Synthesis of Ceramic Pigments by Non-Conventional Methods for New Ceramic Decoration Technologies

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

Introduction

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

The need to develop pigments with upgraded properties led to the search for more homogeneous synthesis methods and more effective chemical reactions than the presently traditional methods.

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 photothermal activation by applying laser for the development of ceramic pigments matching new trends and avant-garde decorations [5–9].

The study was carried out 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 $CaSnSiO_5$. In this study, chromium-doped malayaite ($Cr : CaSnSiO_5$) is the only system used as pigment in the ceramic industry. To be noted is that this pigment has drawn high "chemical attention" 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 researchers 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 during its under-glaze decoration and reaction still continues to pose problems.

Titanite ($CaTiSiO_5$) is isostructural to malayaite ($CaSnSiO_5$), but has never been used as ceramic pigment. Therefore, researchers have sought to verify its effectiveness in this field. The difference between both compounds lies in the fact that the octahedron $[TiO_6]$ in $CaTiSiO_5$ is more distorted than $[SnO_6]$ in $CaSnSiO_5$, due to different ionic radii r Sn^{4+} (0,69 Å) > r Ti^{4+} (0,65 Å) [11] resulting in 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.

Experimental

The two materials, $Cr : CaTiSiO_5$ and $Cr : CaSnSiO_5$, were synthesised using the various preparation methods described below. The stoichiometries selected to obtain the solid solutions were: $CaSn_{1-x}Cr_xSiO_5$ and $CaTi_{1-x}Cr_xSiO_5$ ($x = 0,02$, 0,05, 0,10, and 0,20).

Synthesis methods

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, they were heat-treated in a conventional electric kiln. No fluxes were used in order to appropriately compare the materials developed by the alternative methods.

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 $Cr(NO_3)_3 \cdot 9H_2O$. Stoichiometric quantities of metallic compounds were dissolved in water and subsequently frozen by addition of liquid ni-

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trogen under vacuum of about 1 – 10 Pa in a *Telstar* Cryodos freeze-dryer system. This provided in the frozen sample solvent sublimation and yielded an end product in the form of amorphous powder. The powder was milled and prepared for calcination.

Sol-gel method

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

Spray drying and spray pyrolysis method

Spray drying and spray pyrolysis are two independent procedures. However, due 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 atomisation, the spray is introduced into a heated chamber (for spray drying) or into an electric tubular kiln (for spray pyrolysis). The powder obtained by pyrolysis is dried and calcined in a continuous process, the powder obtained by spray drying is subsequently treated in a conventional muffle kiln.

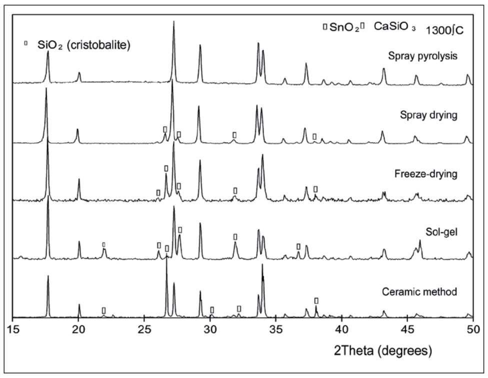

Fig. 1 **Comparative diffractograms of the $CaSn_{0,95}Cr_{0,05}SiO_5$ sample, synthesised by different methods at a temperature of 1300 °C**

Laser method

In the case of malayaite Cr : $CaSnSiO_5$ obtained by sol-gel, freeze-drying, and ceramic method respectively, trials were conducted in order to use laser radiation of CO_2 (λ = 10,6 µm) at a maximum power of 100 W as alternative heat treatment. Samples 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.

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 function of the sample type and desired result.

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 a *Leica* model LEO 440 and a *Jeol* JSM5400 microscope respectively. The materials treated by laser radiation were studied with a *Leica* model Q600S optical microscope. Analysis by UV-visible spectroscopy and measurement of the chromatic coordinates (L*a*b*) were performed for the powder pigments and for those used in industrial glazes [12].

Discussion of results

Malayaite Cr : $CaSnSiO_5$

The thermal evolution of chromium-doped malayaite with the stoichiometry $CaSn_{0,9}5Cr_{0,05}SiO_5$ (chosen as representative) and synthesised at 1300 °C using different methods is shown in Fig. 1. The procedure based on processing using sprays, as spray drying and spray pyrolysis, displayed good compositional control and favourable reactivity. Spray pyrolysis was the best method because only in this way, it was possible to obtain the desired pigment as pure phase.

Fig. 2 shows the thermal behaviour of the malayaite samples calcined applying laser. The stoichiometries displayed correspond to $CaSn_{1-x}Cr_xSiO_5$ (x = 0,02, 0,05, and 0,10). The diffractograms evidence the presence of cassiterite (SnO_2) as major phase, accompanied by the perovskite phases $CaSnO_3$ and $CaSiO_3$, where a very small amount of formed malayaite was noticed. This result may be explained by the short processing time of the samples and the temperature of laser beam (~1500 °C). This indicates that this preparation method is not the most suitable for developing the desired pigment. The efficiency of the tested synthesis methods in relation to the reactivity of the system Cr : $CaSnSiO_5$ without mineralisers can be summed up as follows:

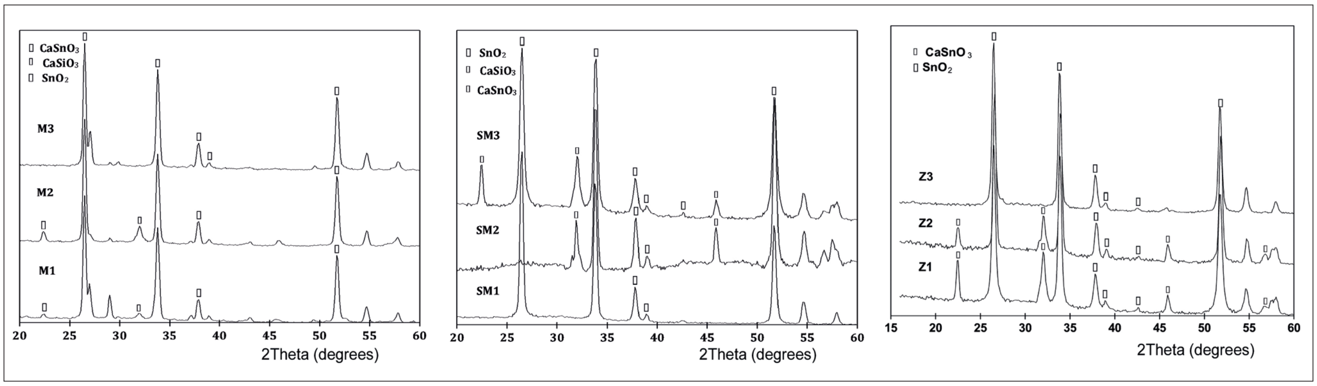

Fig. 2 **Diffractograms of Cr : $CaSnSiO_5$, synthesised using (f.l.t.r.): a) ceramic method; b) sol-gel; c) freeze-drying and thermally treated with laser; the unmarked reflections correspond to $CaSnSiO_5$**

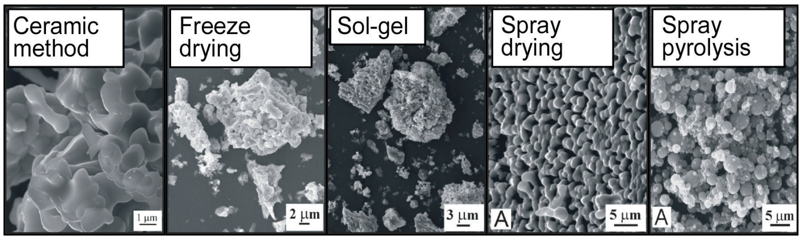

Fig. 3 SEM micrographs of representative samples prepared using different synthesis methods

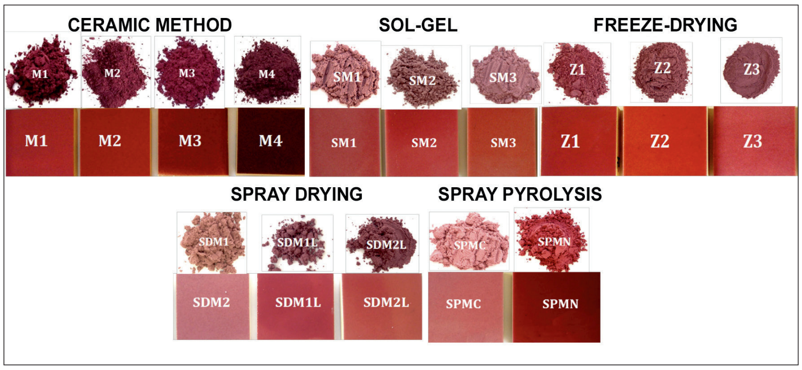

Fig. 4 Digital image of the pigments (powders and glazed tiles) obtained using different synthesis methods

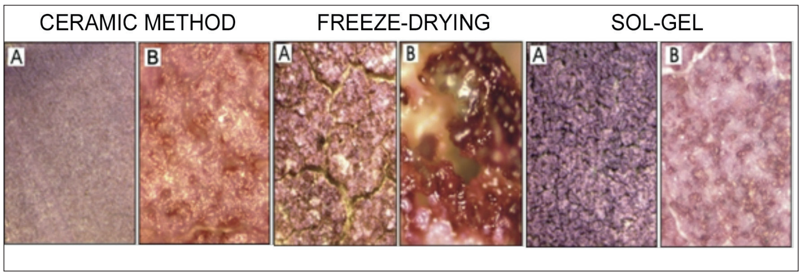

Fig. 5 Digital images at different magnifications, obtained with the optical microscope, of the surface of the laser-treated pellets

spray pyrolysis > spray drying > freeze-drying > ceramic method > sol-gel > laser. The morphology of the developed materials was related to the preparation method. Thus, as may be observed in Fig. 3, the sample obtained by the ceramic method consisted of highly sintered particle aggregates. The sol-gel and freeze-drying methods resulted in polycrystalline grains, of about 20 µm, with coral-like shapes. The spray-based methods 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. As it was proven that these materials could be used as ceramic pigments, they were successfully used in industrial glazes (Fig. 4). However, the best colours were obtained by the spray methods, spray pyrolysis was the optimum method (sample SPMN, $CaSn_{0,95}Cr_{0,05}SiO_5$). This synthesis method does not require mineralisers addition in order to obtain the malayaite solid solution doped with pure chromium, which is an important advantage from an environmental point of view.

Fig. 5 shows digital images of the pressed-pellets surface using precursors synthesised by the ceramic, sol-gel, and freeze-drying methods, and subsequently treated by laser radiation, at different magnifications obtained with the optical microscope. 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.

Titanite Cr : $CaSnSiO_5$

The thermal evolution of the materials obtained by different synthesis methods and calcined at maximum temperatures according to the preparation method (Fig. 6) exhibited single phases at 800 °C for the Cr : $CaTiSiO_5$ compositions prepared by spray pyrolysis and colloidal sol-gel. These materials were treated at a higher temperature (1000 °C) in order to increase 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 due to phase separation during preparation. The pigment body 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 : $CaTiSiO_5$ without mineralisers can be summed up as followsr:

spray pyrolysis = sol-gel > spray drying > ceramic method > freeze-drying.

The microstructure changed as function of the synthesis method (Fig. 7), following the same criterion as in the case of malayaite. An irregular morphology involving aggregates with an average size of 10 µm was found in the non-sprayed materials, the sprayed materials developed spherical particles with an average size of 1 – 5 µm.

The materials synthesised by all tested methods developed hues in the brown-orange range and could be used as ceramic pigments being successfully applied in industrial glazes (Fig. 8). The colour range depends on the Cr quantity, synthesis method and used precursors. The most reddish hues were obtained with the pigments prepared by spray pyrolysis.

Conclusions

The study demonstrates the benefits of non-conventional synthesis methods for the development of ceramic pigments matching the new trends in ceramic decoration. Considering the different tested methods, the most efficient methods regarding the reactivity of the studied pigmenting systems

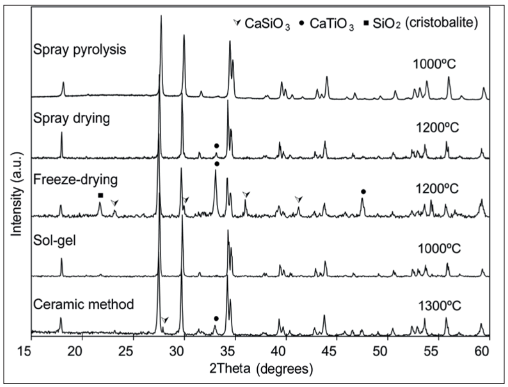

Fig. 6 Comparative diffractograms of the $CaTi_{0,95}Cr_{0,05}SiO_5$ sample, synthesised by different methods and treatments

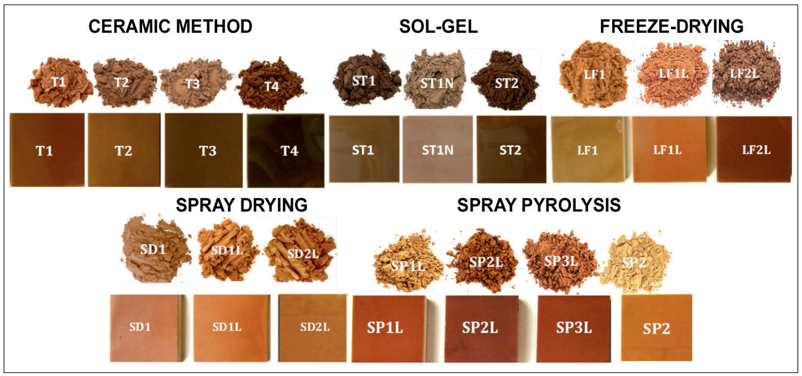

Fig. 7 Morphology of the Cr : $CaTiSiO_5$ pigments obtained using various preparation methods

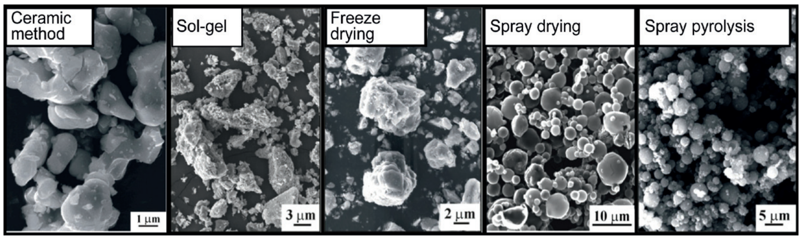

Fig. 8 Digital image of the pigments (powders and glazed tiles) obtained using different synthesis methods

were those based on liquid sprays. They allowed to obtain the colour and desired crystalline phases at lower temperatures without using mineralisers, which is an important advantage from an environmental point of view. In addition, they provided greater morphological control, which is desirable for future industrial application.

All the synthesized pigments applied on fired glazes developed intensely coloured glazes without defects, indicating that these materials are potentially interesting for the ceramic industry. The efficiency and pigmenting stability of Cr : $CaTiSiO_5$ has been successfully verified.

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