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Ceramics International 29 (2003) 385–392

CERAMICS
INTERNATIONAL

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Non-conventional synthesis of Cr-doped SnO_2 pigments

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Received 20 May 2002; received in revised form 17 June 2002; accepted 2 July 2002

Abstract

It is shown that Cr–SnO_2 violet pigments can be synthesised by heating at 1300 °C precursors obtained by pyrolysis at 600 °C of aerosols generated from aqueous solutions of tin (IV) chloride and chromium (III) nitrate. This method is simpler than the conventional one and permits to control the particle size distribution not requiring grinding. In addition, it is a continuous technique which makes it suitable for industry. The effects of the chromophore (Cr) concentration on the colour properties of the pigments were evaluated. The optimum pigment obtained by this procedure corresponds to a Cr/Sn molar ratio in the 0.04–0.05 range. The colour changes originated as a consequence of the heat treatment of the precursors obtained by pyrolysis of aerosols up to the development of the desired pigments were interpreted in terms of the variations of the oxidation state of the Cr species during calcination.

Keywords: Synthesis; Pigments; Spray pyrolysis; Cr–SnO_2

1. Introduction

Chromium-doped cassiterite (SnO_2) pigments, also called chrome tin orchid cassiterite [1], have long been used in the ceramic industry for colouring glazes [2]. Nowadays, this pigment is still the only alternative to cadmium-containing pigments for deep burgundy shades in the pottery industry [3]. As most ceramic pigments, it is industrially prepared by solid state reactions through the traditional ceramic procedure which involves several steps including the initial milling of the mixture of the component precursors (metal oxides and/or salts) for homogenisation, the calcination of this mixture at high temperature to develop the desired phases and colours and a final grinding process to reduce particle size [4]. The morphological characteristics (size and shape) of the particles resulting from this process are not easy to reproduce, which affects negatively to the reproducibility of the optical properties of the so obtained pigments. In addition, the required grinding processes usually introduce chemical contamination in the pigments, which also may influence colour quality.

It has been amply shown that the method known as pyrolysis of liquid aerosols (or spray pyrolysis) is a very convenient procedure for the preparation of ceramic powders [5] including pigments [6–8], which offers several advantages over other synthesis techniques such as simplicity (powders are produced from a solution in a single step), high purity, excellent control of composition and stoichiometry in multicomponent systems, easy control of particle size (determined by the characteristics of the aerosol generator) and shape (always spherical since each droplet act as an independent reactor) and continuous character, which makes suitable for industrial production [5,9].

In this work we describe the preparation of Cr-doped SnO_2 pigments by pyrolysis of aerosols generated from aqueous solutions of chromium (III) nitrate and tin (IV) chloride. Since the so produced powders were beige, they were thermally treated up to the development of the violet colour characteristic of this pigment. The compositional, structural and morphological changes produced as a consequence of this treatment were studied. The pigment was also characterised in terms of their electrokinetic behaviour to determine their isoelectric point. Finally, the effect of the chromium content on the pigments optical properties was investigated in order to optimize the preparation procedure.

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doi:10.1016/S0272-8842(02)00149-9

2. Experimental

2.1. Samples preparation

Cr-doped SnO_2 powders were prepared by spray pyrolysis in an apparatus previously described [7]. The aerosols were generated from aqueous solutions containing Sn(IV) chloride ($SnCl_4{\cdot}5H_2O$, Riedel de Haën, 98%) and Cr(III) nitrate ($Cr(NO_3)_3{\cdot}9H_2O$, Aldrich, 99%). The concentration of $SnCl_4$ was kept constant in all experiments (0.05 mol dm^{-3}), whereas the Cr/Sn molar ratio was varied from 0.03 to 0.10 in order to analyse the influence of the chromophore (Cr) content on the pigments colour properties. The starting solutions were nebulized using a glass nozzle and air at constant pressure (0.5 kg cm^{-2}) as a carrier gas. The resulting aerosols were first introduced into a furnace heated at 250 °C, to evaporate the solvent from the droplets and afterwards into a second furnace at 600 °C, to decompose the metal precursors. The resulting solid particles were collected with a glass filter.

The obtained powders were calcined at different temperatures for 3 h in platinum crucibles using a heating rate of 10 °C min^{-1}.

2.2. Characterization

The particle size and shape of the powders were examined by scanning electron microscopy (SEM, Jeol JSM5400). The volumetric particle size distribution of the samples was obtained from laser diffraction measurements (Malvern Mastersizer S).

The composition of the powders (Cr/Sn molar ratio) was determined by X-ray fluorescence (Siemens, SRS3000). Energy dispersive X-ray analysis (EDX, Philips DX4) installed in a transmission electron microscope (Philips 200 CM) was also used to gain information on the composition of the particles.

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 crystalline phases present in the solids were identified by X-ray diffraction (XRD) (Siemens D501). The crystallite size was determined from the X-ray diffraction reflection at $2\theta \sim 26.57$ by using the Scherrer formula.

The infrared spectra for the powders diluted in KBr pellet were recorded in a Nicolet 510 Fourier transform spectrometer.

X-ray photoelectron spectra (XPS) were obtained with a VG Escalab 210 model using the MgKα excitation source. Calibration of the spectra was done at the C1s peak of surface contamination taken at 284.6 eV. The peaks areas were corrected by the sensitivity factors of the elements as supplied by the instrument manufacturers.

The isoelectric point (i.e.p.) of the powders was determined from electrophoretic mobility measurements carried out for aqueous dispersions as a function of pH. For this, 3 mg of sample were dispersed in 100 ml of a 0.01 mol dm^{-3} NaCl solution to keep the ionic strength constant while the pH was varied by adding HCl or NaOH, as needed.

The pigments colour was measured using a Dr. Lange, LUCI 100 colorimeter, for an illuminant D65 and a white tile ceramic (chromaticity coordinates: $x = 0.315$, $y = 0.335$) as standard reference. The colour was evaluated according to the Comission Internationale de l'Eclairage (CIE) by using $L^*a^*b^*$ parameters [10]. In this system, L^* is the colour lightness ($L^* = 0$ for black and $L^* = 1$ for white), a^* is the green (−)/red (+) axis, and b^* is the blue (−)/yellow (+) axis.

3. Results and discussion

The composition of the as prepared Cr-doped SnO_2 samples in terms of their Cr/Sn molar ratio is shown in Table 1. As observed, the measured values are in good agreement with the nominal ones (Cr/Sn molar ratio from 0.03 to 0.1), which manifest the effectiveness of the pyrolysis method to control the stoichiometry of multicomponent systems. It should be noted that the samples also contained a certain amount of chlorine coming from the Sn precursor as revealed by EDX analyses (Fig. 1) for sample Cr4 (initial Cr/Sn molar ratio = 0.038, Table 1). Most of the characterization data hereafter presented corresponds to this sample, which has been chosen as a representative example. All other studied samples showed a similar characteristics and thermal behaviour except when indicated.

The as prepared samples were composed of spherical particles (Fig. 2A) of broad size distribution with diameters ranging from 0.05 to 8 μm (Fig. 3). As observed by SEM (Fig. 2A), some of these spheres were hollow suggesting surface precipitation of the salts precursors during the drying process of the aerosol droplets [5].

Table 1

Composition of the Cr-doped SnO_2 samples, as prepared and after heating for 3 h at 1300 °C

Sample	$(Cr/Sn)_{nominal}$ molar ratio	Heat treatment	$(Cr/Sn)_{experimental}$ molar ratio
Cr3	0.03	As prepared 1300 °C	0.031 0.036
Cr4	0.04	As prepared 1300 °C	0.038 0.043
Cr5	0.05	As prepared 1300 °C	0.050 0.052
Cr10	0.10	As prepared 1300 °C	0.106 0.138

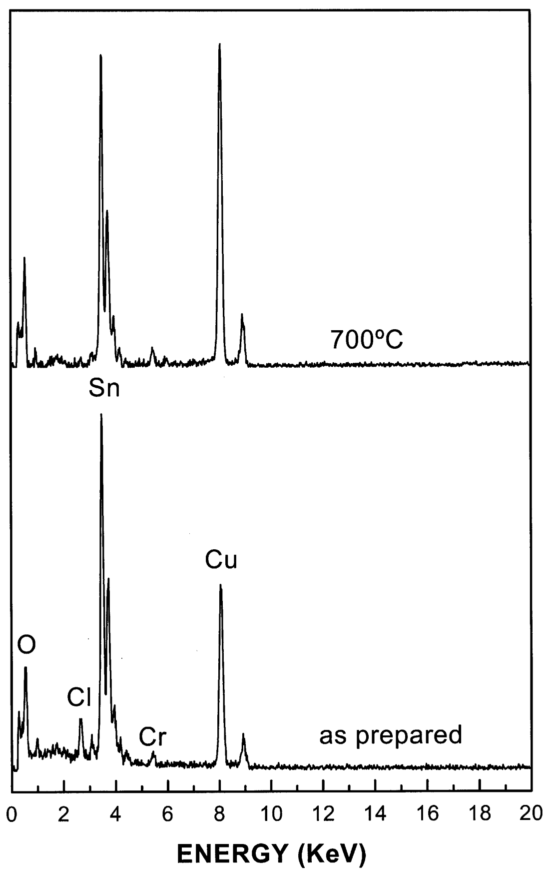

Fig. 1. EDX spectra obtained for sample Cr4, as prepared and after heating at 700 °C. The most intense peaks of the elements have been labelled. The Cu peak is due to the TEM grid.

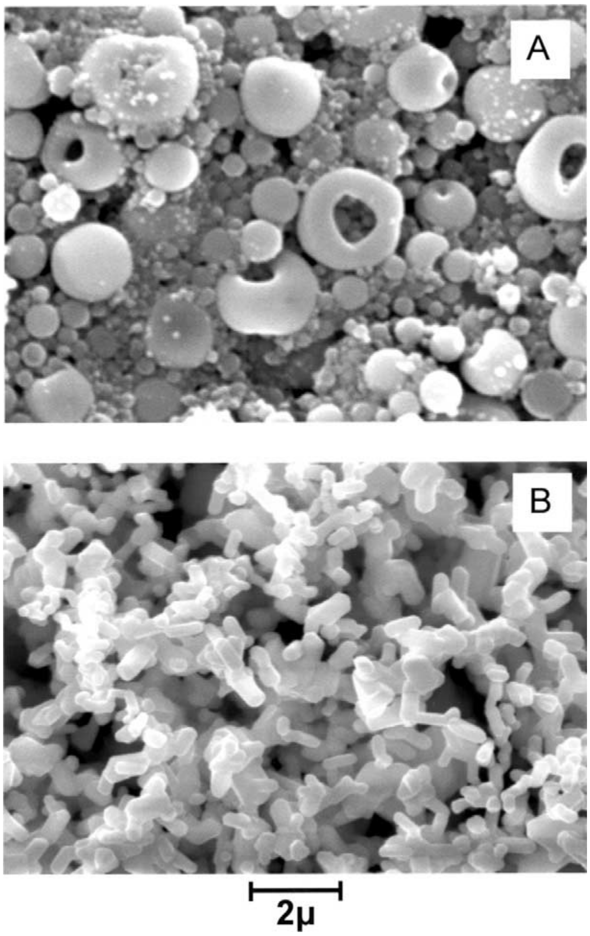

Fig. 2. Scanning electron micrographs obtained for sample Cr4, as prepared (A) and after heating at 1300 °C (B).

X-ray diffraction (Fig. 4) showed that the only crystalline phase present in these powders consisted of poorly crystallized cassiterite [11]. As illustrated for sample Cr4, the crystallite size resulting from the X-ray diffraction pattern (Table 2) was much smaller (3.5 nm) than the mean size of the particles measured by laser diffraction (Fig. 3), indicating their polycrystalline character. Additional structural and compositional information on this sample can be obtained from its infrared spectrum (Fig. 5). As it has been amply reported [12–15], the position of the absorption bands of a microcrystalline inorganic solid varies as a function of the shape of the microcrystals. This effect has been previously recognized for several metal oxides including cassiterite [14,15]. The spectrum of our sample displays main bands at 665, 610 and 315 cm^{-1} which are very close to those expected for spheres [14] manifesting the spherical shape of the crystallites that compose the particles. It should be also noted the absence of absorption bands in the 1300–1500 cm^{-1} region indicating the complete decomposition of the chromium nitrate precursor during pyrolysis. This process should produce Cr_2O_3, which could be responsible for the weak shoulders observed at the low frequency side of the 610 cm^{-1} infrared band [16].

Table 2
Crystallite size and $L^*a^*b^*$ parameters measured for sample Cr4 as prepared and after heating for 3 h at different temperatures

Heat treatment	Crystallite size nm	L^*	a^*	b^*
As prepared	3.5	69.1	2.3	9.5
300 °C		67.5	3.6	10.3
500 °C		53.7	9.4	−1.9
700 °C	17.0	45.8	11.0	−8.0
1000 °C		59.2	4.6	5.3
1200 °C		64.0	4.0	1.6
1300 °C	>1000	59.4	9.2	−6.7

DTA and TGA analyses (Fig. 6) indicate that the as prepared particles contain adsorbed water which was released on heating between 50 and 200 °C as manifested by the endothermic effect centred at 70 °C and its associated weight loss (~4.3%). An additional endothermic peak at 460 °C accompanied by a weight loss from 200 to 700 °C (~5.5%) were also detected, which are attributed to elimination of chlorine, as supported by the absence of the Cl peak in EDX spectrum of the sample heated at 700 °C (Fig. 1).

Since the as prepared samples presented a beige colour, which for sample Cr4 was characterised by $L^*a^*b^*$

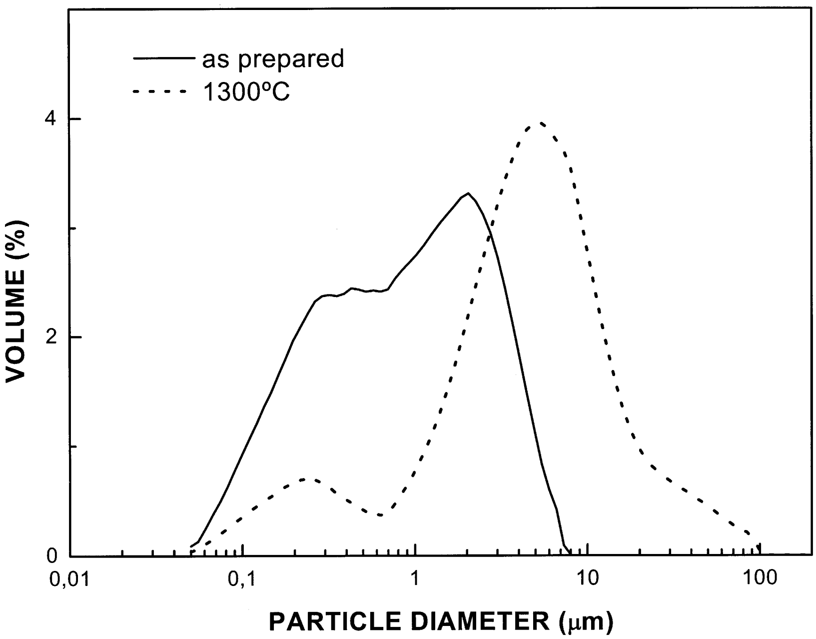

Fig. 3. Volumetric particle size distribution obtained for sample Cr4, as prepared and after heating at 1300 °C.

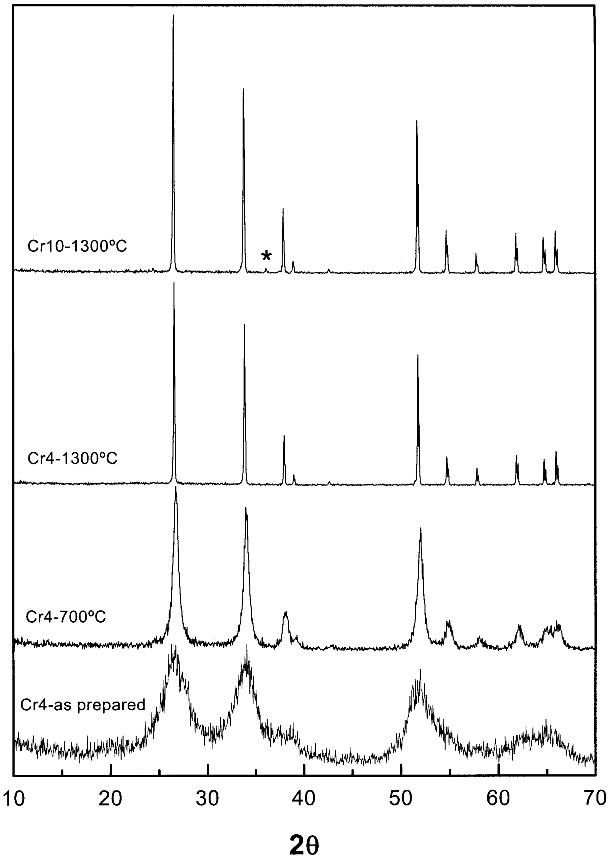

Fig. 4. X-ray diffraction patterns obtained for the sample Cr4, as prepared and after heating at different temperatures and for sample Cr10 heated at 1300 °C. The peaks labelled with an asterisk correspond to α-Cr_2O_3.

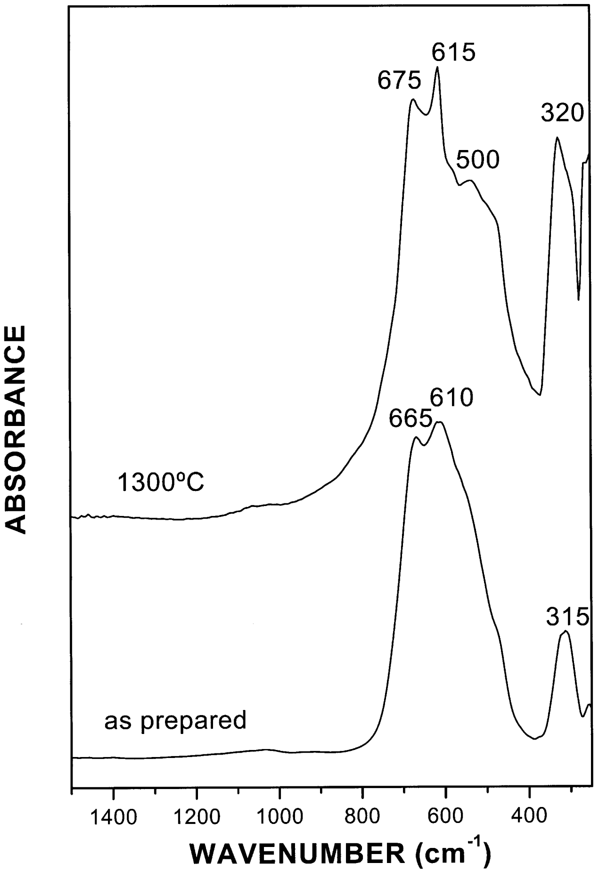

Fig. 5. Infrared spectra recorded for sample Cr4, as prepared and after heating at 1300 °C.

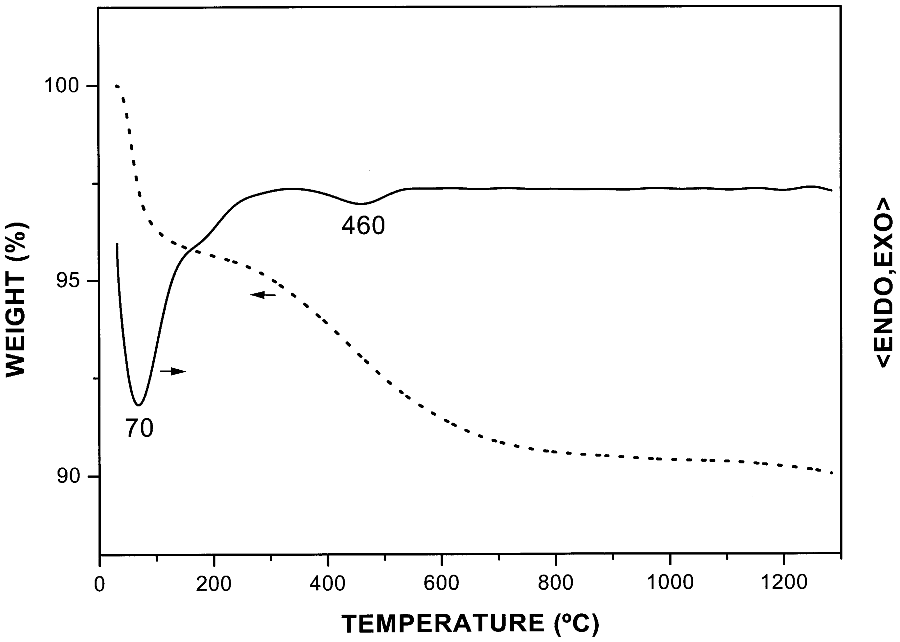

Fig. 6. Differential thermal (DTA) and thermogravimetric (TGA) curves obtained for sample Cr4.

parameters of 69.1, 2.3 and 9.5, respectively (Table 2), they were thermally treated at increasing temperatures up to the development of the violet colour characteristics of the Cr-doped SnO_2 pigments. A progressive increase of a^* (from 2.3 to 11.0) and a decrease of b^* (from 9.5 to −8.0) were detected for sample Cr4 on calcination up to 700 °C, which were accompanied by an important decrease of luminosity (L^*) (from 69.1 to 45.8) (Table 2). These changes involved the apparition of a reddish lilac colour, which progressively turned to light brown on a further heating up to 1200 °C as manifested by the decrease of a^* (from 11 to 4) and the increase of b^* (from −8 to 1.6) and L^* (from 45.8 to 64) (Table 2). The heat treatment at 1300 °C finally produced the characteristic violet colour of Cr-doped cassiterite, which for this sample involved a slightly lower value (9.2) of the red component (a^*) and a significant higher luminosity (59.4) when compared with the sample heated at 700 °C (Table 2).

During this heat treatment a slight increase of the Cr/Sn molar ratio of the sample (from 0.038 to 0.043) was observed (Table 1) probably due to the volatilization of a small amount of Sn [17]. In addition, the spherical shape of the particles was lost as a consequence of particle sintering (Fig. 2B), which also gave rise to an increase of particle size characterised by a bimodal size distribution with maxima centred at 0.25 and 5 μm (Fig 3). The infrared spectrum of the sample heated at 1300 °C (Fig. 5) also manifest the changes in particle shape by variations in the position of the bands with respect to that of the original sample. The resulting spectral features were characteristics of powders with heterogeneous particle shape [15] in agreement with SEM observations. The only structural change detected by X-ray diffraction on calcination was a sharpening of the diffraction peaks indicating a progressive increase of crystallite size (Table 2). Therefore, the colour changes observed during heat treatment should be related to variations in the oxidation state of the Cr species and/or their distribution in the cassiterite matrix.

In order to get information about these aspects, the samples were characterised by X-ray photoelectron spectroscopy. The main differences observed between the spectra recorded for sample Cr4 heated at increasing temperatures were related to the shape and position of the peaks corresponding to the Cr2p level (Fig. 7). Thus, the $Cr2p_{3/2}$ signal appeared as a single peak for the original sample at a binding energy of 577 eV, which would be consistent with the presence of Cr(III) [18], in agreement with the infrared spectroscopy suggestions. At 700 °C, this signal consists of the overlapping of two peaks at 577 eV due to Cr(III) and a more intense one at 580 eV, which must be ascribed to Cr(VI) species [18]. This finding would agree with results previously reported by Harrison et al. [19] who detected chromate species by XANES spectroscopy after heating at 300–800 °C Cr-doped SnO_2 catalysts with higher Cr content (Cr/Sn mole ratio = 0.32) obtained by coprecipitation from Cr(III) and Sn(IV) aqueous solutions. These authors justify the oxidation of Cr(III) to Cr(VI) on this treatment by the relatively oxidising character of SnO_2. It should be noted that the intensity of the $Cr2p_{3/2}$ peak due to Cr(VI) decreased progressively on further heating finally disappearing at 1200 °C. Simultaneously, the

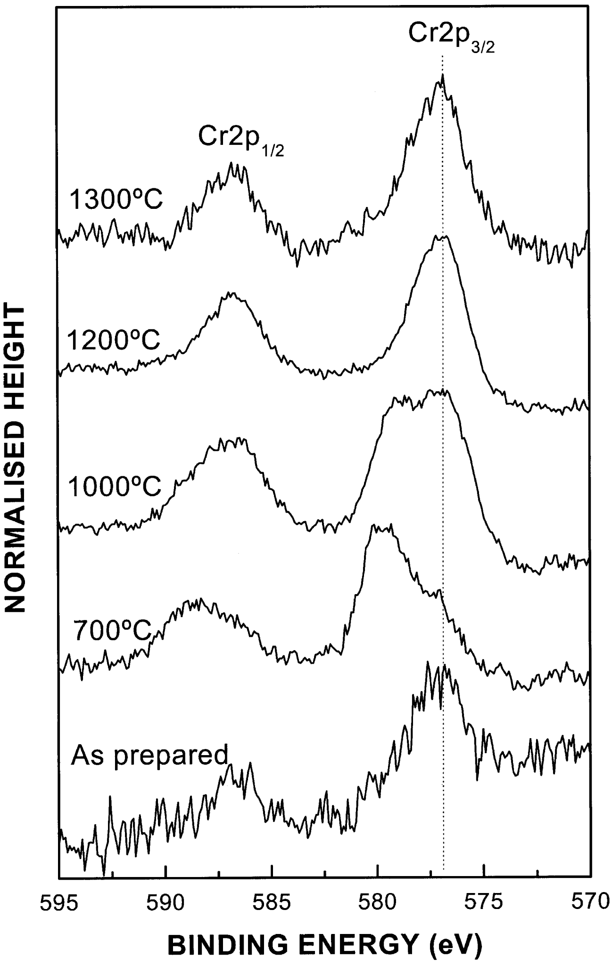

Fig. 7. Cr2p XPS spectra obtained for sample Cr4, as prepared and after heating at different temperatures.

reddish lilac colour of the sample also disappeared. Therefore, it seems reasonable to assume that the Cr(VI) species are responsible for such a colour. It is important to remark that after calcination at 1300 °C, at which temperature the violet colour was developed, no traces of Cr(VI) were detected by XPS (Fig. 7). Thus, an only Cr2p$_{3/2}$ peak was observed at 577 eV, which, as above mentioned, is consistent with Cr(III). This observation would be in agreement with Ren et al. who reported that the violet colour of this pigment is the result of a Cr(IV)/SnO$_2$ solid solution along with the presence of Cr$_2$O$_3$ deposited on the surface grains [20]. It must be mentioned that the Cr(III) and Cr(IV) XPS signals are very similar [21] for which, the possible contribution from Cr(IV) species to the peak at 577 eV can not be disregarded. The Cr/Sn molar ratio obtained from the XPS measurements supports the presence of Cr$_2$O$_3$ on the surface grains, since the value obtained for the sample heated at 1300 °C was higher (0.065) than that obtained from X-ray fluorescence (0.043) indicating a certain enrichment of Cr in the particles outer layers.

The isolectric point (i.e.p.) obtained from electrophoretic mobility measurements for the pigment can be explained on the basis of the above observations. Thus, the i.e.p. for sample Cr4 calcined at 1300 °C was higher (5) than that of the SnO$_2$ blank (4.3) (Fig. 8) probably as a consequence of the presence of Cr$_2$O$_3$ on the particle surfaces, which has a much higher i.e.p. (8.4) [22] than that of undoped cassiterite.

The effect of the chromium content on the pigment colour was also investigated to optimize the reported preparation procedure. The $L^*a^*b^*$ parameters of the samples heated at 1300 °C have been plotted as a function

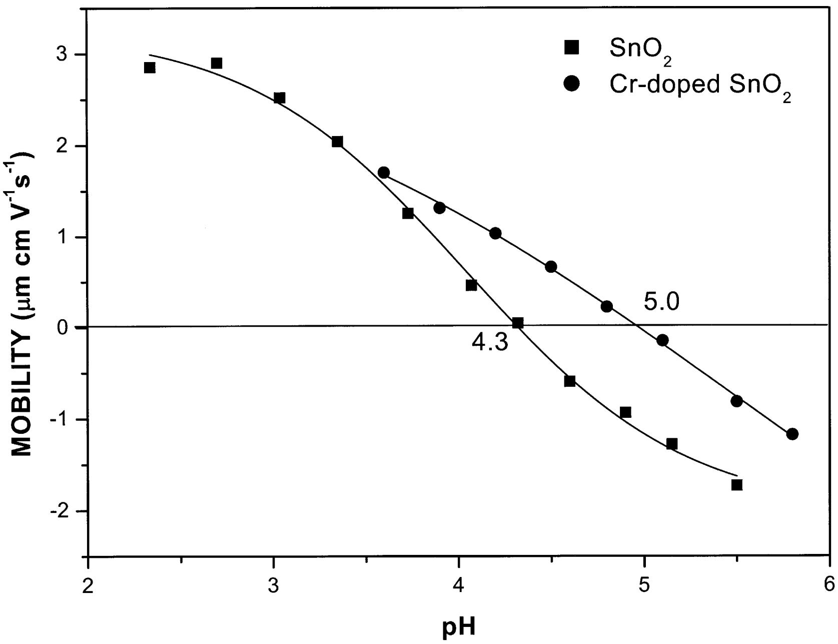

Fig. 8. Electrophoretic mobility measured as a function of pH for sample Cr4 heated at 1300 °C and the SnO$_2$ blank.

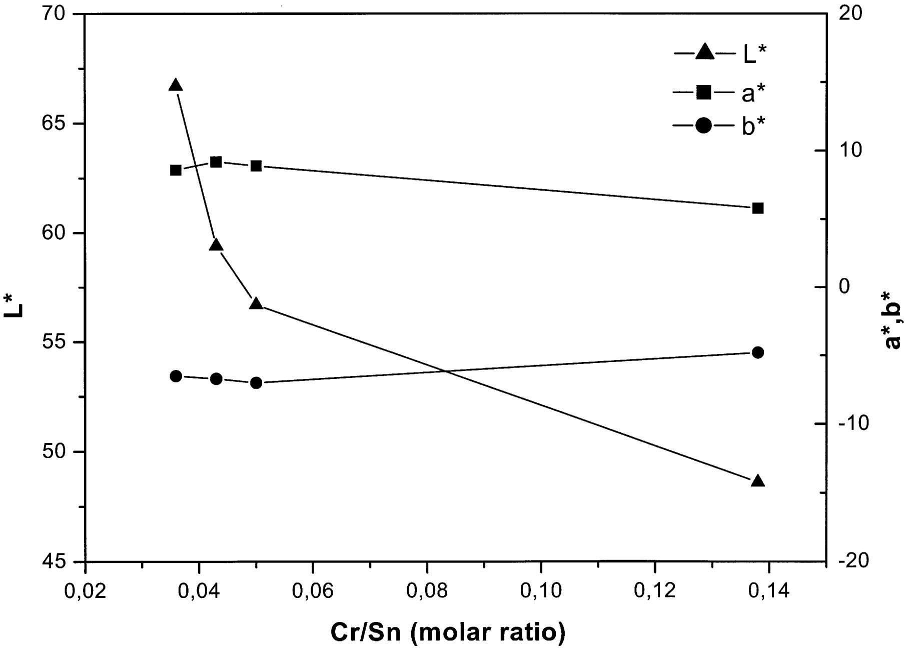

Fig. 9. $L^*a^*b^*$ parameters measured for the Cr-doped SnO_2 samples heated at 1300 °C as a function of the Cr content.

of the Cr/Sn molar ratio in Fig. 9. It should be noted that as for sample Cr4, a certain increase of the Cr/Sn ratio was detected in all cases after calcination with respect to the initial values (Table 1), due to the Sn volatilization. As observed in Fig. 9, the increase of such Cr/Sn ratio in the final pigments from 0.036 to 0.052 did not produce important variations of the colour hue (a^* an b^* values). However, a significant decrease (from 67 to 57) of luminosity (L^*) was detected which indicated an increase of the colour intensity. Although L^* still decreased when the Cr/Sn molar ratio was further increased (0.138), a darkening of the pigment colour (a^* decrease and b^* increase) was also produced likely due to the increase of the chromium oxide content, which for the highest Cr/Sn value was even detected by X-ray diffraction (Fig. 4) as α-Cr_2O_3 [23]. Therefore, it can be concluded that optimum pigment (more intense violet colour with the lower Cr content) obtained with the here reported procedure corresponded to a Cr/Sn molar ratio in the 0.4–0.5 range.

4. Conclusions

A simple and continuous method for synthesizing Cr–SnO_2 violet pigments based on the pyrolysis at 600 °C of aerosols generated from aqueous solutions of tin (IV) chloride and chromium (III) nitrate has been reported. This process produces poorly crystallized beige powders consisting of cassiterite (SnO_2) spherical particles containing Cr_2O_3. The evolution of these powders on thermal treatment up to the development of the violet colour characteristic of Cr-doped cassiterite pigment was analysed. It was found after heating at 700 °C, the colour of the samples turned to reddish lilac, which was attributed to the presence of Cr(VI) species on the particles surface, which disappeared along with such a colour on calcination up to 1200 °C. A further heating at 1300 °C was required to develop the desired violet colour, which also caused an increase of particle size as a consequence of a certain degree of sintering. Under these conditions only Cr(III) and probably Cr(IV) species are present in the particles outer layers. The effects of the chromophore concentration on the colour properties of the pigments were also evaluated finding that the optimum pigment obtained by this procedure corresponds to a Cr/Sn molar ratio in the 0.04–0.05 range.

Acknowledgements

This work was supported by the Spanish CICYT and the European Union under project No 1FD97-0697.

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