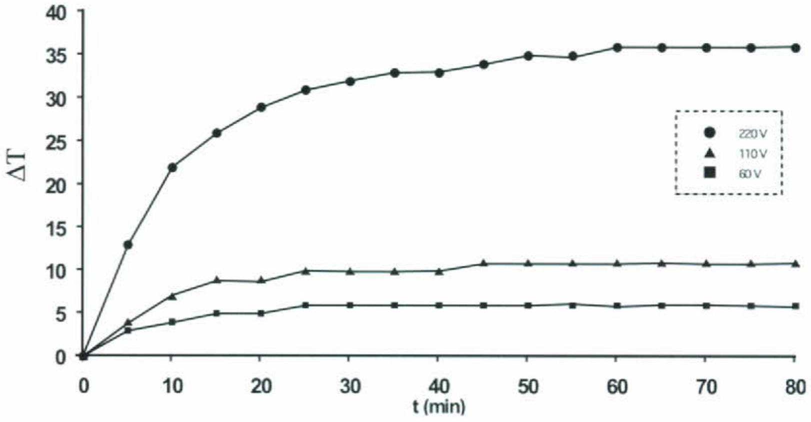

Fig. 12. Variation of DT in terms of applied voltages and time.

With equations [1], [5], [6] and [7], taking into account that the heat consumed by a body in raising temperature is found from equation [8]:

$$Q = mc_e \Delta T \qquad [8]$$

where Q is heat (J), m mass (kg), T_1-T_2 = ΔT (K) the difference in temperature, and c_e specific heat (J/(kg·K)),

leads to equation [9], in which the heat produced by the Joule effect causes temperature to rise in the body (tile) itself and be dissipated by conduction, convection and radiation to the surroundings.

$$\frac{V^2}{R} t = mc_e \Delta T + \frac{c_t S \Delta T t}{L} + h_c S \Delta T t + e\sigma S T^4 t \qquad [9]$$

where V is potential difference (V), R electric resistance (Ω), t time (s), m mass (kg), ΔT the difference in temperature (K), c_e specific heat (J/(kg·K)), S surface area (m²), L distance between two cross sections considered (m), c_t thermal conductivity (J/(K·m·s)), h_c coefficient of convection (J/(K·m²·s)), e emissivity, σ the Stefan constant ($\sigma=5.67 \cdot 10^{-8}$ $J \cdot s^{-1} \cdot m^{-2} \cdot K^{-4}$) and T absolute temperature of the body (K).

Thus, the dependence can be observed of the increase in temperature with V^2, a fact clearly shown in Figure 11, in which ΔT decreases on reducing the applied voltage for the same times.

Moreover, depending on the applied voltage, there is a tendency for the value of ΔT to stabilise, which would be explained by equation [9], since the factors belonging to heat dissipation begin to take on more importance against the heat used in increasing the body's own temperature.

According to these data and with the current standard[11] (MI BT 021), the use of these tiles as flooring in housing can be considered feasible, since with the appropriate protection and commonly used systems, such as grounding or insulation, they would involve no danger at all.

4. CONCLUSIONS

The results found in the study allow drawing the following conclusions:

A ceramic glaze has been developed based on $SnO_2 - Sb_2O_5$ semiconductor system of industrial applicability, adapted to stoneware and porcelain tile bodies, which exhibits good physico-chemical properties of use.

The frit and end glaze compositions were optimised, achieving resistance values of the order of 103 W at the glazed tile surface.

After applying a low potential difference, the developed ceramic glaze generates heat and thus the desired feeling of warmth.

The rise in temperature of the glazed ceramic tile was found to depend on the applied potential, so that at the same times, increasing voltage enabled raising temperature.

After reaching a maximum temperature value, a thermal equilibrium is reached owing to the competition between generated heat and dissipated heat.

According to current regulations (MI BT 021) the use of these ceramic tiles can be considered feasible as floor coverings with the appropriate installation of protection systems for overvoltage.

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