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# MULTIFUNCTIONAL SMART COATINGS ON NOVEL CERAMICS AND GLASS-CERAMIC SUBSTRATES IN THE CONTEXT OF THE CIRCULAR ECONOMY

Teodora Stoyanova Lyubenova[1], Diego Fraga[1], Juan B. Carda Castelló[2],
Vladimir Kozhukharov[3], Maria S. Machkova[3]

[1] *Department of Inorganic and Organic Chemistry,*
*University Jaume I, Castellón de la Plana, Spain*
*E-mail: stoyanov@uji.es*
[2] *Unidad Asociada "Química de materiales procesados por REM*
*(radiación electromagnética)", UJI-ICMA/CSIC,*
*Universidad Jaume I, 1750 Castellón de la Plana, Spain*
[3] *University of Chemical Technology and Metallurgy*
*8 Kliment Ohridski, 1756 Sofia, Bulgaria*

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## ABSTRACT

*Nowadays is time of products generated by "smart coatings" that exhibit multiple functionalities. In particular, the construction industry is reached the point where it is possible to fabricate "smart and sustainable" buildings that fulfill the requirements of a growing marketplace of products and devices for "smart cities" generation. In addition, if the buildings are "green", i.e. in accordance with the today's economic model "made to be made again" or so-called "circular economy" they are very attractive and viable alternative for future businesses and industrial exploring.*

*In this concept, we report a development sustainable ceramic and glass-ceramic tile substrates made by cheap, easily accessible and recycled materials that are further functionalized by different "smart coatings" for specific applications. Devices that generate and save energy, air and pollution cleaning, with anti-slip and phosphorescence properties are some examples of the overview that this publication described.*

*Keywords:* *"Smart coating", glass-ceramic, ceramic tiles, recycling, waste.*

## INTRODUCTION

Multifunctional materials designed to meet specific requirements through tailored properties is a topic of great interest of many scientists from Material Science field. Ones that the materials have the ability to react upon an external stimulus adapting their properties dynamically they become to be "smart materials" [1]. These materials can be for application either in bulk or layer and usually, at macro or nano-scale level [2]. Traditionally, the standard thinking regarding coatings have been as a passive layers unresponsive to the environment and usually used for protection or decoration [3]. The idea to develop coatings with unique properties is being explored mainly for industrial applications. Several smart coating systems have been already developed. Examples include stimuli responsive, antimicrobial [4], antifouling [5], conductive [6], self-healing [7], super hydrophobic and protective systems [8, 1] as well. Some coatings are currently under investigation, but are emerging constantly. The layers can be designed according to functional components, fabrication methods and application. When the smart coatings are in accordance with the future economic model "made to be made again", "design for not to contaminate" or so-called "circular economy", they become of vast industrial importance [9].

Nowadays, the environmental problems and the global warming are originated the debates about the deficiencies in the current economy model of linear economy (produce - use - throw). So, the idea of society based on economy where the use of materials, energy and wastes are optimized, is of great attention. The circular economy in which the elements are used to complete the cycle "cradle to cradle" or "remaking the way we make things" developed by chemist Michael Braungart and architect William McDonough ranked as the next industrial revolution [10]. Creating goods and products with reusing materials and providing more sustainable energy solutions of the technology is the business model of our future industrial generation [11].

When the concept of "circular economy" is shifted towards building industrial sector, this is resulting in creating of more sustainable cities and urban areas (also known as "ecocity") where the minimization of energy, water, food, waste, air and water pollution are of important social, economic and environmental impact [12]. The construction sector is very significant to the European Union economy as provides 18 million direct jobs and solutions for social, climate and energy challenges. One of the main goals of the European Commission (EC) is to help the sector become more competitive, resource efficient and sustainable [13], including European ceramic industry (forecast analysis) and world market [14, 15]. Since it is not possible to present all review papers, our attention was focused on the research and technological development (RTD) activities during of 7FP period of EC and selected actual books issues in the field discussed. For example, some research projects in the field could be marked [16 - 22] and important information from the following books [23 - 25] recently published could be found in.

In this concept, we report a development of sustainable ceramic and glass-ceramic tiles by using wastes and recycled materials from different industrial sectors like ceramic, glass and thermal plants. Self-cleaning, anti-slipping, energy saving, photovoltaics, phosphorescence, laser treated and domotics among others innovations are achieved by functionalization of the ceramic tiles discussed in the report. The main goal of this project is to combine the use of sustainable supports with efficient "smart coatings" to lead novel functional devices with increased added-value for more competitive and eco-friendly marketplace.

## SUSTAINABLE CERAMIC SUBSTRATES

It is well known, that the ceramic tiles are traditional constructive elements that are improving constantly in the last years. The use of ecological products become of a vast importance in the ceramic industry in order to optimize the consumption of natural resources and to the growing attention to the environmental safeguard because the residues cause big environmental impact and increase the industrial running costs.

In order to create novel and improved products according the above mentioned requirement, sustainable ceramic tiles have been designed: called eco-ceramic and eco glass-ceramic tiles that incorporate recycled materials and waste in their compositions such as second hand flat glasses, chamotte, clays, sludge, chimney waste, etc. In the following paragraphs the experimental procedure, characterization, results and discussion of the above mentioned sustainable substrates are exposed. Further, smart coating depositions by functionalization of the substrate surfaces to give utility of the product by creating of devices with different applications are briefly described, as well.

### *Development of Ecologic ceramic tiles*

The ecologic ceramic tiles [26] are made by the introduction of waste generated by ceramic industry such as calcined clay from fired porcelain of stoneware and raw biscuit, sludge and cleaning water. In addition, wastes from glass sector are also used as recycling glasses with different nature (Fig. 1). The waste glass and sludge can form a vitreous microstructure during sintering of porcelain stoneware acting as flux agent and thus decreasing process temperature [27, 28]. The stoneware porcelain composition (for the ceramic body/paste) is shown in Table 1. The porcelain stoneware tiles were made by traditional industrial ceramic method of

Table 1. Eco-Ceramic paste composition (mass %).

| | |
|---|---|
| Clay + Kaolin | 40-45% |
| Felsdpar | 30-35% |
| Sand | 5-10% |
| Recycled products (glass, chamotte, crushed pot) | 15-20% |

Fig. 1. Recycled materials applied in the preparation of the eco-ceramic and glass ceramic bodies (pastes).

preparation. The green bodies were prepared by pressing and further sintering in a conventional roller kiln.

The use of waste, natural and energy resources in the eco-tiles is evaluated [27]. A decreasing of about 16 % of the use of natural resources as raw materials is observed from the formulation of the stoneware eco-ceramic paste. The results achieved 50 % of reduction of in clean water, 20 % in energy consumption, which is totally 86 % of reduction in the use of natural and energy resources. Fig. 2 shows a diagram representing the distribution of the savings made of natural and energy resources. Summarizing, the designed eco-tiles, including industrial wastes in it paste formulation, achieved significant improvement in terms of lower porosity and water absorption, mechanical resistance, lower body thickness and morphology in comparison with the standard ceramic tiles [26].

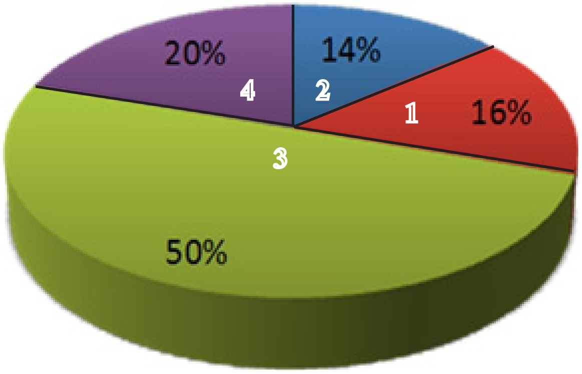

Fig. 2. Degree of reduction in resources (natural and energy) for the stoneware eco-ceramic paste. Reduction in: raw materials (1-red), unusable resources (2-blue), clean water (3-green), energy (4-violet).

### *Development of eco-glass ceramic tiles*

The interest on glass-ceramic material resides in its relative low cost of manufacture, compared to the advanced ceramics and the possibility of higher performances. The manufacturing process of glass-ceramic can be carried out using a variety of economic processes, although the energy consumption cannot be avoided [29, 30]. However, the need of sintering at high temperatures could be balanced by some economic savings as the use

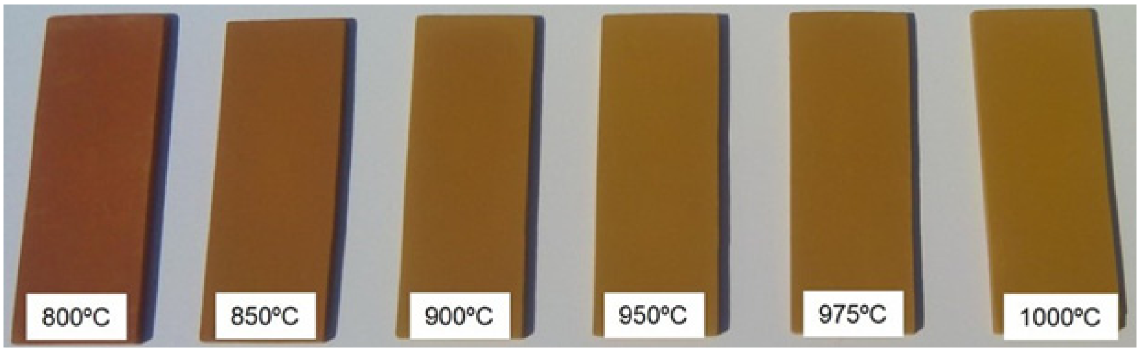

Fig. 3. Image of Sample A treated at different temperatures.

Table 2. Chemical analysis by X-ray Fluorescence of Sample A (mass %).

| | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $K_2O$ | CaO | $TiO_2$ | $SO_3$ | $Fe_2O_3$ | PPC |
|---|---|---|---|---|---|---|---|---|---|---|
| Sample A | 6.83 | 2.10 | 17.05 | 52.75 | 0.78 | 12.34 | 0.36 | 0.00 | 7.69 | 0.05 |

of recycled by-products /wastes as raw materials. In our case, we developed a glass-ceramic material with residue content greater than 90% using ashes from thermal power plants and glass wastes as alternative ceramic tile substrate that are more environmentally friendly [31]. The prepared glass-ceramic substrate is 3 mm thick. The composition (sample A) contains soda-lime glass waste (50 mass %), bottom ash (25 mass %), fly ash (15 mass %), $CaCO_3$ (10 mass %) in $CaO-Al_2O_3-Fe_2O_3-SiO_2$ system (Table 2). The prepared powder was melted at 1500ºC for 1h. The melt was quenched into water obtaining shape glass. Grinding and sintering experiments were performed on rectangular compacts (2x5cm$^2$) obtained by uniaxial pressing of the fine powder. The compacts were treated at different temperatures (from 800 to 1000ºC) to enhance complete crystallization process.

Optimum treatment at 950ºC for 30 min with 20ºC/min of speed is achieved (data not shown). Image of the treated sample is shown in Fig. 3. An increasing in soaking time from 30 min to 7 hours do not shows significant differences in crystallization, thus the minimum interval is selected as representative (Fig. 4).

Evaluation of apparent density versus flexural strength as a function of temperature changes is shown in Fig. 5. It can be observed that the apparent density increase with sinterization starting from 2,43 at 800ºC to 2.62 at 975ºC. These characteristic are superior in comparison with standard porcelain stoneware tile (apparent density: 2,40 g/cm$^3$ and flexural strength: 600 kg/cm$^2$ at 950ºC).

Eco-glass ceramic support is developed as alternative to the conventional ceramic one. The designed glass ceramic, including industrial wastes in its formulation, achieved better results in terms of lower porosity and water absorption, mechanical resistance and lower body thickness. These characteristics are very encouraging form functionality and energy saving points during the manufacturing process [31].

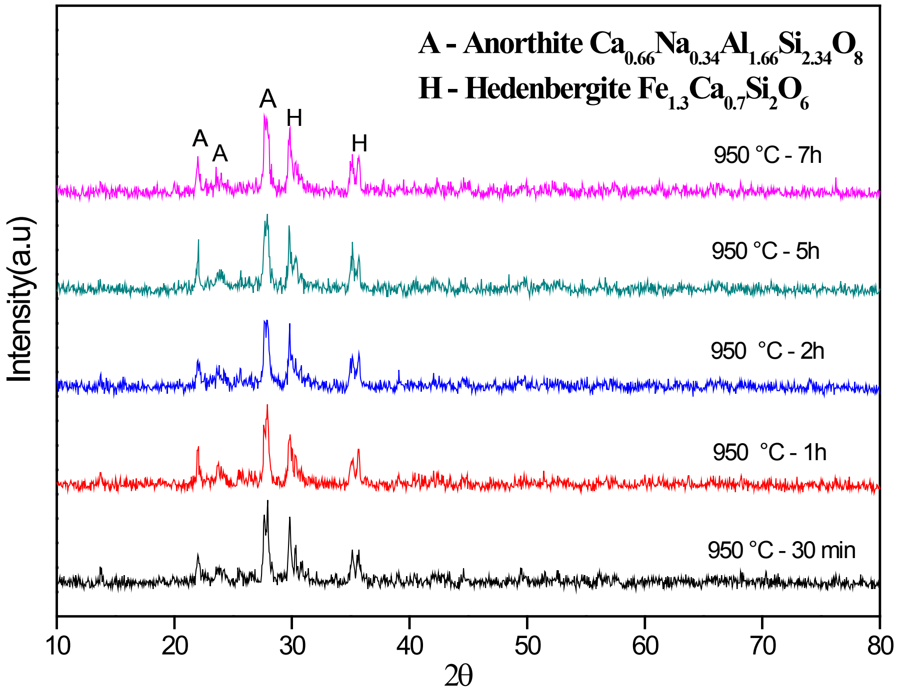

Fig. 4. X-ray diffraction spectra of Sample A treated at 950ºC with different soaking times. Crystalline phases detected: A- Anorthite ($C_{a0.66}Na_{0.34}Al_{1.66}Si_{2.34}O_8$); H- Hedenbergite ($Ca_{0.7}Fe_{1.3}Si_2O_6$).

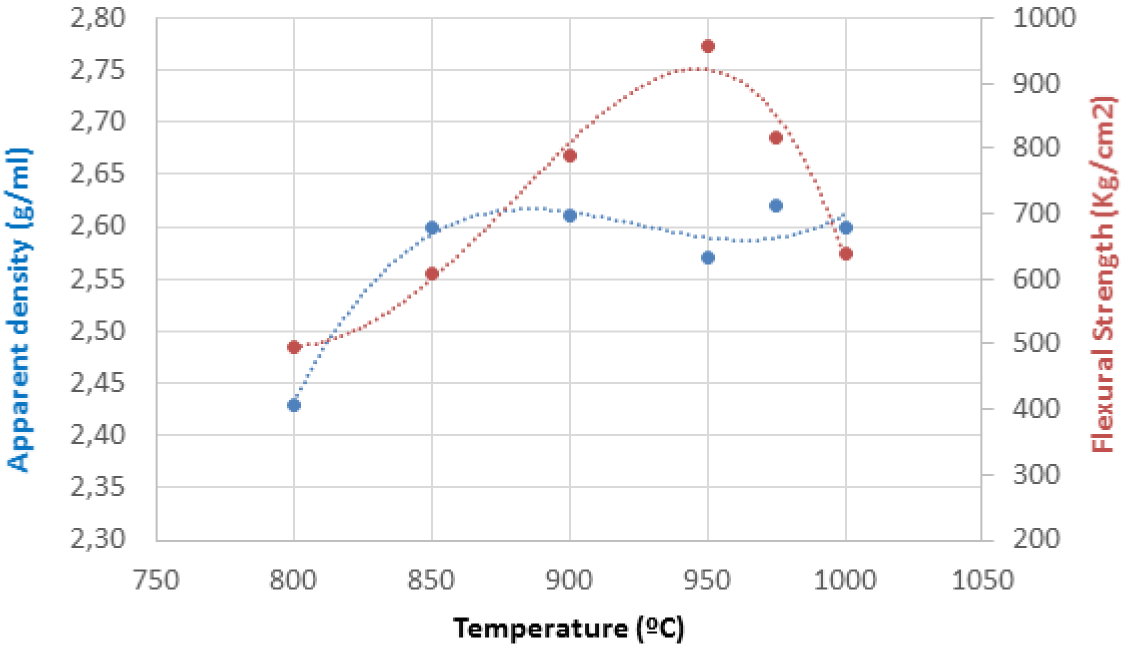

Fig. 5. Apparent density vs. flexural strength as a function of temperature for Sample A.

## "SMART COATINGS" SUBSTRATE FUNCTIONALIZATION

### Photovoltaic eco-ceramic tiles

Conception of new architectural elements with added functionalities creates a strong interest in recent years. To design construction elements that fits with different parts of the buildings and in the same time generate electricity is very attractive project for whole sector. This is so called Building-integrated photovoltaics (BIPV), i.e photovoltaic devices that are used to replace conventional building materials in parts of the building envelope such as the roof, skylights, or facades [32]. A thin film photovoltaic technology is an attractive option for substitution of the classical silicon crystalline solar cells due to the flexibility to achieve large area modules, been able to adapt to uneven surfaces and to reduce materials and production costs [33]. This technology permits easy installation of the photovoltaic modules, bringing not only financial benefits from solar power generation, but also increasing the social values by making the buildings go "green" or "eco" by simple retrofitting.

The prepared eco-ceramic tile had been use as a support for the development of novel thin film solar cell devices [34, 35, 26, 36, 37]. An advantage of the ceramic substrate is the possibility to operate at higher temperatures than the soda-lime glasses and the polymers. The ceramic substrate for solar cells requires adequate adjustment. Thus, an introduction of extra layer based on enamel is needed [26 - 28, 32]. The enamel acts as an intermediate barrier between Mo back contact coating and the substrate providing chemical stability and roughness reduction, simulating glass surface with no porosity [34]. In addition, the enamel also prevents diffusions from the support to the Mo and the absorber CIGS layer and acts as Na and K source. It is demonstrated that small Na and K diffusion favors the CIGS crystallization process [35].

Here, we demonstrate the development of novel solar cell on the eco-ceramic substrate based on CIGS (Cu (In, Ga) $Se_2$ based semiconductors) technology that offers new possibilities for building integration photovoltaic (BIPV) [26]. The schematic design of the photovoltaic ceramic tile is shown in Fig. 6. In addition, easy, sustainable and low-cost ways of preparation using co-precipitation route for CIGS absorber is also used that add valued to the final product [38, 39]. The solar cell device is composed of a substrate that could be made of different materials (glass, polymers, metals or ceramic). To provide uniform, lower roughness and avoid any diffusion coming from the substrate during thermal treatments enamel is applied. Consequence, a metallic conducting layer (Mo), *p* and *n* type semiconductors (p-

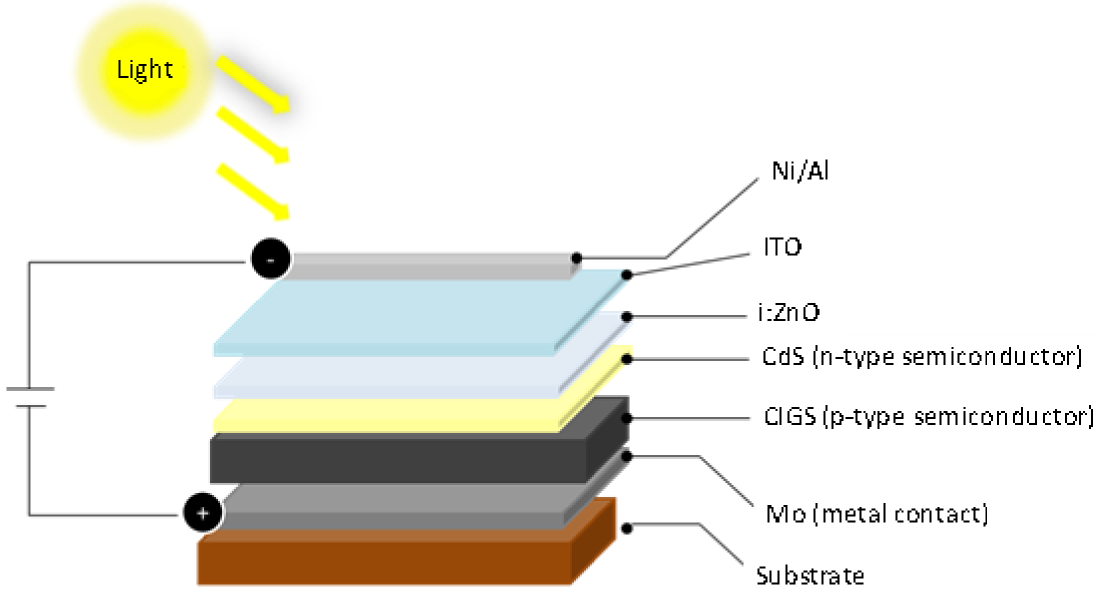

Fig. 6. Schematic layout of developed photovoltaic ceramic tile.

type is CIGS and n-type is CdS) and TCO (transparent conducting oxides, i-ZnO and ITO ($In_2O_3$:Sn) and metal contact finish the solar cell sandwich structure.

The morphology of the cell is analyzed by Scanning Electron Microscopy in Fig. 7. Dense layers well attached to the Mo are formed. Absence of holes cracks and other defect is evident which is very important for the final devices performances. Different textures resulting from crystallization of each layer is also apparent.

The eco-photovoltaic device was optoelectronically characterized through current density-voltage (J-V) curves under an AM1.5 global spectrum. The photovoltaic tile exhibit an open-circuit voltage (Voc) = 270 mV, short-circuit current density (Jsc) = 13.43 mA/cm2, fill factor (FF) = 36 %, efficiency (η) = 1.3 %. It can be observed that it is possible to prepare a photovoltaic device based on film layer technology using an ecological tile that contains industrial waste as part of raw materials. Integration criteria and guidelines of the solar energy system in the architecture are discussed in [40], as well.

### In-situ laser synthesis of materials synthesis

The conventional synthesis method based on solid-state reaction of oxides or carbonates requires high temperatures with prolong retention times and presence of unreacted phases. In addition, this synthesis routes usually involve the use of a flux that enhance the kinetic reaction or a reducing atmosphere if valence control

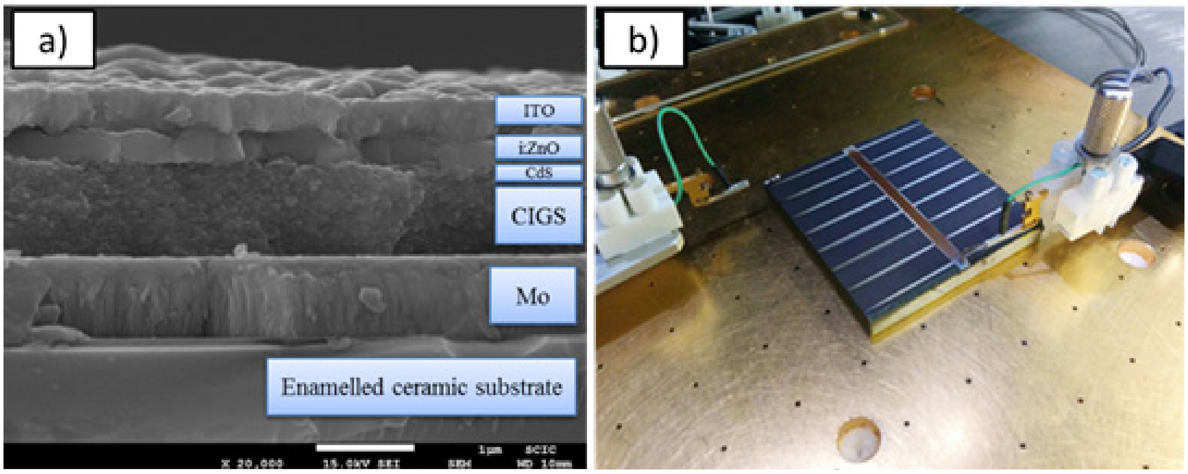

Fig. 7. Image of the developed solar cell: a) made by SEM and b) digital image of the prototype.

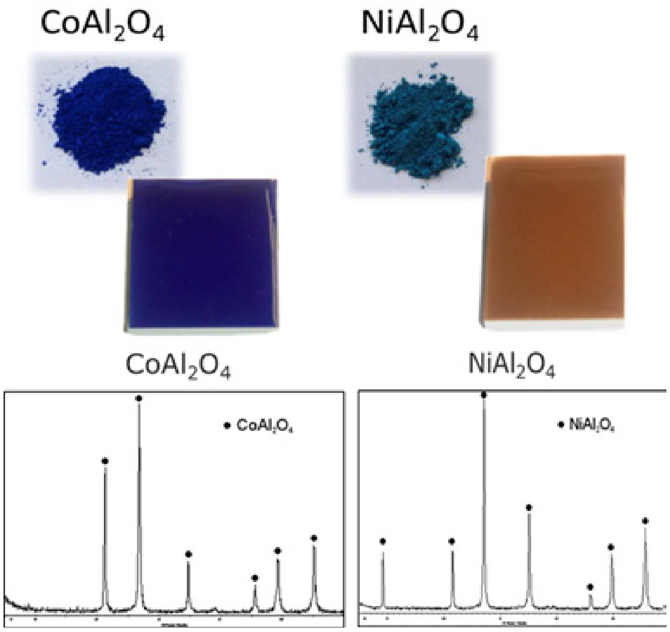

Fig. 8. Ceramic pigments developed by laser treatment: X-ray diffraction pattern of and digital images of $CoAl_2O_4$ and $NiAl_20_4$ spinel pigments.

is necessary to form the desired solid solution. Alternatively, many others alternative methods have been developed for preparation of ceramic pigments, but all of them requires previously the use of more-expensive precursors, preparation and further treatment which is not very feasible from industrial point of view [41, 42] .

As a solution to those problems is the laser heating application. Laser-assisted synthesis is based upon the thermal effects caused by the laser radiation absorbed by the material. It can thus be considered as a photothermal synthetic route, where temperatures well above 2000 °C may be reached. The preparation of high melting point oxides has been successfully achieved by using this laser melting method, as demonstrated with the synthesis of different ceramic pigments directly obtained in ceramic substrates [43] . Examples are demonstrated in Fig. 8. Two different ceramic pigments that crystallized in spinel structure have been successfully developed by laser treatment. It can be observed that the desired crystalline phases were obtained as almost pure ones, without relevant impurities. The grains present also excellent crystallinity that reflects in the developed intense colors. The industrial application in ceramic glazes was also successful for the $CoAl_2O_4$ pigment. However, loosing of blue coloration is detected after glazing due to chemical reaction occurred with someone of the components from the pigment systems and the glaze composition. In addition, large, crack-free surface molten eutectics coatings are also made by laser. Examples are the in situ synthesis of rare earth aluminate perovskite and garnet based eutectic as $MTiO_3$ (M = Ca, Sr, Ba) coatings on $Al_2O_3$ substrates by laser melting of metal carbonates (Fig. 9) [44].

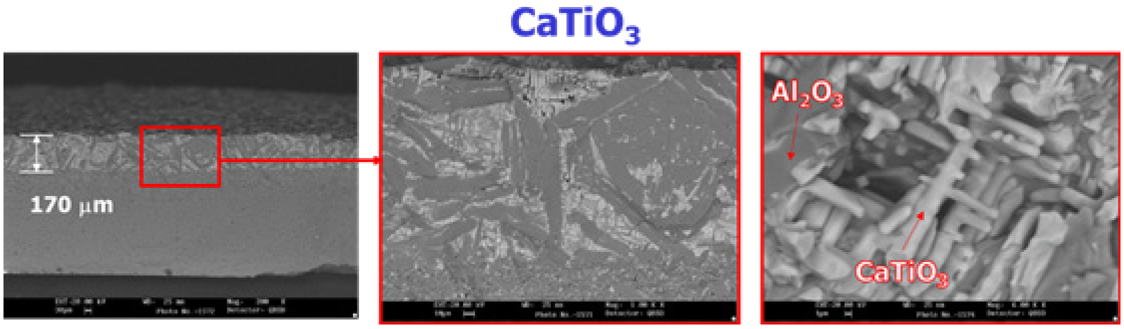

Fig. 9. In-situ laser synthesis of $CaTiO_3$ (SEM images at different magnifications).

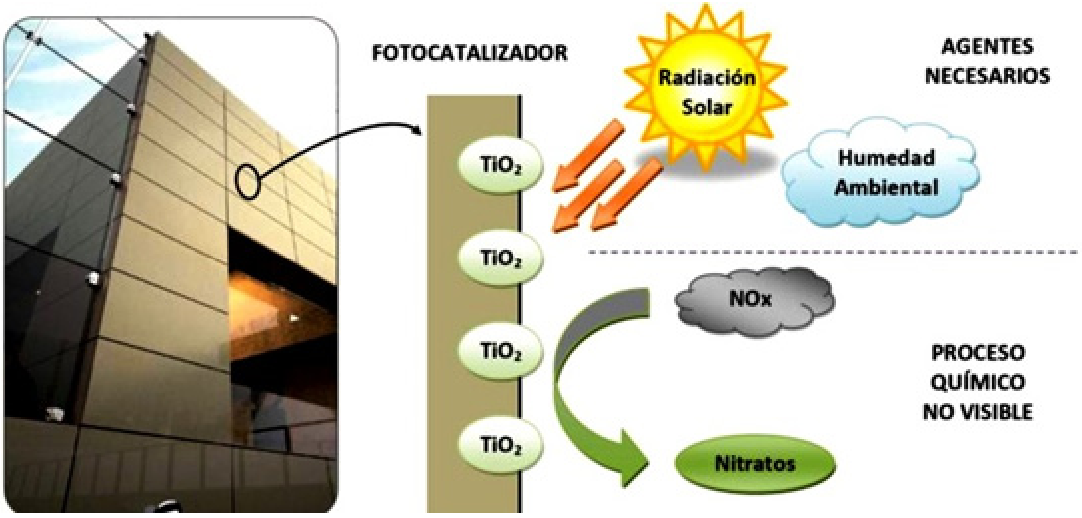

Fig. 10. Schematic layout of the photocatalytic functions of BIONICTILE®.

In the figure is observed tree different areas after laser treatment: i) fused upper layer; ii) diffusion zone attached by the heat (intermediate); iii) undisturbed substrate (bottom). If we take closer look at the intermediate layer, we can observe preferred crystalline orientation either of perovskite and alumina crystals.

### Self-cleaning/Air cleaning

The photocatalytic properties of titania ($TiO_2$) together with its unique properties like high chemical stability, non-environmental impact, and low cost make it very attractive for many uses [45]. Since it was found, that is able to oxidize aqueous or gaseous pollutants under Ultraviolet irradiation (UV) and to inactivate microorganisms is focus of investigation. This effect is applied in development of "smart coatings" with multiple properties as: air purification, anti-fogging, self-cleaning, self-sterilizing surfaces, amongst other applications [46, 47].

In the ceramic tile industrial sector, this effect is also used for air cleaning by breaking down harmful pollutants creating "air-cleaning" tiles. The tiles are treated with a titanium dioxide glaze that breaks down nitrous oxide in the presence of sunlight and humidity through a photocatalytic process. In order to maximize the tiles' air-cleaning capability the ceramics feature a biomimetic structure modeled after the leaves of trees – you can see tiny rivulets and crannies in the tiles' surface that serve to trap pollutants.

As an example is a photocatalytic ceramic tiles called BIONICTILE® (commercial product form Ceracasa, S.A., Alcora, Spain [48]) that converts nitrogen oxides (NOx), emitted in combustion processes into harmless nitrates thanks to the action of ultraviolet light. It is demonstrate a significant reduction of NOx oxides (270, 91 mg/m2 per hour) and a reduction of 76.7% of $HNO_3$ in air, causing acid rains (Fig. 10).

These photocatalytic tiles (BIONICTILE®) are applied for creating vertical gardens (Lifewall®, Fig. 11) as a support for a number of different plants. When they work in conjunction, they are able to suck pollution out of the air by breaking down nitrous oxide in the air, improving the local air quality. In the same time, both products create a symbiotic relationship, where the Lifewall® has plant matter that soaks up $CO_2$, and the BIONICTILE® converts $NO_x$ to fertilizer, which is used by the plants.

Tests show that BIONICTILE® [48] ceramics are able to decompose 25.09 micrograms of NOx per $m^2$ per hour, and if 200 buildings were coated by ceramic BIONICTILE®, an equivalent volume of 2,638 million cubic meters of air per year would be decontaminated. In other words, more than 400,000 people could breathe air free of harmful NOx from vehicles and industries in one year.

### Energy-Saving Ceramic Tiles (bio-climate tiles)

Novel type of high-tech tiles that could cut your energy bill by 16% have been also commercialized by Ceracasa S.A ceramic company (Ecom4 Tiles®) [49]. The phase-changing tiles feature nano- energy storage cells that excel at absorbing thermal energy – meaning they keep interior spaces comfortable for longer with less energy input from climate control systems. They

Fig. 11. Image of Lifewall® by Ceracasa S.A [48].

are also stain-proof and incorporate a glaze that breaks down bacteria and odors. Ecom4 Tiles have been tested to reduce energy use by 16 % in a 1,000 square foot space, and they are so efficient at absorbing and releasing ambient heat that air conditioners or heaters can be switched off for 1 - 2 hours each day. It is necessary to underlined that these ceramic tiles work through the phase-changing materials contained within the tiles start to fuse together when a room hits 22ºC, at which point they begin to store thermal energy. This stored heat is then released to warm the room later when the temperature drops below 22ºC. This evens out the thermal profile of a room over time and reduces the amount of energy needed to maintain a comfortable temperature. The phase-changing capabilities of Ecom4 tiles also gives them a surface temperature that is roughly equivalent to the temperature of ambient air in a room, so they are comfortably warm to the touch. The tiles are suitable for floor or wall installations, and the more surface area you cover, the better your energy savings will be for the family as is illustrated in (Fig. 12). Some benefits in the production of innovative ceramic tiles from waste is expected to be realized in an EC project [50] as well.

**Phosphorescence ceramic tiles**

Phosphorescence ceramic tile are made by glazes where a phosphorescent pigments with organic or inorganic nature is dispersed. These "smart" coatings are able to absorb energy after being excited by photons and emit a portion of that energy as radiation in the visible–ultraviolet (visible-UV) range [51]. One common type of phosphorescent pigment is aluminates with spinel structures ($MAl_2O_4$), which emit in the visible range when doped with appropriate activator ions – usually the so-called rare-earth elements (R) or transition metals (e.g. $SrAl_2O_4$: $Eu^{2+}$, $Dy^{3+,}$ $Nd^{3+}$) [52 - 54]. Many phosphoresce pigments are available since 1950´s as an yellow and red Emission Copper-Activated Zinc Sulfide Phosphors (ZnS:Cu) [55] and thermoluminescent behavior is also investigated [56].

The ceramic industry develops tiles that accumulate energy during the day and emit it during the night. The tiles absorb the sun's energy during daylight hours and artificial light from a lamp. At night, the stored energy is slowly released. This pigment could be also used epoxy resin, wood, plastics and textile. They are resistant to heat, atmospheric effects and chemicals. Thus, these characteristic make them very attractive for the consumers, as they are stable over time; easy to clean and do not requires special maintenance and very resistant to wear. There many applications where these tiles are useful as: light markers and labels, decorative functions, etc., as is illustrated in Fig. 13.

Fig. 12. Commercial advertisement of Ecom4Tile® by Ceracasa S.A.

Fig. 13. Some applications of phosphorescent ceramics.

**Anti- Slip**

Slips and falls on wet surfaces are a major problem for all types of commercial establishments, residences, swimming pools or even at home´s bathroom. Thus, slip-resistant floors and bathtub products are object of interest. The ceramic anti-slip tiles can be used indoors or outdoors and will make any type of floor slip-resistant when wet is present. The tiles are made by, either conventional anti-slip enamels or glass-ceramic coatings [57, 58] or by inkjet printing technology [59]. The conventional anti-slip tiles are generally obtained from mat enamels that are modified superficially by adding desegregated frit, corundum, silica fume (also known as microsilica), which gives them a remarkable surface roughness, and thus, anti-skid properties. However, these types of surfaces are difficult for cleaning and usually embedded dirt in the roughness of the surface. In addition, their touch surface is rather rough and this makes difficult it commercialization. In this context, Martínez et al. [57] developed seeds of α-cordierite phase by the sol-gel process, which were subsequently introduced (3wt %) together with a commercial gloss transparent frit in a glaze composition. The study found that the gels were able to give rise to cordierite crystallization, but saphirine ($4MgO{\cdot}4Al_2O_3{\cdot}2SiO_2$) was also present as major phase and cerianite ($CeO_2$) (Fig. 14), introduced in the gel composition as a nucleating agent, remained as a minor phase [57, 60].

In order to solve that problems, glass-ceramic nature enamels has been designed, characterized by being stain-resistant and presenting a smooth texture and touch soft [61].

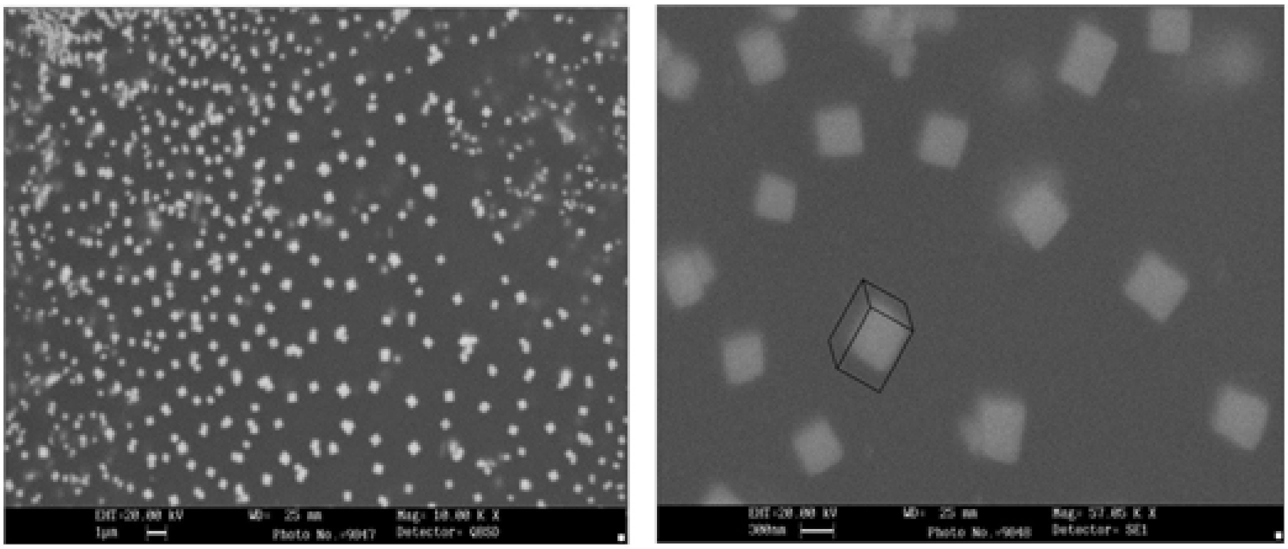

Fig. 14. Devitrification of $CeO_2$ nanoparticles (~ 300 nm) in the vitreous matrix that lead ceramics with high degree of hardness.

Fig. 15. Image of “Smart” tile interface (TAU Ceramica).

## “SMART” TILES (domitic ceramic tiles)

The ceramic tile innovations are also entered in a building automation mainly for homes, i.e. called “smart home or smart house”. It involves the control and automation of lighting, heating (such as smart thermostats), ventilation, air conditioning and security, as well as home appliances such as washer/dryers, ovens or refrigerators/freezers. Wi-Fi routers are often used for remote monitoring and control. The systems generally consist of switches and sensors connected to a central hub sometimes called a “gateway” from which the system is controlled with a user interface that is interacted either with a wall-mounted terminal, mobile phone software, tablet computer or a web interface, often but not always via Internet cloud services. A ceramic domotic tile (development of TAU Ceramica and LARTEC) has been designed to adapt our homes to the last generation modern and careful design. The home automation ceramic tile system can be incorporated into any room of the house integrated perfectly with the décor, and it includes icons with different functions such as “soft touch”, they are activated almost without touching them and it includes braille reading to be more accessible for any user [62].

## CONCLUSIONS

This publication has presented an overview of the most interesting and recent approaches to developing of functional materials in terms of “smart coatings” on ceramic tiles for improving the properties and for giving add –value of this traditional construction product. The developed ceramic tiles exposed in the report are also in accordance with the novel society model that optimized the use materials, energy and wastes by creating goods with specific functional properties. Thus, sustainable porcelain stoneware and glass-ceramic tiles have been developed by introduction of recycled materials and wastes from different industrial sectors. Therefore, the developed tiles have been functionalized by creating coatings inspired by the “smart phenomena” and offer technological capabilities, which conventional coatings cannot. Energy generators (Photovoltaic ceramic tile devices), self and air cleaning floors and facades, anti-slipping, domotic smart surfaces and tiles with phosphorescence and energy saving functions are some points of interest of this paper. Automation and acclimatization of inside spaces with intelligent surfaces, anti-slipping, anti-bacterial and self- regular heating floors, fluorescence lightening, among others innovations makes us easier the tasks of daily life increasing our comfort. Some of the coatings and related functional materials continue to be an innovative area in research and technology for the implementation in the production processes as it is the case of solar cell devises. However, others approaches have already been applied in industrial processes that is an example of real scientific and technological success.

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