

DEVELOPMENT OF CERAMIC GLAZES WITH OPTICAL ABSORPTION AND EMISSION PROPERTIES: APPLICATION AS WALL TILE GLAZES WITH SANITARY (BACTERICIDAL) PROPERTIES

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ABSTRACT

The present study describes the development of a ceramic glaze (frit), which on application exhibits optical properties with a bactericidal effect.

The material obtained, compared to similar existing products, presents improved wear resistance in service, high gloss and potential use in sanitary products and ceramic wall tiles.

The material was developed by selecting rare-earth oxides, whose compatibility was studied in different frit formulations, subsequently measuring their absorption and emission properties in the ultraviolet to infrared radiation range.

The properties of the materials obtained were characterised and measured by UV and visible absorption spectrophotometric techniques, emission (photoluminescent spectrum), and infrared as well as nuclear magnetic resonance spectroscopic techniques (¹H RMN).

Structural, microstructural and microanalytical studies were also conducted on the prepared samples by X-ray diffraction (XRD) and scanning electron microscopy (SEM) in an instrument equipped with energy dispersive X-ray microanalysis (EDX).

*Finally, the properties were assessed which the materials developed exhibited as finished products. These involved refractive properties (gloss) and bactericidal capability, selecting for the latter case certain strains of bacteria (*Scherichia coli*, *Pseudomona aeruginosa* and *Stafilococcus aureus*), and analysing the degree of growth or absence of growth of these colonies by optical microscopy and image analysis.*

[1]. "Progress in Inorganic Chemistry". Vol. 44. Published by: G. J. MEYER, JOHN WILEY AND SONS, Nueva York, 1997.

1. INTRODUCTION

At present a new field known as photochemistry is being developed in Solid State Chemistry. The research results not only have fundamental implications but also open up a vast potential of real technological applications. Recently "Progress in Inorganic Chemistry" published a monograph entitled: "Molecular Level Artificial Photosynthetic Materials", dealing with aspects of the molecular nature of Chemistry and Materials Science in the field of artificial photosynthetic materials design, which can convert solar energy into other products that yield energy or directly in electricity. This requires integrating a variety of factors in the material that is developed. Such factors include light absorption, electron and/or energy transfer processes, and finally the obtainment of useful products with interesting properties^[1].

The literature has traditionally described sensitised wide-bandgap semiconductors^[2]. Typical wide-bandgap semiconductors are the n-types such as TiO₂, ZnO and SrTiO₃, which exhibit high stability, easy processibility, and do not decompose under radiation. The sensitisation process of a semiconductor material involves an absorption capacity in a range of wavelengths exceeding the gap. This phenomenon became known in 1873 following Vogel's^[3] investigations into organic inks deposited on semiconductor halogen mineral grains, when he managed to raise the photosynthetic sensitivity of these particles in low energy regions of the spectrum (visible region). This system simply consists of an optically active molecule that can be excited electronically, and on being adsorbed onto the semiconductor surface allows introducing the excited electron into the conduction band, thus generating photoelectrochemical and photocatalytic processes.

Vogel's work led to extensive research that has continued up to the present decade^{[4], [5], [6]}. These studies have produced important advances in the degree of understanding of the fundamental processes involved, such as degree of sensitisation, light absorption efficiency and development of single-layer manufacturing techniques.

In recent years research has focused on TiO₂ production with nanoparticle sizes to raise specific surface area and increase the gap. Progress has also been made in developing new synthesis methods (sol-gel methods), and transparent film applications. This has allowed developing photoanodes and thin layer solar cells combined with an appropriate photosensitive pigment, thus achieving sunlight-electricity conversion efficiencies of the order of 7 to 10 %.

The literature^[7] reports numerous examples of molecular photosensitisers designed using TiO₂ with transition metal complexes, together with chlorophyll derivatives and natural porphyrins.

These studies have led to a new line of research focused on synthesising

[1]. "Progress in Inorganic Chemistry". Vol. 44. Published by: G. J. MEYER, JOHN WILEY AND SONS, Nueva York, 1997.

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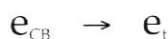
[5]. T. A. HEIMER, C. A. BIGNOZZI Y G. J. MEYER, J. PHYS. Chem., 97, 11987, (1993).

[6]. R. ARGAZZI, C. A. BIGNOZZI, T. A. HEIMER, E. N. CASTELLANO AND G. J. MEYER, *Inorg. Chem*, 33, 5741, (1994).

[7]. A. KAY Y M. GRÄTZEL, J. PHYS. Chem., 97, 6277 (1993).

semiconductor pairs that exhibit different electronic gaps such as CdS-ZnO, CdSe-TiO₂, which exhibit non-linear optical properties^{[8], [9]}.

A new method was developed by the Toto company, based on superhydrophilic photocatalytic technology (Honda-Fujishima effect invented by professor Honda and professor Fujishima of Tokyo University in the 70s, and patented by Toto). It has a bactericidal effect by capturing charge bearers. The optical excitation of electrons is produced by means of colloidal semiconductor particles having a high fault density. The free bearers are trapped in the faults in which they undergo radiative and non-radiative recombination, as set out in the scheme:



where e_{CB} and h_{VB} are free charge bearers in the valence and conduction bands, and e_t and h_t are respectively the trapped electrons and holes. In this fashion, there arises a great charge accumulation in the minute structure of a semiconductor colloid, which produces increased efficiency in interface redox reactions on the colloid surface. This fact, consisting of simultaneously trapping photogenerated holes and electrons has recently been demonstrated in colloidal TiO₂ suspensions. Moreover, these trapped charge bearers exhibit characteristic absorption bands in the infrared and ultraviolet regions. Studies have also been performed by trapping electrons in ZnO, WO₃ and SnO₂ colloids, investigating the photolysis phenomenon by laser flashes. These experiments have led to technology applications such as the development of photochromic materials^{[10], [11]}.

As an example, the photocatalysis phenomenon consists of a semiconductor that breaks down organic compounds in water or those in the air by oxidation through exposure to light.

On the other hand, the rare-earth oxides present electron transfer bands at f-f level transitions of levels. Fig. 1 schematically depicts interaction between photons (light) and matter. There are certain properties of electron activity, which are desirable such as energy-level promotion of electrons, usually between the fundamental atomic state and a higher level. Such charge transfer generally produces optical absorption phenomena in the visible and near UV spectrum, as well as emission phenomena. This has allowed developing all the laser technology (ruby, Cr⁺³, RE⁺³ rare earths).

In rare earth and transition metals compounds, the absorption bands can be attributed to electron transitions centred on individual atoms having incomplete "d" or "f" levels. Thus the rare-earth oxides exhibit broad absorption bands in the visible spectrum, which indicate electron transfer under low energy conditions.

[8]. D. LIU Y P. V. KAMAT, J. PHYS. Chem., 97, 10769 (1993).

[9]. E. CORDONCILLO, J. B. CARDIA, M. A. TENA, G. MONRÓS AND P. ESCRIBANO, J. Sol-Gel Science and Technology, 8, 1043, (1997).

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[11]. M. R. HOFFMANN, S. T. MARTÍN, W. CHOI AND D. W. BAHUEMANN, "Environmental applications of semiconductor photocatalysis". Chem. Rev, 95, 69-96, (1995).

In this way, sensitised luminescence involves enabling the absorbed energy of an ion (sensitiser) in an absorption band to be emitted in the emission band of another ion (activator). Energy transfer from the sensitiser to the activator occurs through the following types of transfer: emission-reabsorption, non-radiative resonant, and non-radiative non-resonant transfer^[12].

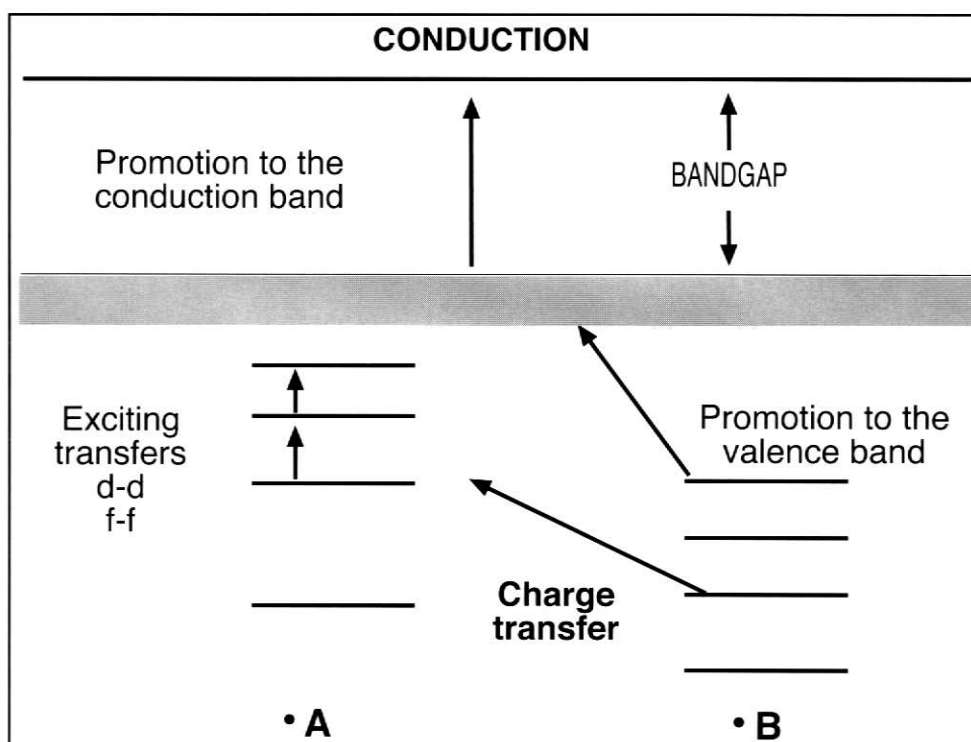


Figure 1. Electron transfers in solids affecting optical properties. Energy levels are shown for two atoms, A and B, together with some characteristic electronic states in solids.

In recent years, hospital hygiene has received special attention, as a result of the spread of infections, basically staphylococcal, streptococcal, pseudomonal infections, etc., whose origin is to be sought in hospital staff themselves, as healthy bearers of agents causing these infections owing to continuous contact with patients.

Traditionally the spread of this type of infection was fought by effective traditional prophylactic action and using air conditioning, which together with the use of UV lamps allow sterilising the environment.

Air is a potential source of micro-organisms that can contaminate surgical wounds. The relationship between environmental microbial contamination and the infection of surgical wounds has been shown in surgery, and in clean orthopaedic surgery with knee or hip transplants. The extent of microbial air contamination depends on many factors, such as the number of persons present, their movement, or presence of air streams and measuring system used.

Hospital hygiene could at present be improved by installing wall tiling with bactericidal (bacteria killing) or bacteriostatic (bacterial growth inhibiting) characteristics, since this would eliminate or reduce the spread of a great number of

[12]. "Spectroscopy, luminiscence and radiation centers in minerals". Mc. Furning, Springer-Verlag, Berlín, 1979.

common bacteria in these centres, such as *Scherichia coli*, *Pseudomona aeruginosa* and *Stafilococcus aureus*, etc.

In the present study, a suitable glassy matrix composition was chosen, modulating the addition into the formulation of a rare earth in the fritting process, in order to use the already mentioned absorption and emission properties of rare-earth oxides. The resulting composition was applied as a glaze to ceramic wall tile specimens, using both single and double firing. The aim was the development of materials, which after application as glazes and subsequent firing would exhibit good quality performance and aesthetic properties (mechanical strength and gloss) and have a bactericidal affect.

These wall tiles are of particular interest in operating theatres, hospitals, food-processing rooms, slaughterhouses, school dining halls and canteens, kitchens, bathrooms and other sanitary facilities, etc.

2. EXPERIMENTAL DEVELOPMENT

2.1. CHARACTERISATION TECHNIQUES USED

To suitably characterise the materials developed in the present study and measure their properties, the following analytical and instrumental techniques were used:

- DILATOMETRY: BÄHR, Model DIL801L, instrument with a heating rate of 10°C/min.
- Mechanical measurements by Vickers measurements with a MATSUZAWA MHT-1 microhardness tester, up to 2 kg force.
- Microcharacterisation by scanning electron microscopy with a LEO, series 6300, instrument and an Oxford ISIS spectrometer, characterising the materials by image formation with back-scattered and secondary electrons. Images were also obtained by cathodeluminescence with a PHILIPS scanning electron microscope fitted with a cathodeluminescence detector.
- Absorption measurements in the UV and visible range were run on a PERKIN-ELMER, Model UV/VIS LAMBDA 19, spectrophotometer applying the diffuse reflectance method for solids.
- SIEMENS Model D5000X-ray diffractometer, running at 20 mA and 40 kV, with a Cu k_{α} cathode and Ni filter, fitted with a graphite secondary monochromator. Low angle determinations were performed to determine the glassy halo exhibited by the specimens, as well as scanning between 20 and 70° (2 θ) to analyse for crystalline phases.
- Emission measurements were run in a photoluminescent spectrophotometer collected by specimen excitation with 1000 W tungsten lamp light passing through an 0,5 m double monochromator.
- Microbiological analysis was carried out in a recognised microbiology laboratory. Optical microscopy and image analysis and processing with a LEICA instrument via the Quantimex Q600 software were used to assess bacteria growth or non-growth.

2.2. MATERIALS AND METHODS

The objective at the outset was to obtain a glaze, which on application to a ceramic wall tile, would be capable of interacting with light and would produce optical phenomena, either as emissions or photocatalytically (with electron transfer), and would be capable of destroying the bacteria that settled on the tile surface. Moreover, the glaze coating needed to also be suited to the industrial ceramic production process.

It was therefore decided to develop a ceramic a ceramic glaze, which on application to a ceramic wall tile body would be capable of withstanding firing in an industrial kiln, while exhibiting the requisite bactericidal property.

The methodology adopted in conducting the present study has been set out in Fig. 2.

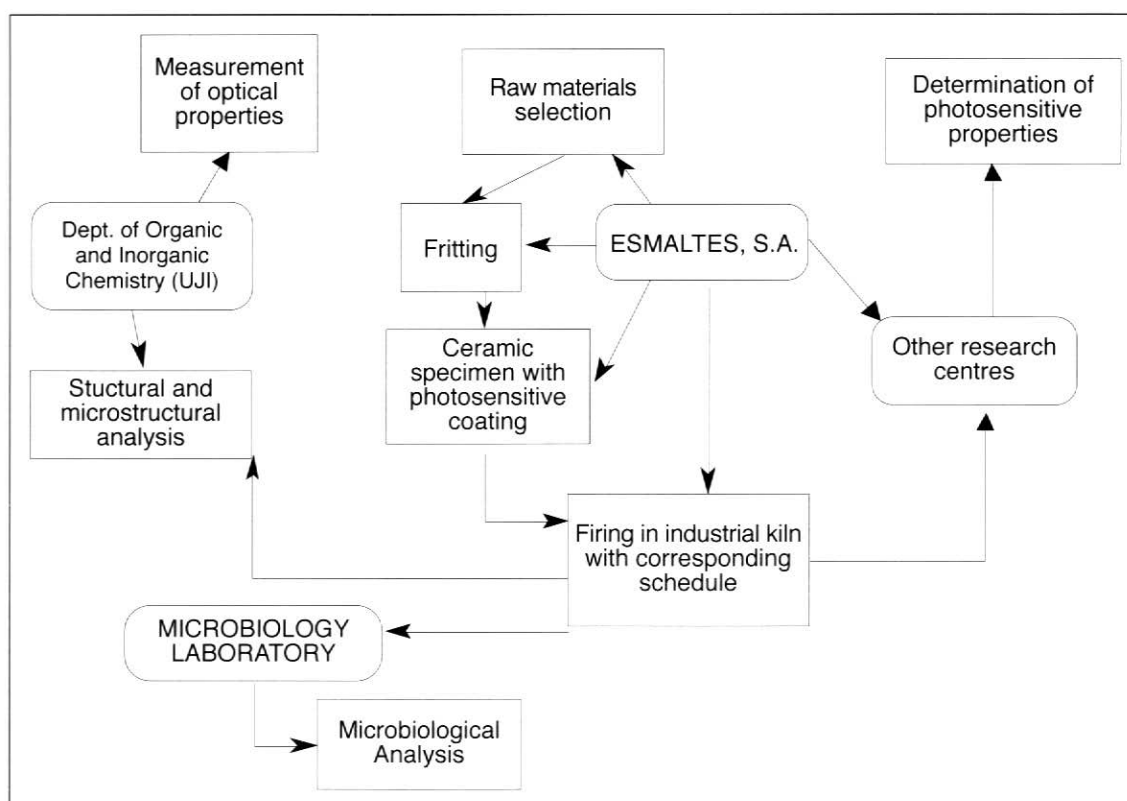


Figure 2. Diagram setting out the methodology adopted in the study.

A thorough study was therefore undertaken. The behaviour was analysed of different chemical elements (rare-earth oxides), capable of developing optical absorption and emission as well as photocatalytic properties on being incorporated into glassy matrices formed from acid (RO_2), basic (R_2O/RO) and amphoteric (R_2O_3) oxides, which were stable at high temperatures, subsequently studying their bactericidal behaviour.

2.3. RESULTS AND DISCUSSION

A qualitative formula was found as a result of all the experimentation, whose partial composition lay within the following ranges (Table I):

Oxide	wt%
SiO ₂	35-55
Al ₂ O ₃	5-10
CaO	5-10
Na ₂ O	0-5
K ₂ O	0-5
B ₂ O ₃	5-10
ZrO ₂	0-5
ZnO	5-10

Table I. Compositional ranges of the selected glaze.

2.3.1. BACTERICIDAL GLAZE PREPARATION

The rare-earth oxide that was to develop the bactericidal property was added to the above formulation.

After fritting, the material was applied by screen printing and spraying (fume) onto a substrate consisting of a fast double- or single-fired ceramic body, engobe and conventional glaze.

The prepared specimens were fired in industrial kilns according to standard tile production firing schedules, without modifying either schedules or firing atmosphere.

On firing the specimens were run through the various analytical and biological control techniques listed above. Their optical behaviour was studied in terms of composition and interaction with different luminous radiations (infrared, visible and UV light).

On establishing the bactericidal frit formula, three reference glazes A, B and C were developed, conditioned to fast double firing (reference glaze A), and porous single firing (reference glazes B and C).

2.3.2. STRUCTURAL AND MICROSTRUCTURAL MATERIALS CHARACTERISATION

A dilatometric study was carried out of the three bactericidal glazes developed. The results are detailed in Table II.

Glaze	T _G (°C)	SP (°C)	α (50-300°C)·10 ⁻⁷	γ (50-300°C)·10 ⁻⁷
A	610.1	700	68.04	204.12
B	609.5	710	72.2	216.61
C	613.2	704	68	204.01

Table II. Dilatometric analysis of the formulated glazes.

Morphological and compositional studies were run on the three glazes developed by SEM. As an example Fig. 3 shows a micrograph of glaze A, obtained by secondary electrons at low magnification (500x). Owing to the poor resolution found in this type of detection owing to the nature of the materials involved, micrographs were obtained by back-scattered electrons (Fig. 4). This technique allows the various compositional constituents to be differentiated by their atomic weight. The elements having lighter atomic weights showed up in darker shades (Si, Al), while the heavier ones (Ca, Mg, Zr, Zn) appeared in paler or lighter shades. Thus, helped by microanalysis techniques through point analysis with light spots below 1 μm, it was established that the dark points

consisted of aluminium and silicon particles, which could correspond to silica and aluminosilicate microcrystallisations. The detected lighter points signalled the presence of silicon and zircon, which might in this case correspond to the formation of small zirconium oxide and zircon crystals.

Analysis of element surface distribution by mapping showed a regular distribution of all elements, with the silicon and zirconium content being concentrated in the darker points, which were the source of silica, zircon and zirconate crystals. A highly regular distribution was also found for the rare-earth element added to the composition (Fig. 5).

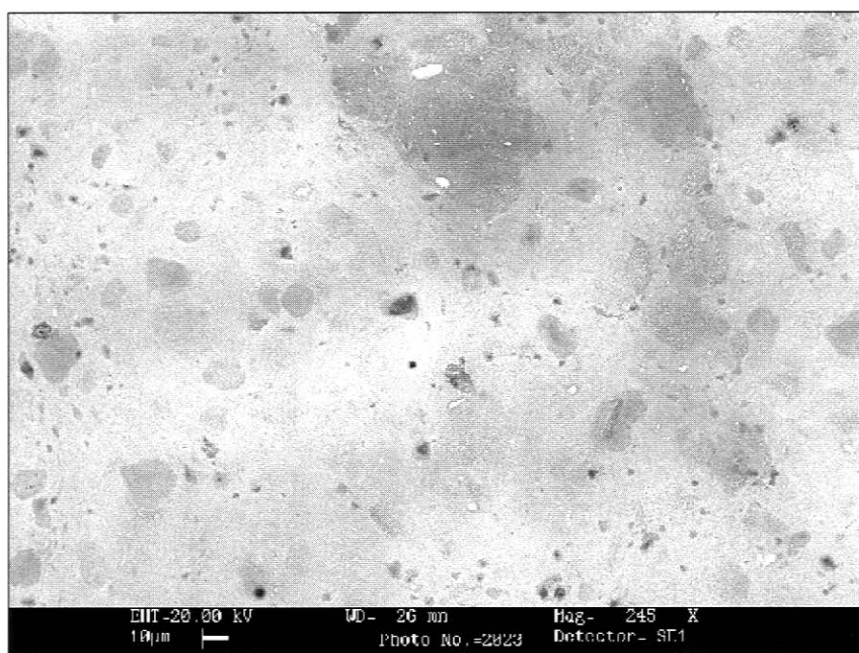


Figure 3. SEM micrograph obtained by secondary electrons.

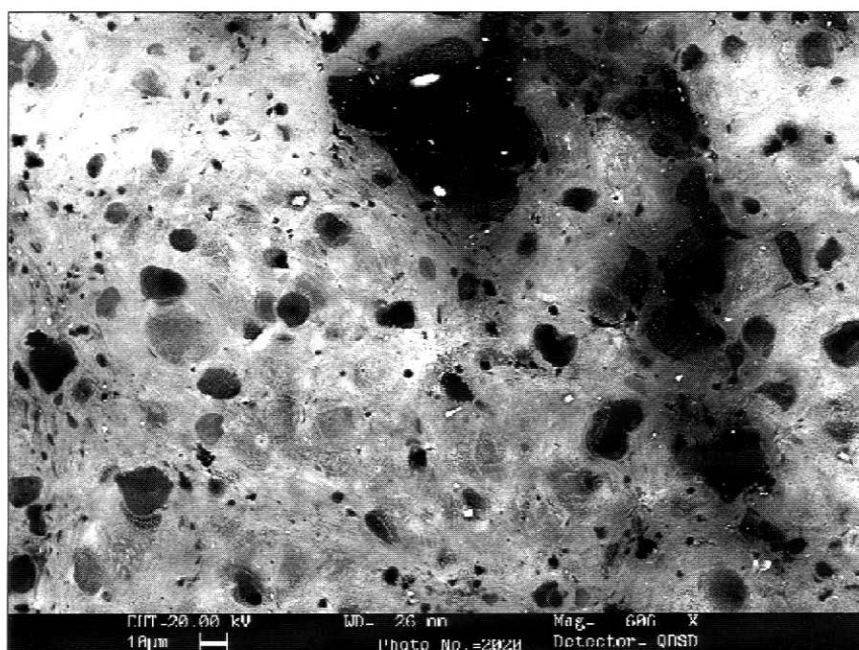


Figure 4. SEM micrograph obtained by back-scattered electrons.

In view of the possible luminescent properties that these materials could exhibit, the materials were examined by SEM fitted with a cathodeluminescent detector. Fig. 6 shows the resulting micrographs. The luminescent material appears in the micrograph with a greater gloss signal compared to the reference value, indicating greater emission by the former.

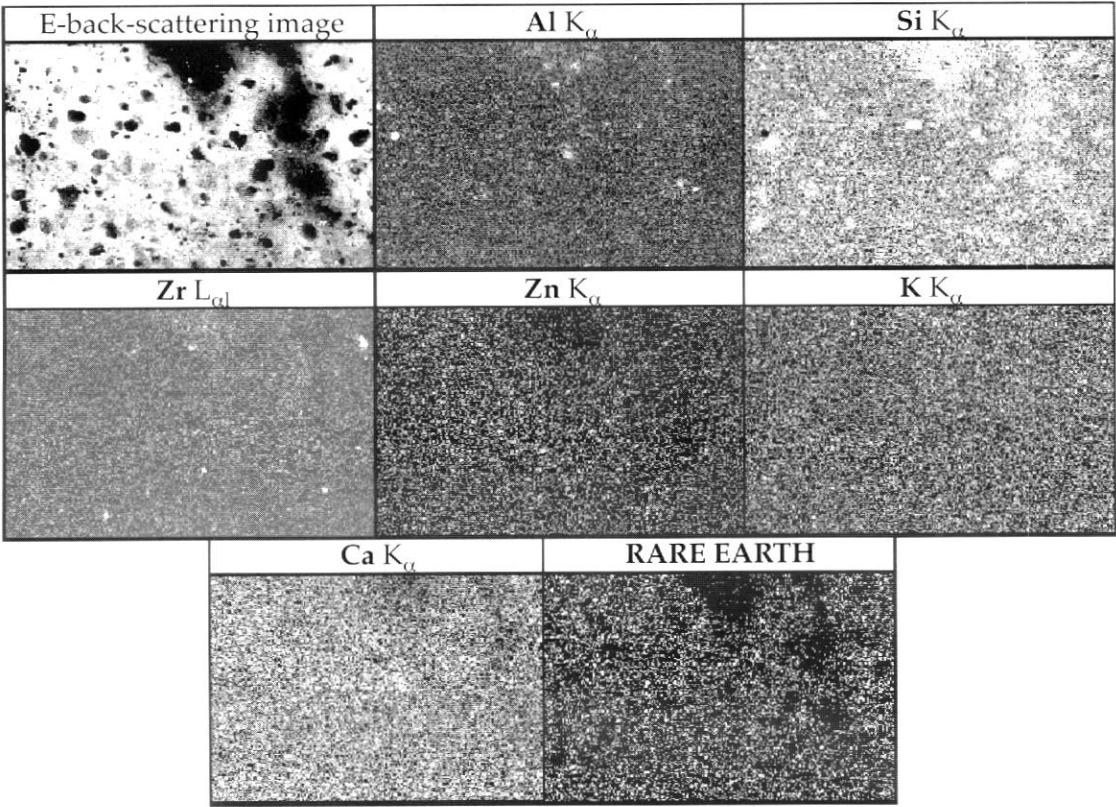


Figure 5. Elemental surface distribution analysis by mapping.

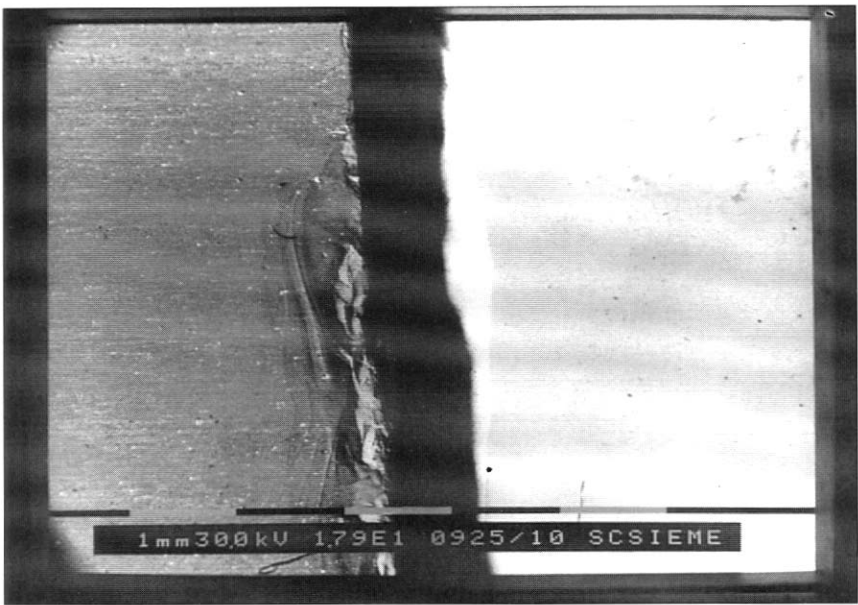


Figure 6. SEM micrograph obtained with a cathodeluminescent detector. Reference a is the image of the glazed ceramic tile with the conventional glaze, while reference b corresponds to the ceramic specimen also coated with the bactericidal glaze.

2.3.3. MEASUREMENTS BY INFRARED, VISIBLE AND UV SPECTROPHOTOMETRY

The absorption properties were determined in the finished products in the UV and visible spectrum region (Fig. 7), showing a broad shoulder between 200 and 400 nm (wavelength values), which indicates intense absorption by the material in the UV range. Beyond 400 nm and in the visible spectrum region, the material exhibited little absorption.

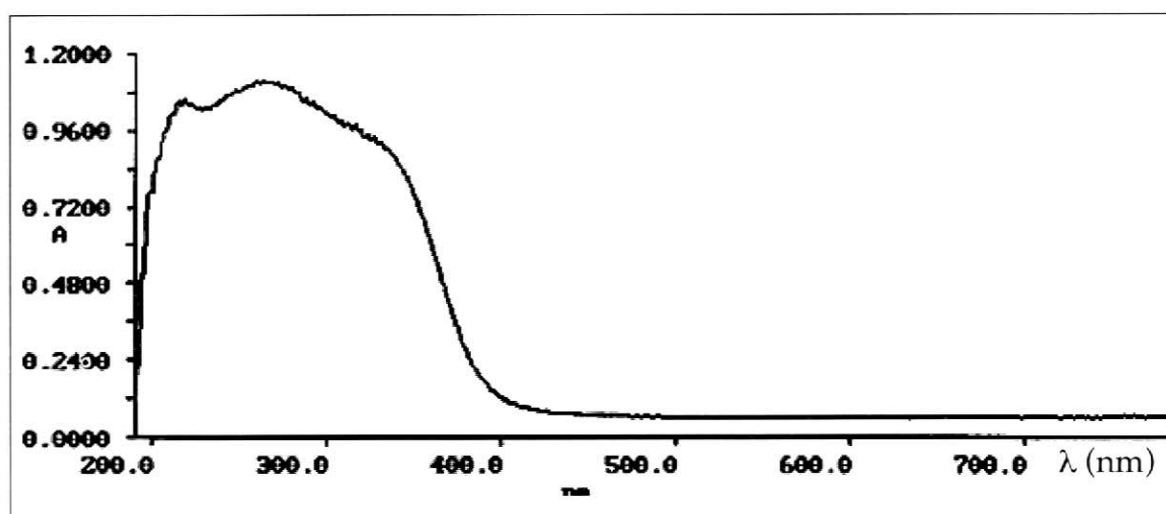


Figure 7. Bactericidal glaze absorption spectrum.

The transmittance spectrum of the same finished product was also determined in the visible to infrared range (Fig. 8). The material exhibited little absorption over this whole range, although two small distinguishable shoulders could be observed in the infrared region (around 1800-1900 nm and 2500-3000 nm).

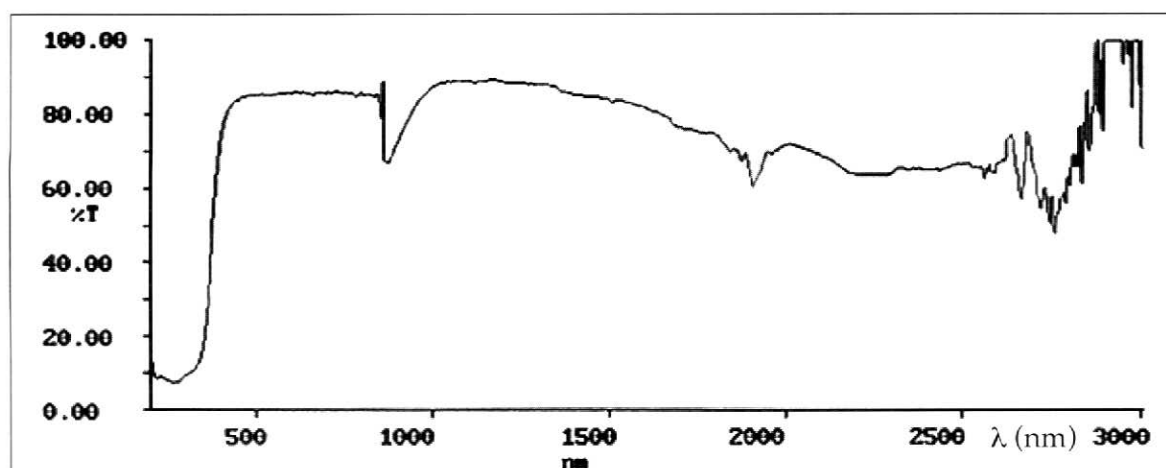
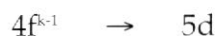


Figure 8. Bactericidal glaze transmittance spectra.

It should be noted that the spectral aspects of the lanthanides are fundamentally different from those of block d corresponding to the transition elements. The basic reason for this difference lies in the electrons that are responsible for ion properties being 4f electrons, and that the 4f orbitals are protected very effectively against external influences by external shells 5s² and 5p⁶. For this reason the states arising

form the various $4f^n$ configurations are only slightly affected by the medium surrounding the ions, and remain virtually invariable for a given ion in all their compounds^[13].

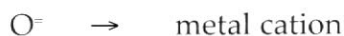
Rare-earth elements of general electron configuration $4f^n(5s^25p^6)5d^0$ permit mixed electron transitions:



and also between:



as well as forbidden bands owing to f-f transitions, both in absorption and luminescence, yielding an intense broad band in the absorption spectrum. The presence of absorption bands owing to charge transfer between anion and cation are also to be taken into account:



which because of its energy values tends to fall in the UV region.

Another effect also to be taken into account is the presence of impurities in the material, which can logically appear on producing such a multi-component material as the product developed in this study.

2.3.4. MEASUREMENT OF EMISSION PROPERTIES

The excitation and emission spectra were determined of the developed bactericidal material. Fig. 9 presents the respective spectra.

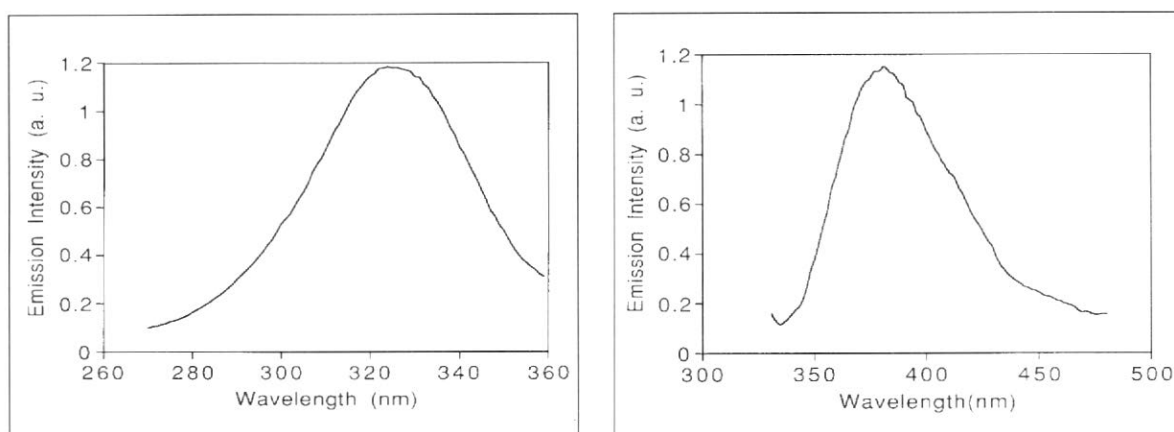


Figure 9. Excitation (A) and emission (B) spectra of the developed material.

As Fig. 9 shows, excitation peaked at 330 nm while emission peaked at 380 nm, both in the UV region, thus perfectly matching the above absorption spectra.

[13] A. S. MARFUNIN, "Spectroscopy, Luminescence and Radiation Centers in Minerals", De. Springer-Verlag, Berlin, 1979.

2.3.5. QUALITY CHARACTERISTICS OF THE DEVELOPED GLAZE

Indentations were run on the finished specimens with a Vickers microhardness tester, at a force of 100g for 25 sec, obtaining the data detailed in Table III.

Body	Vickers microhardness HV (kgf/mm ³)	
	Specimen with conventional glaze	Specimen with bactericidal glaze
Single firing	521	507
Fast double firing	509	513

Table III. Comparison of Vickers microhardness test data on a normal glazed ceramic specimen and a similar glazed specimen that was also coated with the bactericidal glaze.

The data show that the resulting bactericidal glaze exhibited similar characteristics to the conventional glaze.

The gloss exhibited by the specimens coated with the bactericidal glaze was measured in a Multi-Gross 268 glossimeter, which measures reflected light photoelectrically, measuring at a 20° angle. A gloss value was obtained of 97.6 GU for the fast double-fired specimens and 95.3 GU for those obtained by porous single firing. These values allowed characterising the materials as glossy glazes with a high gloss index.

In view of these data, it can be observed that the mechanical properties of the developed materials were not impaired on incorporating the bactericidal material.

2.4. BACTERIOLOGICAL RESULTS

After firing, the resulting specimens were cut into 5 cm x 5 cm pieces and taken to an accredited microbiology laboratory. The aim was to study whether these ceramic coatings could under artificial lighting have a bacteriostatic or bactericidal effect on the germs put onto them. ATCC international strain bacteria *Staphylococcus aureus* were used in testing.

The method employed in determining glaze coating bactericidal effect was as follows:

- A 24-hour culture was first prepared with ATCC strain *Staphylococcus aureus* in Agar Chocolate supplementing with Isovitalex.
- A suspension was made up with the bacteria to allow applying them to the ceramic specimen, determining the quantity deposited by the Mac Farlan scale.
- The ceramic specimens were sterilised in an autoclave.
- Filter paper moistened with a salt solution (1 ml) was put on the 9 cm diameter petri dishes, placing a ceramic specimen sized 5 cm x 5 cm in each dish, all under sterility conditions (Fig. 10).
- Bacteria were applied onto the ceramic specimens coated with the developed glazes by the Kirby Bauer method for Antibigrams, involving sowing with a cotton brush. Growth controls were always used in the trials in which bacteria were sown in an Agar Chocolate culture medium, keeping steady conditions at all times.

- Sowing was also done on the conventionally glazed specimens (normal tile) without a bactericidal glaze coating. This was to establish whether depositing bacteria on these led to a decrease in bacteria. As no decrease was found, these specimens were used for controls.
- To start with, sowing was performed in petri dish with a culture medium without any ceramic specimen. After many tests, as the number of bacteria was observed to be similar to that found on non-bactericidal ceramic specimens, these tests were stopped. It was thus shown that the ceramic specimens did not produce any interference with regard to the bacteria.
- The ceramic specimens sown with bacteria were left for a set time under a light source (in the first tests a 100 W tungsten light bulb was used, and in the others two 36 W fluorescent tubes).
- After exposure to light for the pre-set time, the ceramic specimens were placed in direct contact on the petri dishes with Agar Chocolate culture medium supplemented with Isovitalax. These were then put into an oven for times ranging from 1-3 hours. The ceramic specimen was then separated and the dishes were left to incubate for 24 hours.
- The colonies were counted with an optical microscope by image analysis.



Figure 10. Glazed ceramic specimen distribution. Trials were run with the conventional glaze (control trials) and with the bactericidal glaze.

The following variables were used in the tests:

- Degrees of light intensity
- Types of light sources
- Distance from light sources to the ceramic specimens
- Different glaze coatings
- Different number of germs in different experiments measured by the Mac Farlan scale
- Controlled room temperature at 25°C

- Culture sown on the ceramic surface
- Different contact times between the ceramic specimens and culture media for bacterial transfer from the ceramic piece to the culture medium. On keeping this time sufficiently long, the bacteria started feeding on the culture medium and remained stuck in it.

On setting the variables, this detection method was then used in the experiments. The experimental assembly is depicted in Fig. 11.

The method ultimately used was:

- 24-hour culture of ATCC strain *Staphylococcus aureus* in Agar Chocolate supplementing with Isovitalax.
- ATCC *Staphylococcus* measured in Mac Farlan 0.001 MF units.
- Sowing with a cotton brush (just one pass)
- Lighting with two 6000°K, 2500 lumen, Osram L36 W/72-965 “daylight” fluorescent tubes at a lighting distance of 1 m, providing a total of 400 lux, for 12 hours.
- Ceramic specimen in contact with the Agar Chocolate medium in an oven at 36 °C for 1 hour, separation of the ceramic piece, and culture placed in the oven at the same temperature for 24 hours.



Figure 11. Experimental assembly used for lighting the petri dishes containing the ceramic specimens sown with the selected bacteria.

The trials run on the ceramic specimens with the greatest bactericidal effect were performed at a bacterial concentration of 0.001 and 0.002 Mac Farlan units. Fig. 12 shows the bacteria that survived the experiment. Table IV details colony number analysis.

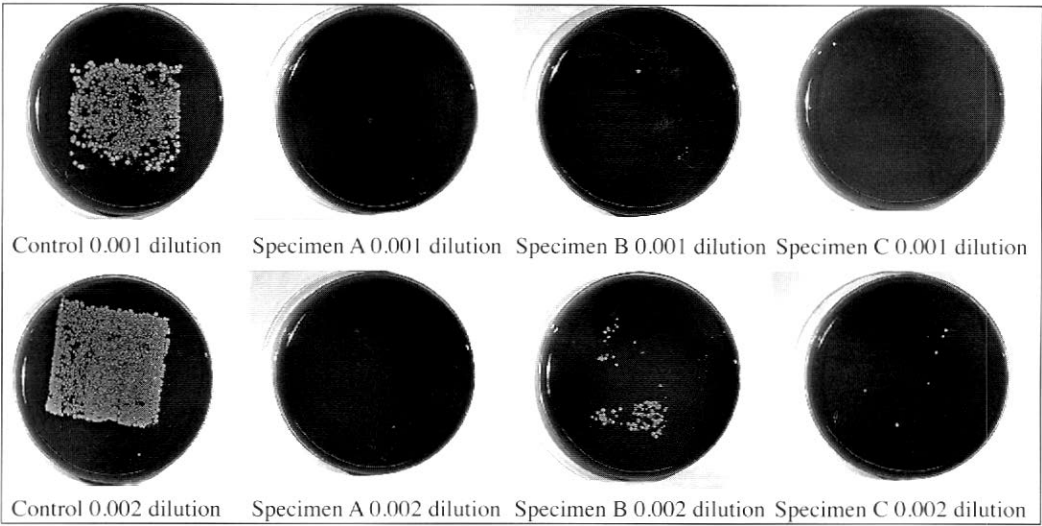


Figure 12. Experiments conducted at bacteria concentrations of 0.001 and 0.002 measured in Mac Farlan units.

Table IV details the results of the colony counts.

Ceramic specimen	No. of surviving colonies	
	Bacteria concentration 0.001 Mac Farlan units	Bacteria concentration 0.002 Mac Farlan units
Normal	900	1800
Bactericidal A	0	0
Bactericidal B	1	96
Bactericidal C	0	6

Table IV. Number of measured and quantified colonies by image processing and analysis.

The table reveals that ceramic specimen coated with bactericidal glaze A (over the conventional glaze) yielded the best results, although in all three bactericidal coatings the number of colonies was strikingly smaller than those in the ceramic specimens coated with the conventional (non-bactericidal) glaze.

CONCLUSIONS

- 1. A glassy material (frit) was developed with high gloss optical properties
- 2. The resulting frit can be applied to single-fire and double-fire tiles in industrial wall tile manufacturing cycles, while maintaining the required quality performance compared to a conventional glaze.
- 3. The glazed wall tile exhibited great bactericidal power for the tested strains under normal “daylight” and UV lighting.
- 4. There is no doubt as to the durability of this phenomenon with age, as studies elsewhere in this field have shown.

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