

SYNTHESIS OF CERAMIC PIGMENTS BY NON-CONVENTIONAL METHODS FOR USE IN THE NEW CERAMIC DECORATION TECHNOLOGIES

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1. INTRODUCCIÓN

The ceramic tile industry increasingly commits to modernisation and the implementation of new technologies in the ceramic decoration process. Current demands of advanced processes in this field, such as rotational decoration, inkjet printing, PVD (physical vapour deposition), laser systems, etc., have led to a great interest in developing ceramic pigments with controlled compositions and microstructures, which are thermally and mechanically stable in the production cycles, with reproducible and multifunctional properties, and which meet ecological and economic demands. Research into these materials has made the ceramic sector dynamic and competitive with regard to opening new markets.

Nowadays, conventional ceramic technology is still considered the most appropriate pigment synthesis approach [1]. This method is still preferred by the industry, owing to its low cost and easy processing. However, this process requires high calcination temperatures, and the addition of fluxes that have adverse effects on the environment and make it difficult to control and reproduce the end product [2-4]. This has led to the development of alternative preparation methods that avoid these problems and contribute added value to the material for a wider-ranging multi-functionality.

The need to develop pigments with upgraded properties has led to the search for more homogeneous synthesis methods and more effective chemical reactions than the traditional methods used at present. This study describes the benefits of non-conventional methods such as sol-gel, freeze-drying, spray drying and spray pyrolysis, and *in situ* synthesis using photo-thermal activation mediated by laser, for the development of ceramic pigments matching the new trends and avant-garde decorations [5-9]. The study was performed using the pigmenting structure of sphene (ABCO_5), which is known in the form of two compounds: the mineral titanite CaTiSiO_5 and its isostructural analogue, malayaite CaSnSiO_5 .

Chromium-doped malayaite (Cr:CaSnSiO_5) is the only system in this study that is used as a pigment in the ceramic industry. To be noted is the great chemical attention that it has drawn for decades. It has probably become one of the most widely studied inorganic pigments since the discovery of its interesting optical properties, related to the peculiar, intense pink-magenta hue. Many authors have worked to elucidate its formation mechanism. However, recent studies have renewed the debate on its crystal-chemistry [10]. On the other hand, the stabilisation of the system through fluxing agents still continues to pose problems during its under-glaze decoration and reaction.

Titanite (CaTiSiO_5) is isostructural to malayaite (CaSnSiO_5), but it has never been used as a ceramic pigment. We have therefore sought to verify its effectiveness in this field. The difference between both compounds lies in the fact that the octahedron $[\text{TiO}_6]$ in CaTiSiO_5 is more distorted than $[\text{SnO}_6]$ in CaSnSiO_5 , owing to different ionic radii $r\text{Sn}^{4+}(0.69\text{\AA}) > r\text{Ti}^{4+}(0.65\text{\AA})$ [11], which leads to the appearance of a different hue.

The developed pigments were structurally and microstructurally characterised. Their stability and pigmenting performance were evaluated before and after direct application on reference fired glazes.

2. EXPERIMENTAL

The two materials, Cr:CaTiSiO_5 and Cr:CaSnSiO_5 , were synthesised by various preparation methods, which are described below. The stoichiometries selected to obtain the solid solutions were as follows: $\text{CaSn}_{1-x}\text{Cr}_x\text{SiO}_5$ and $\text{CaTi}_{1-x}\text{Cr}_x\text{SiO}_5$ ($x = 0.02, 0.05, 0.10, 0.20$).

2.1. SYNTHESIS METHODS

2.1.1. Ceramic method

The traditional ceramic method was used for comparative purposes. Metallic oxides were used as precursors for this purpose. After mechanical micronisation and without the introduction of mineralisers, these were heat-treated in a conventional electric kiln. No fluxes were used in order to appropriately compare the materials developed by the alternative methods.

2.1.2. Freeze-drying method

The precursors used in freeze-drying synthesis were $C_8H_{20}O_4Si$, Ludox, $Ca(NO_3)_2 \cdot 9H_2O$, $SnCl_4 \cdot 5H_2O$, $C_{12}H_{28}O_4Ti$, and $Cr(NO_3)_3 \cdot 9H_2O$. The metallic compounds were dissolved in stoichiometric quantities in water and subsequently frozen by adding liquid nitrogen in a Telstar Cryodos freeze-dryer system under vacuum of about 1-10Pa. This provided sublimation of the solvent from the frozen sample and yielded an end product in the form of an amorphous powder. The powder was then milled and prepared for calcination.

2.1.3. Sol-gel method

To prepare the pigments with a sphene structure, two variations of the sol-gel methodology were used. Polymeric sol-gel was used to obtain malayaite $Cr:CaSnSiO_5$ and colloidal sol-gel was used to obtain titanite $Cr:CaTiSiO_5$. The polymeric sol-gel method is based on the hydrolysis and condensation processes of metallic alkoxides, while the colloidal method is based on the destabilisation of a colloidal dispersion of metallic salts and colloidal silica in an aqueous liquid medium.

2.1.4. Spray drying and spray pyrolysis method

Spray drying and spray pyrolysis are two independent procedures. However, owing to their similar methodology, they are described together in this section. Both processes originate from solutions of soluble salts of the corresponding metals, which are then atomised. In both procedures, the solutions are nebulised through nozzles, using air as carrier gas at constant pressure (0.5 kg.cm^{-2}). After the atomisation, the spray is introduced into a heated chamber (for spray drying) or into an electric tube kiln (for spray pyrolysis). The powder from pyrolysis is dried and calcined in a continuous process, while the powder obtained by spray drying is subsequently treated in a conventional muffle kiln.

2.1.5. Laser method

In the case of malayaite $Cr: CaSnSiO_5$, obtained by the sol-gel, freeze-drying, and ceramic methods, trials were conducted of alternative heat treatment with laser radiation of CO_2 ($\lambda=10.6\mu m$) at a maximum power of 100W. For appropriate treatment of the prepared powders corresponding to each composition, these were prepared in the form of pressed pellets for subsequent treatment with laser radiation, which was performed until the characteristic pink-magenta malayaite colour appeared.

2.1.6. Industrial application

The resulting pigments were applied on glazes to evaluate their stability and colour development. Various industrial frits were chosen for this purpose, as a function of the type of sample and desired result.

2.2. CHARACTERISATION TECHNIQUES

The materials were structurally characterised using a Siemens model D5000D diffractometer with a Bragg-Brentano geometry with two goniometers and copper cathode.

Morphological analysis was conducted by scanning electron microscopy (SEM) with Leica model LEO 440 and Jeol JSM5400 microscopes. The materials treated by laser radiation were observed with a LEICA model Q600S optical microscope.

Analysis by UV-visible (UV-VIS) spectroscopy and measurement of the chromatic coordinates ($L^*a^*b^*$) were performed for the pigments in powder form and for those applied on industrial glazes. The details can be found in the literature [12].

3. DISCUSSION OF RESULTS

3.1. MALAYAITE Cr:CaSnSiO₅

The thermal evolution of chromium-doped malayaite with stoichiometry CaSn_{0.95}Cr_{0.05}SiO₅ chosen as representative) and synthesised using different methods at 1300°C is shown in Figure 1. It maybe observed that the procedures based on processing using sprays, as in spray drying and spray pyrolysis, displayed good compositional control and favourable reactivity of the system. In addition, it may be noted that spray pyrolysis was the best method, this being the only method that produced the pure phase of the desired pigment.

Figure 2 shows the thermal behaviour of the malayaite samples calcined by laser photo-thermal energy. The stoichiometries displayed correspond to CaSn_{1-x}Cr_xSiO₅ ($x=0.02, 0.05, 0.10$). The diffractograms evidence the presence of cassiterite (SnO₂) as major phase, accompanied by the perovskite phases CaSnO₃ and CaSiO₃, in which the quantity of malayaite that formed was very little. This result may be explained by the short processing times that the samples were subjected to and the temperatures that the laser beam reached ($\sim 1500^\circ\text{C}$). This indicates that this preparation method is not the most suitable for the obtainment of the desired pigment.

It may be concluded that the efficiency of the tested synthesis methods in relation to the reactivity of the system Cr:CaSnSiO₅, without mineralisers, can be summed up in the following order:

Spray pyrolysis > Spray drying > Freeze-drying > Ceramic method > Sol-gel > Laser

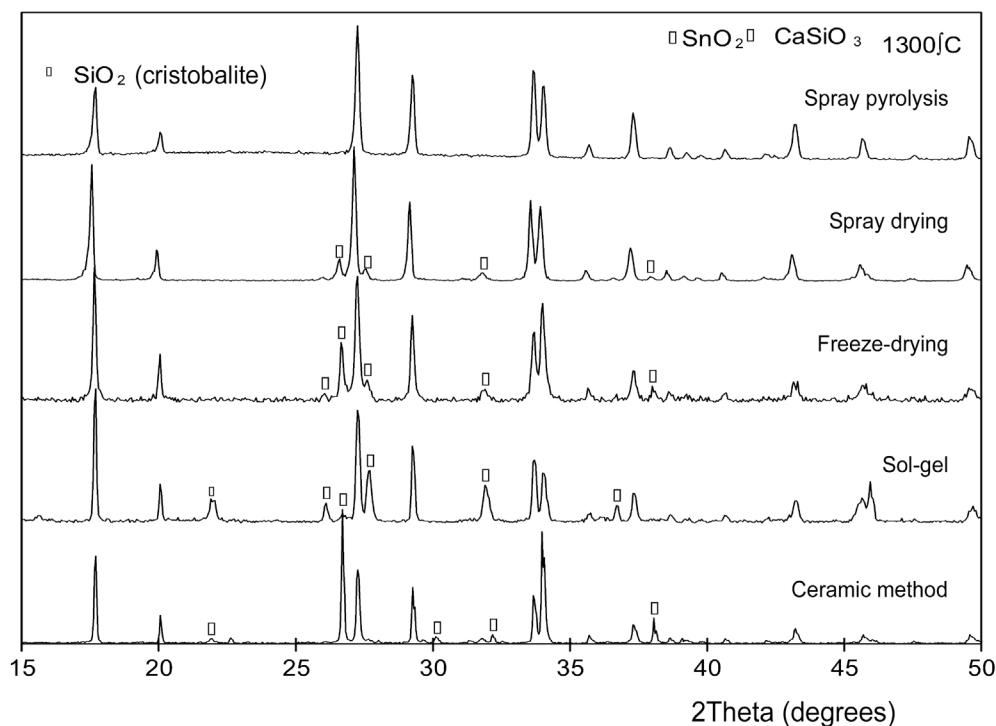


Figure 1. Comparative diffractograms of the $\text{CaSn}_{0.95}\text{Cr}_{0.05}\text{SiO}_5$, sample, synthesised by different methods at a temperature of 1300°C .

The morphology of the materials developed was related to the preparation method. Thus, as may be observed in Figure 3, the sample obtained by the ceramic method consisted of highly sintered particle aggregates. The sol-gel and freeze-drying methods gave rise to polycrystalline grains, about $20\mu\text{m}$ in size, with coral-like shapes. The spray-based methods (spray drying and spray pyrolysis) provided greater control of particle shape and size, yielding spherical crystals with a smaller size.

The materials synthesized by all the tested methods developed pink colours and have shown they could be used as ceramic pigments, as they have been successfully used in industrial glazes (Fig. 3). However, the best colours were obtained by the spray methods, spray pyrolysis being the optimum method (sample SPMN, $\text{CaSn}_{0.95}\text{Cr}_{0.05}\text{SiO}_5$). Note that this synthesis method does not require the addition of mineralisers to obtain the malayaite solid solution doped with pure chromium, which is an important advantage from an environmental viewpoint.

Figure 4 shows digital images at different magnifications, obtained with the optical microscope of the surface of the pellets pressed with the precursors synthesised by the ceramic, sol-gel, and freeze-drying methods, and subsequently treated by laser radiation. Laser treatment led to the development of pigmenting nuclei, albeit with varying hues, which differed from the characteristic pink-magenta colour of malayaite. The results were consistent with the presence of secondary phases and the absence of the desired phase, which was confirmed by XRD analysis. The predominant morphology was heterogeneous and highly sintered.

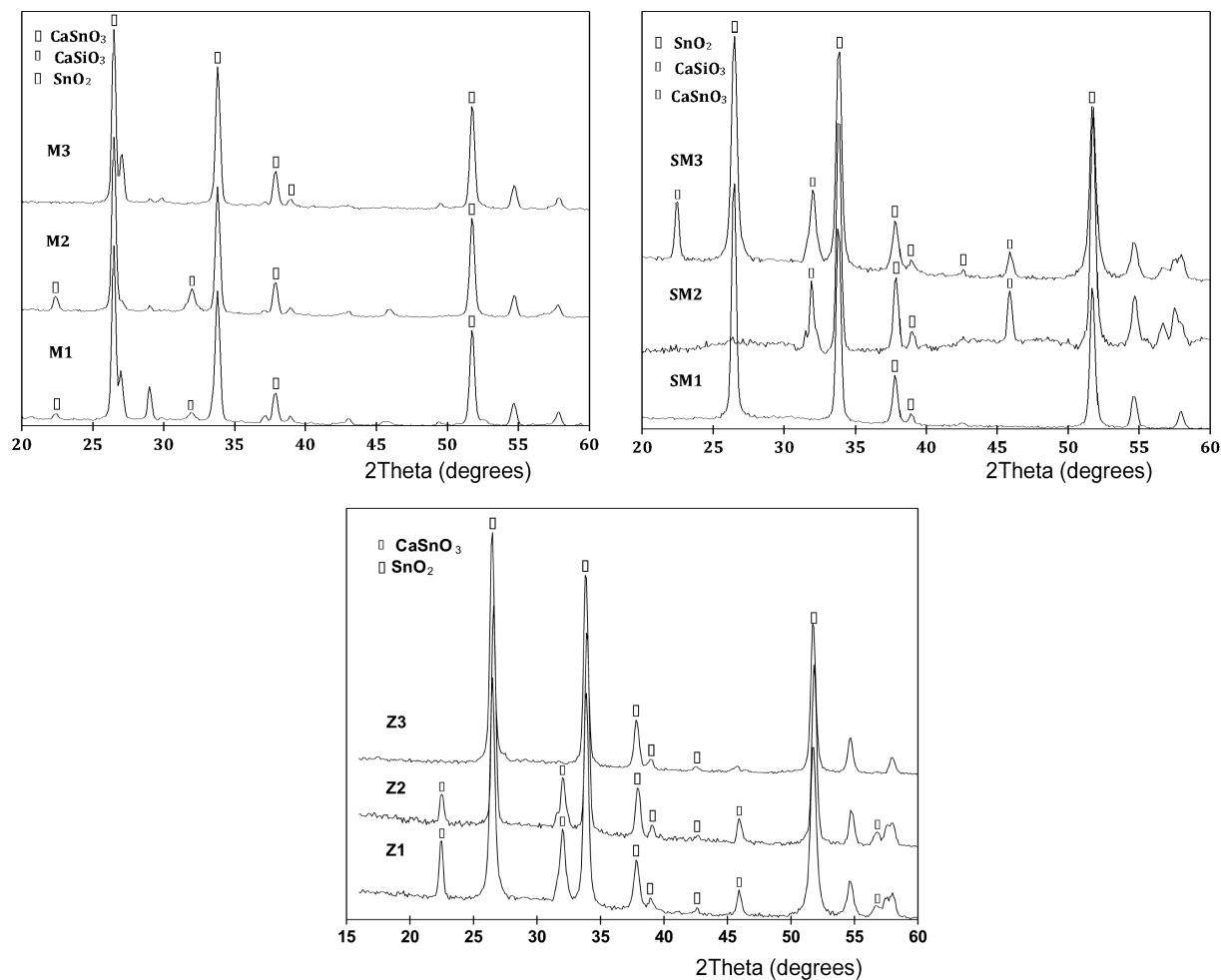


Figure 2. Diffractograms of Cr:CaSnSiO₅, synthesised using: (a) ceramic method; (b) sol-gel; (c) freeze-drying and thermally treated with laser. The unmarked reflections correspond to CaSnSiO₅.

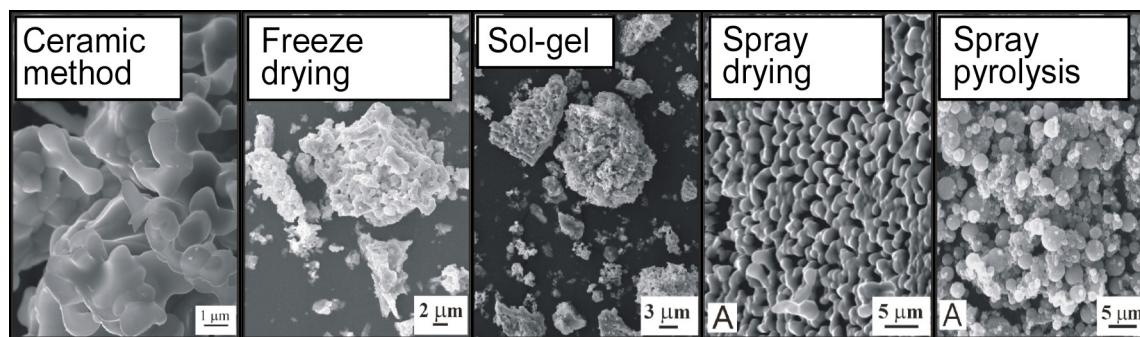


Figure 3. SEM micrographs of representative samples prepared using different synthesis methods.

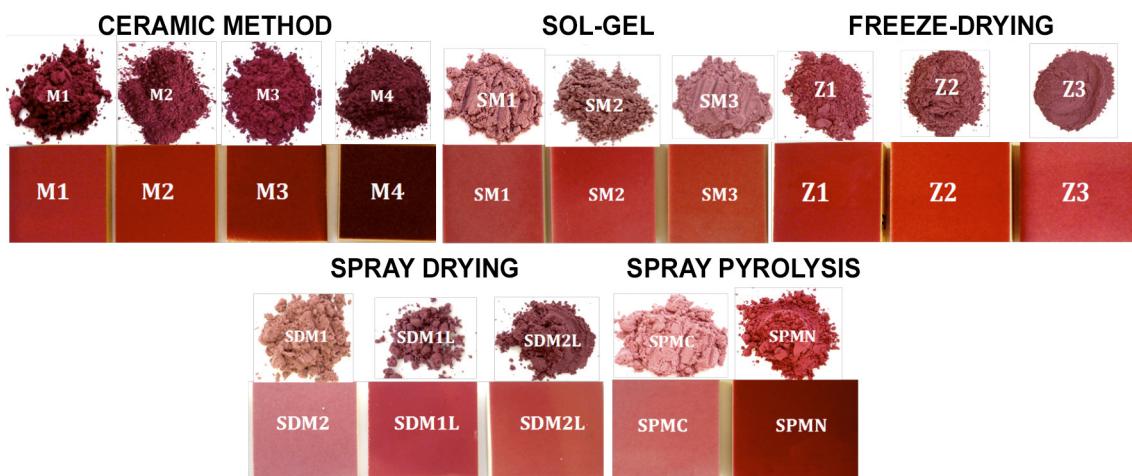


Figure 3. Digital image of the pigments (powders and glazed tiles) obtained using different synthesis methods.

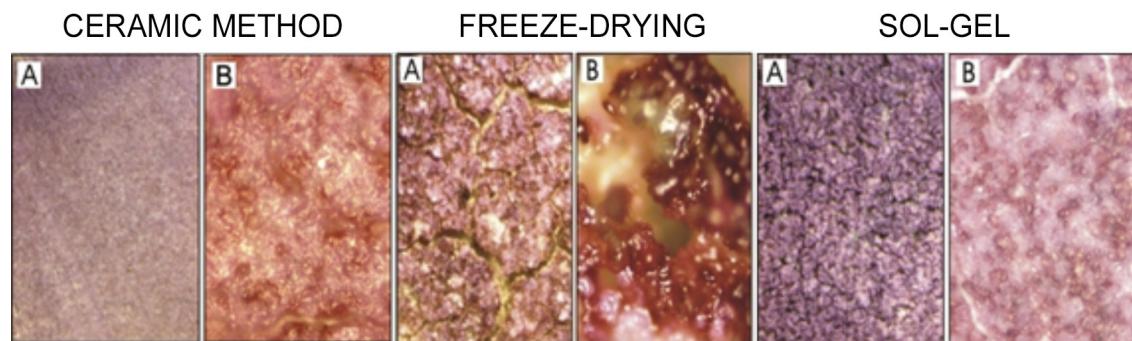


Figure 4. Digital images at different magnifications, obtained with the optical microscope, of the surface of the laser-treated pellets.

3.2. TITANITE Cr:CaSnSiO₅

The thermal evolution of the materials obtained by different synthesis methods and calcined at maximum temperatures according to the preparation method (Fig. 5) exhibited single phases at 800°C for the Cr:CaTiSiO₅ compositions prepared by spray pyrolysis and colloidal sol-gel. These materials were treated at a higher temperature (1000°C) with a view to increasing the crystallinity of the system. The sample prepared by spray drying displayed 97% reactivity at 1200°C. Only freeze-drying synthesis was less favourable, possibly owing to phase separation during preparation. The results obtained by the ceramic method contained minor impurities, though at higher temperatures (1300°C).

The efficiency of the tested synthesis methods in relation to the reactivity of the system Cr:CaTiSiO₅ without mineralisers can be summed up in the following order:

Spray pyrolysis = Sol-gel > Spray drying > Ceramic method > Freeze-drying

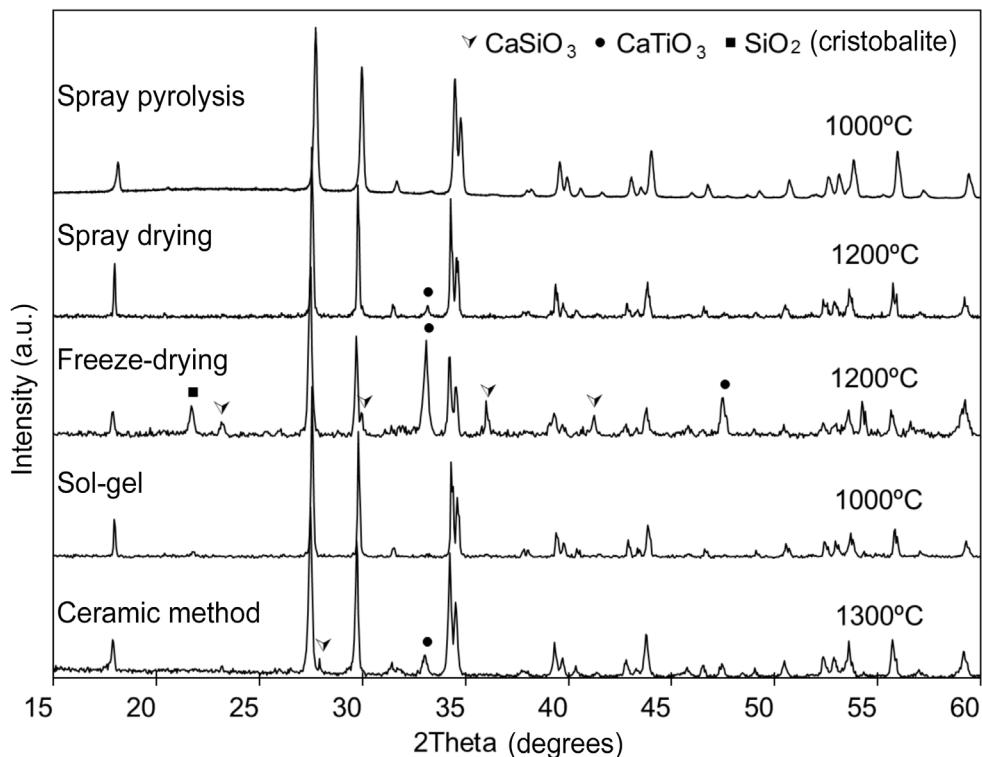


Figure 5. Comparative diffractograms of the $\text{CaTi0.95Cr0.05SiO}_5$, sample, synthesised by different methods and treatments.

The microstructure changed as a function of the synthesis method (Fig. 6), following the same criterion as in the case of malayaite. An irregular morphology involving aggregates with an average size of $10\mu\text{m}$ was found in the non-sprayed materials, whereas the sprayed materials developed spherical particles with an average size between $1\mu\text{m}$ and $5\mu\text{m}$.

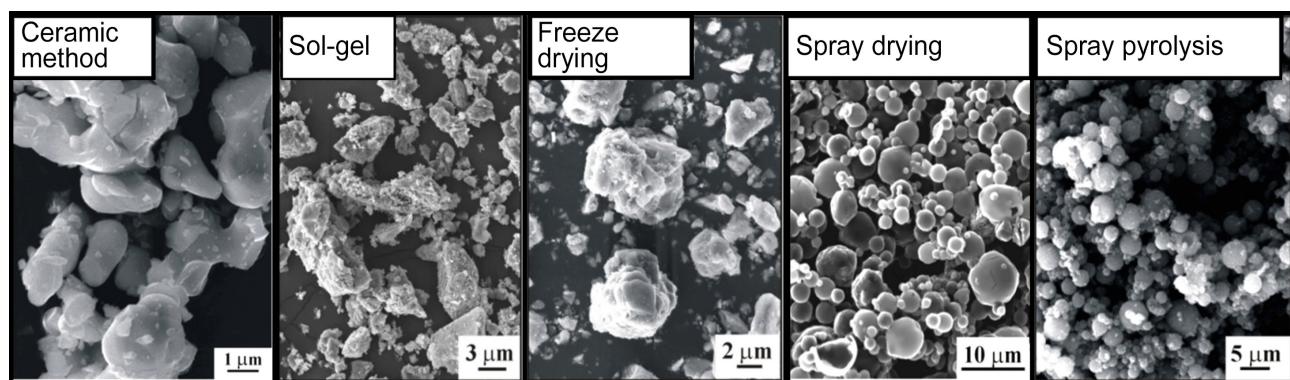


Figure 6. Morphology of the Cr: CaTiSiO_5 pigments obtained using various preparation methods.

The materials synthesised by all the tested methods developed hues in the brown-orange range and have shown that they could be used as ceramic pigments, as they have been successfully applied in industrial glazes (Fig. 7). The colour range depends on the quantity of Cr, synthesis method and precursors used. The most reddish hues were obtained with the pigments prepared by spray pyrolysis.



Figure 7. Digital image of the pigments (powders and glazed tiles) obtained using different synthesis methods.

4. CONCLUSIONS

The study demonstrates the benefits of non-conventional synthesis methods for the development of ceramic pigments that match the new trends in ceramic decoration. Of the different tested methods, the most efficient methods with regard to the reactivity of the studied pigmenting systems were those based on liquid sprays, as they allowed the colour and desired crystalline phases to be obtained at lower temperatures without mineralisers, which is an important advantage from an environmental viewpoint. In addition, they provided greater morphological control, which is desirable for future industrial application.

All the synthesized pigments that were applied on fired glazes produced intensely coloured glazes without defects, indicating that these materials are potentially interesting for the ceramic industry. It may be noted that the efficiency and pigmenting stability of Cr:CaTiSiO₅ has been successfully verified.

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