A simple procedure for the preparation of Cr-doped tin sphene pigments in the absence of fluxes

E. López-Navarrete, M. Ocaña*

Instituto de Ciencia de Materiales de Sevilla (CSIC-UNSE), Americo Vespucio s/n, Isla de La Cartuja, 41092 Seville, Spain

Abstract

A procedure for the preparation of Cr-doped tin sphene pink pigments based on the pyrolysis at 600°C of liquid aerosols generated from solutions of silicon tetraethoxide, calcium chloride, tin(IV) chloride and chromium(III) nitrate in a mixed solvent (ethanol/water) is reported. The as produced powders were amorphous and consisted of spherical particles of broad size distribution (<2 μm). On calcination at 1200–1300°C, these powders transformed into crystalline tin sphene ($CaSnSiO_5$) irregular particles (<11 μm) developing the pink colour characteristic of the commercial pigments with similar composition. The main advantage of this method is that it does not require the addition of the fluxes used in the traditional ceramic procedure, which is highly desirable from the environmental point of view. Additional advantages are its simplicity (no grinding required) and continuous character. The effects of the chromium content on the colour properties of the pigments were also evaluated, finding that the optimal pigment (best colour with minimum Cr content) was obtained for a Cr/malayaite mole ratio of 4.4%. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Chromium; $CaSnSiO_5$; Pigments; Sphene; Spray pyrolysis

1. Introduction

Cr-doped tin sphene ($CaSnSiO_5$) is an important pink ceramic pigment generally used for colouring ceramic glazes.[1] This pigment is industrially produced by the traditional ceramic method, which involves the mixing by milling of the raw materials (individual metal oxides or salts), the heating of the mixture at high temperature and a final grinding process to homogenize particle size. This procedure requires high calcination temperatures for the formation of the desired crystalline phase. In fact, incomplete reactions have been observed after heating at 1300°C.[2] For this reason, certain amounts of fluxes are usually added to the starting component mixture to favour diffusion, which results in high reaction degrees at 1200°C.[3–5] However, the use of fluxes (alkaline and alkaline earth chlorides, fluorides, nitrates, borates and carbonates) causes some additional environmental effects mainly associated to the emission of pollutants into the atmosphere (NO_x, halides, etc.), which are not desirable.[6] Several synthesis routes such as the sol–gel process,[4] coprecipitation[4] and impregnation techniques,[7]

have been developed in order to obtain higher reaction yields on calcination, although even in these cases, the addition of fluxes was still required.

In this paper, we describe a method for the preparation of pink pigments with Cr-doped tin sphene composition in the absence of fluxes based on the pyrolysis at 600°C of liquid aerosols generated from solutions of silicon tetraethoxide, calcium chloride, tin(IV) chloride and chromium(III) nitrate in a mixed solvent (ethanol/water). This procedure produces Cr-doped amorphous powders with tin sphene (malayaite) composition ($SnO_2:CaO:SiO_2$), which on heating at 1200–1300°C transformed into the pink pigments with $\sim100\%$ reaction yields not requiring the addition of fluxes. The optical properties (colour) of the prepared pigments have been evaluated as a function of the chromium content in the precursors and compared to those of a commercial pigment, in order to optimise the pigment preparation procedure.

2. Experimental

2.1. Powders preparation

Silicon tetraethoxide (TEOS, Fluka, $>98\%$), $CaCl_2\cdot2H_2O$ (Fluka, $>99\%$), $SnCl_4\cdot5H_2O$ (Riedel de Haën,

* Corresponding author. Tel.: +34-9-5448-9527; fax: +34-9-5446-0665.

E-mail address: mjurado@cica.es (M. Ocaña).

98%) and $Cr(NO_3)_3 \cdot 9H_2O$ (Aldrich, 99%) were used as metal precursors as received.

The Cr-doped $CaSnSiO_5$ samples were prepared by pyrolysis of liquid aerosols consisting of solutions of the metal precursors in the apparatus schematized in Fig. 1, according to the following procedure. The starting solutions (250 cm^{-3}) were prepared by dissolving in a mixture ethanol/water (30/70 volumetric ratio) equimolecular amounts (0.05 mol dm^{-3}) of TEOS, calcium chloride and tin chloride and variable concentrations of chromium nitrate. The use of ethanol was needed since, as it is well known, TEOS is not water-soluble. It should be noted that the solutions became slightly cloudy a few minutes after mixing as a consequence of the partial hydrolysis of TEOS and $SnCl_4$ as revealed by EDX analyses of the colloidal precipitate (data not shown). The aerosols were generated from these cloudy solutions by nebulisation, using a glass nozzle (a) and air at constant pressure (0.5 kg cm^{-2}) as a carrier gas. Then, they were introduced into an expansion chamber (b) and transported through two consecutive furnaces (c and d) kept at 250 and 600°C, respectively, in which, the liquid droplets were dried and thermally decomposed. The resulting solid particles were finally collected in a glass filter with a very high efficiency (e). The obtained powders were heated for 3 h at different temperatures in platinum crucibles. The furnace containing the samples was heated at 10°C min^{-1} up to the desired temperature.

A sample was also prepared using the traditional ceramic method for comparison purposes. For this, equimolecular amounts of CaO, SiO_2 and SnO_2 were mixed with the desired quantity of Cr_2O_3. This mixture was homogenised with acetone by mild grinding in an agate mortar and calcined at 1300°C for 3 h.

The commercial Cr-doped tin sphene pigment was supplied by Ferro Enamel Española S.A.

2.2. Characterization techniques

Transmission (TEM, Philips 200 CM) and scanning (SEM, Jeol JSM5400) electron microscopy were used to examine the particle size and shape of the powders. The particle size distribution of the pigments was evaluated using a Malvern Mastersizer instrument.

The quantitative composition of the samples in terms of the Si, Ca, Sn and Cr contents was determined by X-ray fluorescence (Siemens, SRS3000). Energy dispersive X-ray analysis (EDX, Philips DX4), installed in the TEM microscope, was also used to gain information on the particles composition.

Differential thermal (DTA) and thermogravimetric (TGA) analyses (Seiko, EXSTAR 6000) were carried out in air at a heating rate of 10°C min^{-1}.

The colour of the pigments was evaluated according to the Commission Internationale de l'Eclairage (CIE) thorough $L^*a^*b^*$ parameters.[8] In this system, L^* is the colour lightness ($L^* = 0$ for black and $L^* = 100$ for white), a^* is the green (−)/red (+) axis, and b^* is the blue (−)/yellow (+) axis. These parameters were measured for an illuminant D 65, using a Dr. Lange, LUCI 100 colorimeter and a white tile ceramic (chromaticity coordinates: $x = 0.315$, $y = 0.335$) as standard reference. Before measurements, the samples were gently ground in an agate mortar.

3. Results and discussion

Table 1 shows the composition of the four precursors prepared with the stoichiometry of malayaite ($CaSnSiO_5$) and different chromium content (nominal Cr/malayaite mole ratio = 1, 1.5, 5 and 10%) in order to evaluate the effect of this parameter on the optical properties of the final pigments. In this table, the samples are named after the Cr/malayaite mole ratio determined by X-ray fluorescence after heating at 1300°C. As observed, the agreements between the nominal and the measured values are rather good.

The colour of the prepared samples changed from beige to light green on increasing the Cr content. In all cases, they were amorphous to X-ray diffraction and consisted of spherical particles with broad size distribution (diameter < 2 μm) as those illustrated in Fig. 2.

The structural and compositional changes originated in these solids on thermal treatment up to full development
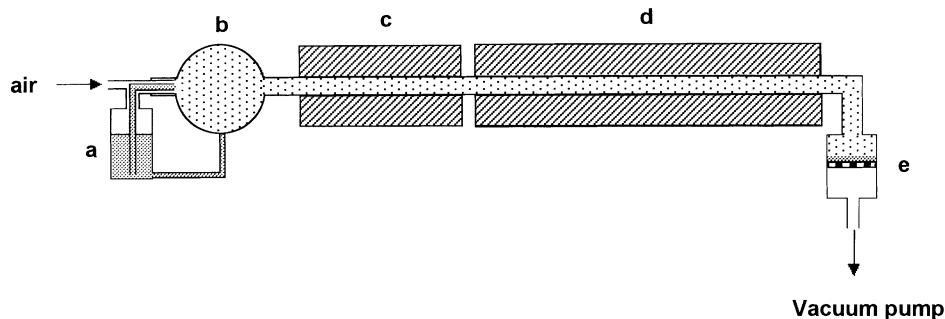

Fig. 1. Schematic diagram of the apparatus used for the preparation of Cr-doped samples by pyrolysis of aerosols. Symbols: a, solution container and glass nozzle; b, expansion chamber; c and d, furnaces; e, filter.

Table 1
Composition (nominal and measured by X-ray fluorescence) of the Cr-doped tin sphene samples prepared by pyrolysis of aerosols and heated at 1300°C, and that measured for a commercial pigment

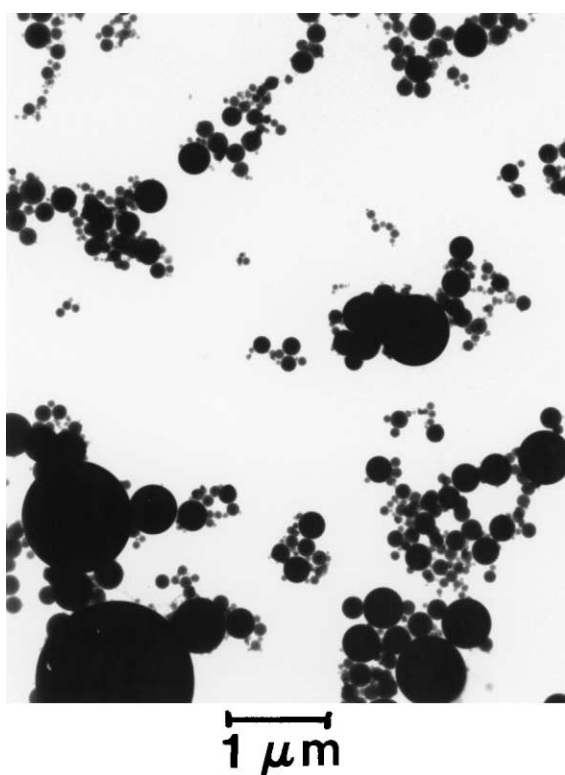|	Sample	Si/Ca mole ratio	Sn/Ca mole ratio	Cr/malayaite mole ratio (%)
Nominal	Cr1	1.0	1.0	1.0
Measured	Cr1	1.0	1.1	1.0
Nominal	Cr1.4	1.0	1.0	1.5
Measured	Cr1.4	1.0	1.0	1.4
Nominal	Cr4.4	1.0	1.0	5.0
Measured	Cr4.4	1.0	1.0	4.4
Nominal	Cr10	1.0	1.0	10.0
Measured	Cr10	1.0	1.0	10.0
Measured	Commercial	1.8	1.0	7.8

Fig. 2. TEM micrograph of the powders prepared by pyrolysis at 600°C of an aerosol generated from a solution of TEOS (0.05 mol dm⁻³), tin(IV) chloride (0.05 mol dm⁻³), calcium chloride (0.05 mol dm⁻³) and Cr(III) nitrate (Cr/malayaite mole ratio = 1.5%) in ethanol/water (30/70 volumetric ratio).

of the sphene structure were followed by differential thermal and thermogravimetric analyses and X-ray diffraction. Most of the results presented hereafter correspond to sample Cr1.4 (Table 1) chosen as a representative example. The other prepared samples showed a similar thermal behaviour except when indicated.

The DTA curve of sample Cr1.4 (Fig. 3) displayed a broad endothermic peak centred at 75°C, which was accompanied by a weight loss of ∼3.5% (in the 25–400°C range) as detected by TGA measurements (Fig. 3). These effects were caused by the release of water. The TGA analysis also indicated that the sample lost ∼10% of weight on heating between 400 and 1000°C, which can be associated to the release of chlorine still retained in the sample, as suggested by EDX analyses. Thus, the spectrum of the sample heated at 400°C showed the chlorine peak, which disappeared after heating at 1100°C (Fig. 4). Although no thermal effects were detected in the DTA curve at 200–500°C, X-ray diffraction showed the crystallization of SnO_2 (cassiterite)[9] at the latter temperature (Fig. 5). Two exothermic effects were also observed in the DTA curve at 740 and 960°C, respectively. The first one was very weak and could be tentatively associated to the crystallisation or transformation of a chromium-containing phase, since its intensity slightly increased with chromium content (data not shown). However, this assumption could not be confirmed by X-ray diffraction, which only showed the presence of cassiterite at 750°C (Fig. 5), probably due to the small amount of chromium present in the sample (Cr/malayaite mole ratio = 1.4%, Table 1). Finally, the peak at 960°C can be attributed to the crystallization of malayaite as suggested by the appearance of the peaks of this phase[10] in the X-ray diffraction pattern of the sample heated at 1000°C, in which some reflections of SnO_2 and $CaSiO_3$ (wollastonite-2M)[11] were also detected (Fig. 5). The intensity of the latter progressively decreased as the heating temperature increased, finally disappearing at 1300°C (Fig. 5). A similar X-ray diffraction pattern was obtained for samples Cr4.4 and Cr10 heated at this temperature (Fig. 6). However, the reflection of cassiterite at $2\theta \sim 26.8$, was still present with very low intensity in the pattern of sample Cr1 after this treatment (Fig. 6). This observation is in agreement with the X-ray fluorescence analyses carried out for the heated samples, which showed that whereas samples Cr1.4, Cr4.4 and Cr10 presented the stoichiometry of malayaite ($CaSnSiO_5$), sample Cr1 contained a slight excess of Sn (Sn/Ca mole ratio = 1.1) (Table 1). It is important to mention that the formation of malayaite was incomplete when a mixture of the component oxides (SiO_2, SnO_2, CaO and Cr_2O_3) with the same composition of sample Cr1.4 was heated at 1300°C following the traditional ceramic procedure. Thus, the X-ray diffraction pattern of the heated sample showed important amounts of unreacted cassiterite in addition to malayaite (Fig. 7). This sample must also contain α-quartz[12] and lime (CaO),[13] which are difficult to detect by X-ray diffraction in this case, since theirs main peaks overlap with other cassiterite or malayaite reflections. This decrease of the temperature of malayaite formation in our precursors may be attributed to the high degree of mixing of the component cations attained at the particle level, for powders prepared by pyrolysis of aerosols,[14] since in this procedure each aerosol droplet
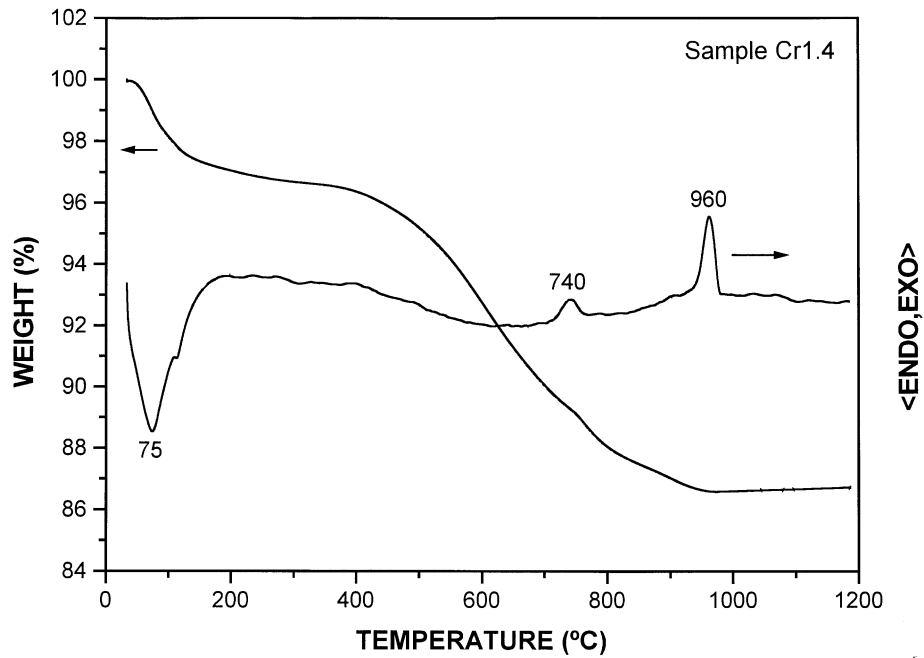
Fig. 3. Differential thermal and thermogravimetric curves obtained for sample Cr1.4.
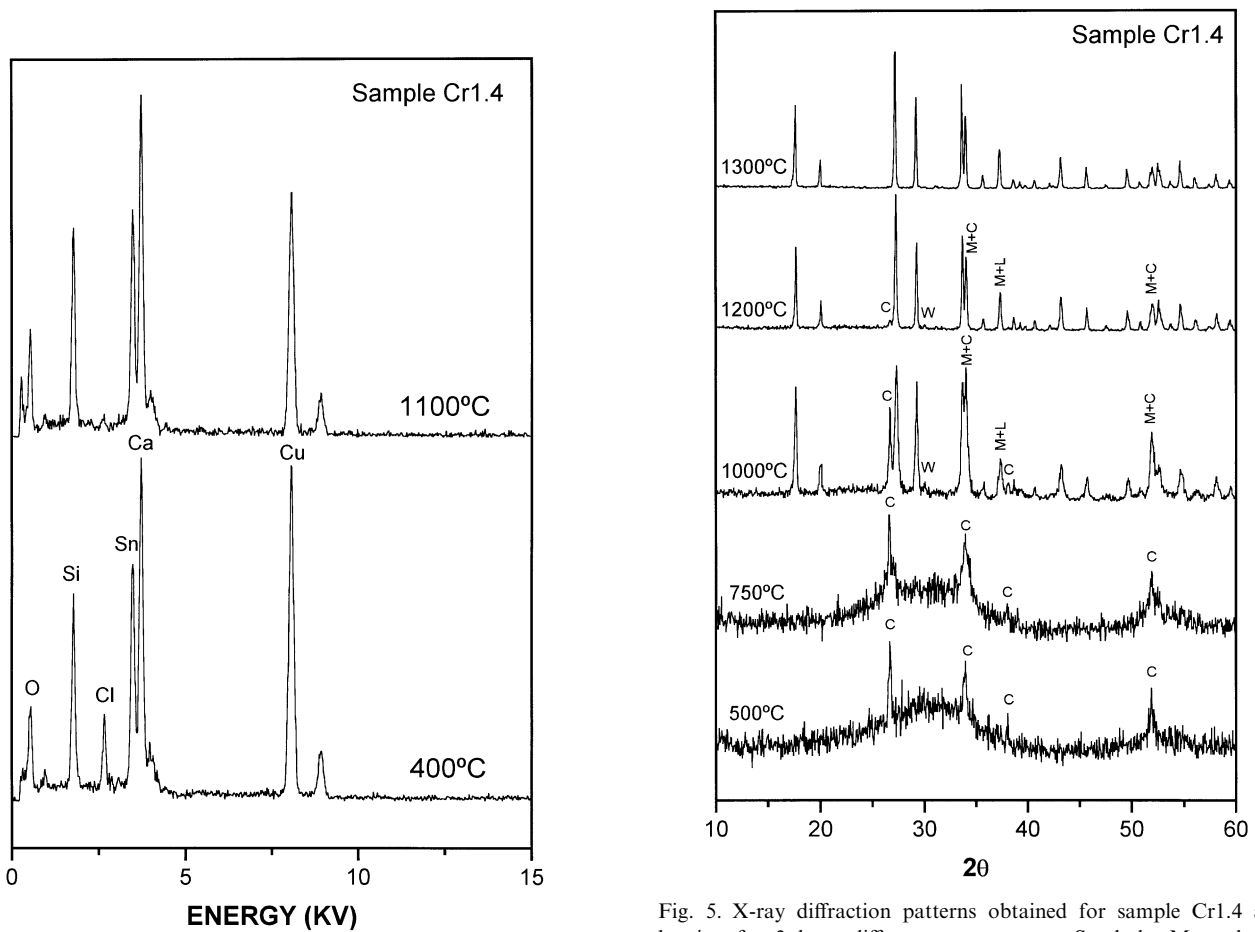

Fig. 4. EDX spectra obtained for sample Cr1.4 after heating at different temperatures.

Fig. 5. X-ray diffraction patterns obtained for sample Cr1.4 after heating for 3 h at different temperatures. Symbols: M, malayaite ($CaSnSiO_5$); C, cassiterite (SnO_2); L, lime (CaO); W, wollastonite-2M ($CaSiO_3$). The pure malayaite peaks have not been labelled.
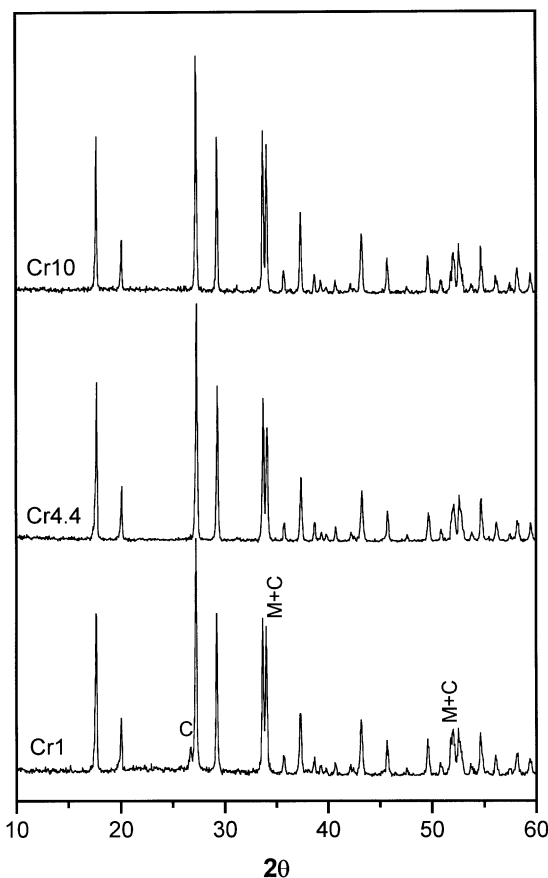
Fig. 6. X-ray diffraction patterns obtained for samples Cr1, Cr4.4 and Cr10 after heating for 3 h at 1300°C. Symbols: M, malayaite (CaSnSiO$_5$); C, cassiterite (SnO$_2$). The pure malayaite peaks have not been labelled.
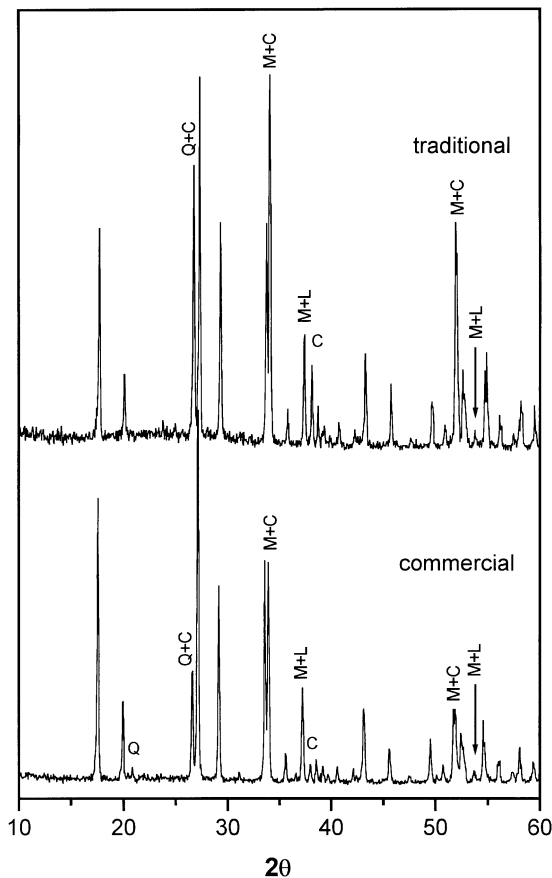

Fig. 7. X-ray diffraction patterns obtained for a sample having the same composition of sample Cr1.4 prepared at 1300°C by the traditional ceramic procedure and for a commercial sample. Symbols: M, malayaite (CaSnSiO$_5$); Q, α-quartz; C, cassiterite (SnO$_2$); L, lime (CaO). The pure malayaite peaks have not been labelled.

behaves as an independent reactor. This intimate mixing would favour the diffusion process required for the formation of the crystalline phase, as it has been previously reported for other systems as mullite,[15] zircon[16] and iron doped zircon pigments[17] prepared by similar method.

It should be noted that the heat treatment of the samples at 1300°C also produced particle sintering, which resulted in Cr-doped malayaite particles of irregular shape as those illustrated in Fig. 8A, which correspond to sample Cr4.4. The particle size analysis of this sample revealed a bimodal distribution with two maxima centred at 0.3 and 3.8 μm, respectively, in the volumetric curve and that the maximum particle size was ∼11 μm (Fig. 9).

The $L^*a^*b^*$ parameters and the colour of sample Cr1.4 (Table 1) as prepared and after heating at different temperatures are shown in Table 2. As observed, the as prepared sample was almost achromatic (small a^* and b^* values) showing a beige colour of low intensity (high L^*). No important changes of these magnitudes were observed when the sample was heated up to 700°C. However, at 1000°C, an important increase (from 1.2 to 16.5) of a^* (green–red axis) took place accompanied by

a decrease (from 4.9 to 0.9) of b^* (blue–yellow axis) and L^* (from 75.9 to 65.7) indicating the development of the pink colour characteristic of the Cr-doped tin sphene, which is in agreement with the beginning of the malayite formation (Fig. 5). No significant variations of a^* or b^* resulted when the sample was heated at higher temperatures (up to 1300°C), although a progressive decrease (from 65.7 to 58) of luminosity (L^*), i.e. an increase of colour intensity, was detected, which may be ascribed to the progress in malayaite crystallisation (Fig. 5). It should be noted that the heating of this sample at 1200°C produced a pigment with similar $L^*a^*b^*$ parameters to those obtained after calcination at 1300°C (Table 2), although at 1200°C a small amount of unreacted SnO$_2$ was still present (Fig. 5).

The effects of the amount of chromophore on the colour properties of the Cr-doped tin sphene pigments are also included in Table 2. It can be noticed that after full development of the sphene structure (1300°C), the only appreciable change of the $L^*a^*b^*$ parameters is related to a decrease of luminosity (from 59 to 50.8), i.e. increase in the colour intensity, as the initial Cr/
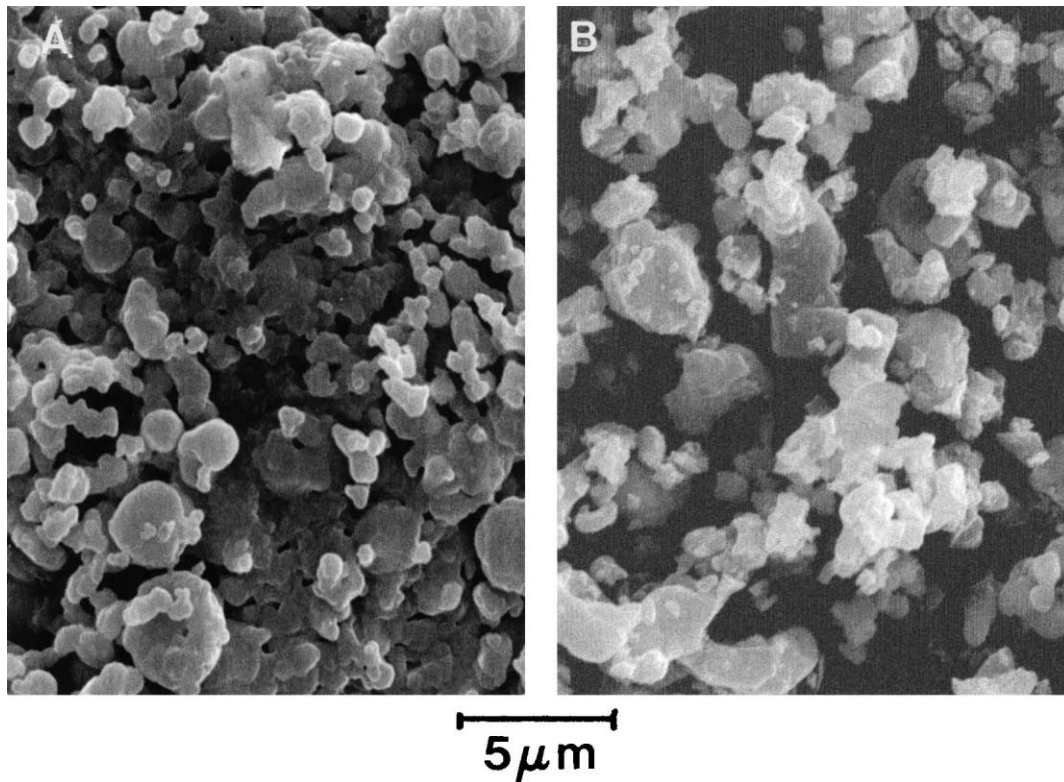
Fig. 8. SEM micrographs of sample Cr4.4 heated for 3 h at 1300°C (A) and of a commercial sample (B).
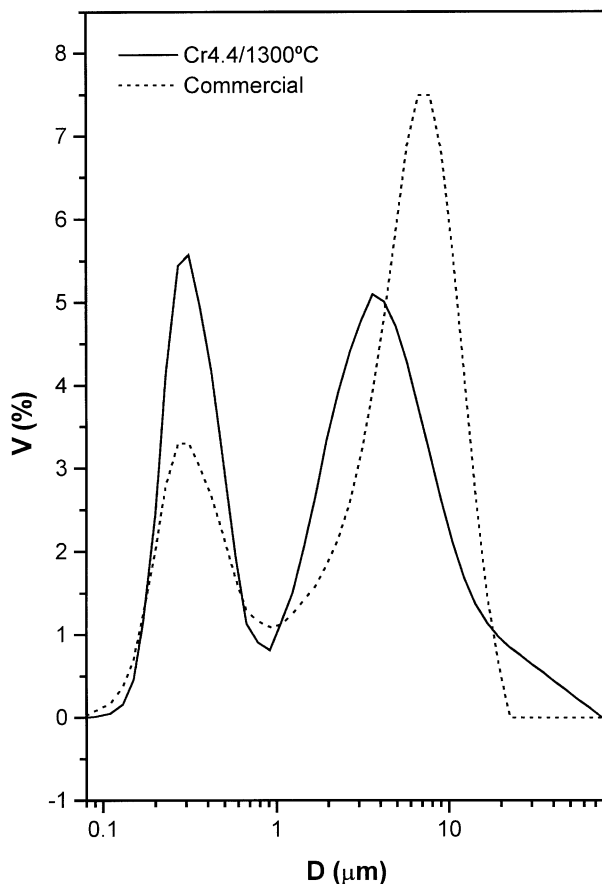

Fig. 9. Particle size distribution curves of sample Cr4.4 heated for 3 h at 1300°C and of a commercial sample.

Table 2
$L*a*b*$ parameters and colour of the Cr-doped tin sphene samples heated at different temperatures and those of a commercial pigment

Sample	Temperature (°C)	$L*$	$a*$	$b*$	Colour
Cr1.4	As prepared	78.1	−0.2	6.0	Beige
Cr1.4	500	75.8	1.2	5.8	Beige
Cr1.4	700	75.9	1.2	4.9	Beige
Cr1.4	1000	65.7	16.5	0.9	Pink
Cr1.4	1200	59.7	18.3	−0.7	Pink
Cr1.4	1300	58.0	17.1	−1.0	Pink
Cr1	1300	59.0	16.6	0.1	Pink
Cr4.4	1300	50.8	21.4	1.1	Pink
Cr10	1300	49.0	16.5	0.7	Pink
Commercial		49.9	15.0	0.8	Pink

malayaite mole ratio increased from 1 to 4.4% (Table 1). Higher values of this magnitude (10%) (sample Cr10, Table 1) did not result in a more intense colour ($L* = 49$), for which we can conclude that the optimum pigment (best colour with lowest Cr content) is obtained by the here reported procedure for a Cr/malayaite mole ratio of 4.4% (sample Cr4.4, Table 1).

Finally, it must be mentioned that our best pigment, prepared under the above conditions, showed similar $L*a*b*$ parameters that a commercial sample (Table 2), which contained a higher amount of chromium (Cr/malayaite mole ratio = 7.8%) (Table 1). Since the grain size distributions were similar for both pigments (Figs. 8 and 9), such a behaviour must be attributed to the presence of an important excess of silica (Si/Ca mole

ratio = 1.8) in the commercial sample (Table 1), which also contained small amounts of cassiterite (Fig. 7).

4. Conclusions

We have shown that the pyrolysis at 600°C of aerosols generated from solutions with appropriated concentrations of silicon tetraethoxide, calcium chloride, tin(IV) chloride and chromium(III) nitrate in a mixed solvent (ethanol/water) yields amorphous precursors, which on calcination at 1200–1300°C transform in Cr-doped tin sphene pigments consisting of irregular particles (<11 μm), which showed colour properties similar to those of the commercial samples. This procedure does not require the addition of the fluxes involved in the conventional method, which is highly desirable from the environmental point of view. Such a behaviour is attributed to the intimate mixing of the metal cations attained in our case, which favour the further diffusion process required for the formation of the desired crystalline phase (malayaite). Additional advantages of our procedure are its simplicity (it eliminates the grinding processes associated to the conventional method) and its continuous character, which are of interest for industrial purposes. From the analysis of the effects of the chromium content on the colour properties of the pigments, it was also concluded that the optimum pigment (best colour with minimum Cr content) was obtained for a Cr/malayaite mole ratio of 4.4%.

Acknowledgements

References

1. *Classification and Chemical Description of the Complex Inorganic Color Pigments*. Dry Color Manufacturer's Association, Alexandria, VA, 1991.
2. Escribano, P. and López, C., Monzonís, G. and Alarcón Navarro, J., Cr–SnO$_2$–CaO–SiO$_2$-based ceramic pigments. *Ceram. Bull,* 1984, **63**, 1492–1494.
3. Ren, F., Ishida, S., Takeuchi, N. and Wakamatsu, M., Colors of chromium in the SnO$_2$–TiO$_2$-based systems. *Ceram. Eng. Sci. Proc,* 1992, **13**, 132–138.
4. Stefani, R., Longo, E., Escribano, P., Cordoncillo, E. and Carda, J. B., Developing a pink pigment for glazes. *Am. Ceram. Soc. Bull.,* 1997, **76**(9), 61–64.
5. Cordoncillo, E., del Rio, F., Carda, J., Llusar, M. and Escribano, P. J., Influence of some mineralizers in the synthesis of sphene-pink pigments. *J. Eur. Ceram. Soc.,* 1998, **18**, 1115–1120.
6. Llusar, M., Badenes, J. A., Calbo, J., Tena, M. A. and Monrós, G., Environmental optimization of flux additions. *Am. Ceram. Soc. Bull.,* 1999, **78**(7), 63–68.
7. Shangani, D. V., Abrams, J. R. and Smith, P. J., A structural investigation of some tin-based coloured ceramic pigments. *Trans. J. Br. Ceram. Soc.,* 1981, **80**, 210–214.
8. C.I.E., *Recommendations on Uniform Color Spaces, Color Difference Equations, Psychometrics Color Terms*. Supplement No 2 of C.I.E. Publ. N. 15 (E1-1.31) 1971. Bureau Central de la C.I.E., Paris, 1978.
9. JCPDF file No 21-1250.
10. JCPDF file No 25-176.
11. JCPDF file No 27-88.
12. JCPDF file No 33-1161.
13. JCPDF file No 4-777.
14. Messing, G. L., Zhang, S. C. and Jayanthi, G. V., *J. Am. Ceram. Soc.,* 1993, **76**, 2706–2726.
15. Kanzaki, S. and Tabata, H., Synthesis and mechanical properties of stoichiometric mullite. *J. Am. Ceram. Soc.,* 1985, **68**, C6–C7.
16. Gonzalez-Carreño, T., Tartaj, P., Sanz, J., Serna, C. J. and Ocaña, M., Zircon formation from amorphous spherical ZrSiO$_4$ particles obtained by chemical reactions in aerosols. In *Proceedings of the 8th CIMTEC — World Ceramic Congress and Forum on New Materials: Advances in Science and Technology 3B*, ed. P. Vicentini. Techna, Faenza, 1995, pp. 1211–1220.
17. Tartaj, P., González-Carreño, T., Serna, C. J. and Ocaña, M., Iron zircon pigments prepared by pyrolysis of aerosols. *J. Solid State Chem.,* 1997, **128**, 102–108.