

# Synthesis by pyrolysis of aerosols and ceramic application of Cr-doped $\text{CaYAlO}_4$ red–orange pigments

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## Abstract

The synthesis of red–orange Cr-doped  $\text{YCaAlO}_4$  pigments has been improved (softer thermal conditions and lower environmental impact) and optimised by using the pyrolysis of aerosols method. We also study the crystallochemical features of the Cr chromophore with special emphasis on its oxidation state which has not been yet clarified, finding that Cr(III) and Cr(IV) species are present in the octahedral and interstitial tetrahedral sites of the  $\text{YCaAlO}_4$  lattice, respectively. Finally, the applicability of this system as ceramic pigment was tested using conventional industrial glazes. A change from orange to pink shades was detected after glaze firing, which is mainly attributed to the  $\text{Cr}^{3+}$  to  $\text{Cr}^{4+}$  oxidation.

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## 1. Introduction

The search for crystalline structures that may incorporate transition metal cations resulting in coloured compounds is one of the most important research lines in the ceramic pigments field. The interest on this activity is based on economical, aesthetic or environmental reasons. For example, it is remarkable the important research effort carried out during the last years to find new red pigments to replace those commercially used since most of them are toxic.<sup>1–5</sup>

$\text{YCaAlO}_4$  belongs to the series of  $\text{A}^{3+}\text{B}^{2+}\text{AlO}_4$  aluminates ( $\text{A}^{3+} = \text{Y, Nd, La}$ ;  $\text{B}^{2+} = \text{Ca, Sr}$ ), which crystallize in the  $\text{K}_2\text{NiF}_4$  type structure consisting of a 1/1 intergrowth of  $\text{ABO}_3$  perovskite and AO rock-salt (NaCl) type layers connected by anisotropic A–O<sub>apical</sub>–B bridge bonds, where A and B elements present ninefold coordination whereas Al is octahedrally coordinated.<sup>6,7</sup> These complex oxides are versatile compounds which, when doped with different transition elements, result in materials with interesting electric, magnetic,<sup>8–10</sup> optical<sup>11</sup> and infrared<sup>6</sup> properties. In particular, it has been

shown that the doping of  $\text{YCaAlO}_4$  with Cr cations yields solid solutions with an orange–red coloration, which might be interesting for ceramic applications.<sup>11</sup> Nevertheless, the performance of these materials when they are incorporated to ceramic bodies has not been tested yet. It should be also noted that, in previous works, the samples were synthesised by the traditional ceramic procedure, requiring high temperatures (1400 °C) and the addition of fluxes (NaF),<sup>11</sup> which are accompanied by undesired environmental effects,<sup>12</sup> to obtain the required crystalline phase. Recently, we have demonstrated that the pyrolysis of aerosols technique is a more ecological synthesis route for ceramic pigments since it involves softer thermal conditions and even the removal of fluxing agents.<sup>13–16</sup>

In this work, we first address the preparation of Cr-doped  $\text{YCaAlO}_4$  pigments through pyrolysis of aerosols in order to improve their synthesis process. In this context, the Cr content of the solid solutions was systematically varied in order to optimise their colour response. We also study the crystallochemical features of the Cr chromophore with special emphasis on its oxidation state which has not been clarified yet. Thus, whereas in the pioneering work by Olazcuaga et al.,<sup>11</sup> a trivalent state was assumed, in further works, the possibility of a partial  $\text{Cr}^{3+}$ – $\text{Cr}^{4+}$  oxidation was suggested.<sup>7,9</sup> Finally, the behaviour of

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this system, once applied in conventional industrial glazes, was assessed.

## 2. Experimental

### 2.1. Powders preparation

Three powdered samples having a nominal Y/Ca/Al atomic ratio of 1/1.1/1 and variable chromium concentrations (Cr/CaYAlO<sub>4</sub> molar ratios = 0.05; 0.08; 0.11) were prepared by pyrolysis of aerosols. These samples will be referred as R1, R2 and R3, respectively. It should be noted that the selected Ca content was slightly above the stoichiometric value aiming to facilitate the Cr<sup>3+</sup> incorporation to the crystallographic sites of isovalent cations. The synthesis procedure can be summarised as follows. Aqueous solutions of AlCl<sub>3</sub>·6H<sub>2</sub>O (0.05 mol/L, Panreac, >95%); CaCl<sub>2</sub>·2H<sub>2</sub>O (0.055 mol/L, Riedel-de Haën, 99%), YCl<sub>3</sub>·6H<sub>2</sub>O (0.05 mol/L, Aldrich, >99.9%) and variable CrCl<sub>3</sub>·6H<sub>2</sub>O (Chem-Lab NV, >98%) were atomized in a previously described apparatus<sup>13</sup> using a glass nozzle and air (0.5 kg cm<sup>-2</sup>) as a carrier gas. The resulting aerosols were introduced into a first furnace heated at 300 °C for solvent evaporation and immediately in a second one heated at 600 °C for precursors decomposition. The resulting powders were collected in a glass filter and further calcined at constant temperature in an electric kiln using a heating rate of 10 °C/min and a soaking time of 4 h.

For comparison, a sample (referred as C1) with a Cr/CaYAlO<sub>4</sub> molar ratio = 0.05 was also prepared by the traditional ceramic route in absence of fluxing agents. For this purpose, the desired amounts of CaO (J.T. Backer, 99%), Al<sub>2</sub>O<sub>3</sub> (Panreac, >99%), Y<sub>2</sub>O<sub>3</sub> (Strem Chemicals, >99.9%) and Cr<sub>2</sub>O<sub>3</sub> (J.T Baker, >99%) were mixed and homogenized by milling using acetone as dispersing medium. The mixture was dried at 100 °C and further calcined up to 1400 °C applying the same firing conditions as above.

About testing in glaze, aqueous suspensions containing 95 wt% of a transparent industrial frit (with elemental composition: Si, Al, Ca, Na, B, Zn) and 5 wt% of pigment were prepared. The obtained slurries were deposited on double-firing wall tile bodies, which were further fired at 1050 °C for 5 min followed by natural cooling.

### 2.2. Characterisation techniques

The crystalline phases present in the powders were characterized by X-ray powder diffraction (XRPD) using a Siemens

D501 diffractometer. The measurements were performed in the 10–60° 2θ range with Δ2θ step of 0.05°. Unit cell parameters were determined by a least-squares refinement from the X-ray diffraction data collected at intervals of 0.02° (2θ) for an accumulation time for interval of 10 s, using silicon (20% by weight) as internal standard. The crystallographic data for the YCaAlO<sub>4</sub> structure, which presents tetragonal crystallographic symmetry ( $a=b \neq c$ ;  $\alpha=\beta=\gamma=90^\circ$ ) and belongs to the space group *I4mmm*, were taken from the JCPDF file reported for this compound.<sup>17</sup>

The particle morphology was assessed using scanning electron microscopy (SEM, Jeol JSM5400) and transmission electron microscopy (TEM, Philips 200 CM). The composition of the solids (Cr/Y, Ca/Y and Al/Y molar ratio) was determined by X-ray fluorescence (XRF) (Model SRS3000, Siemens). Energy dispersive X-ray analysis (EDX, Link Isis, Oxford), installed in the SEM microscope, was also used to gain information on the particle composition.

UV–visible spectroscopy of the fired samples was measured using a Cary 500 Scan Varian spectrophotometer in the 200–1400 nm range (step 0.1 nm). The UV–visible spectra were obtained using an integrating sphere, BaSO<sub>4</sub> as a white reference and a D65 illuminant (observer at 10°).

The colour coordinates of the pigments were measured using a Dr.Lange, LUCI 100 colorimeter for the same illuminant (D65) and a white ceramic tile (coordinates:  $x=76.3$ ,  $y=81.1$ ,  $z=85.0$ ) as a standard reference. The colour was evaluated, according to the Commission Internationale de l'Eclairage (CIE) through  $L^*a^*b^*$  parameters. In this system  $L^*$  is the colour lightness ( $L^*=0$  for black,  $L^*=100$  for white);  $a^*$  is red (+) and green (–) axis and  $b^*$  is the yellow (+) and blue (–) axis.<sup>18</sup>

## 3. Results and discussion

### 3.1. Pigments preparation and characterisation

The compositions of the as prepared samples in terms of their Cr/Y, Ca/Y and Al/Y atomic ratios are shown in Table 1. As observed, the measured values are in agreement with the experimental data, since the small detected deviations can be considered within the experimental error. This finding confirms the effectiveness of the pyrolysis method to control the stoichiometry of multicomponent systems.<sup>19</sup>

EDX analyses provided additional information on sample composition. Thus, a chlorine peak was clearly observed in

Table 1  
Composition of the Cr-doped CaYAlO<sub>4</sub> samples as-prepared measured by XRF.

Sample	Composition	(Cr/YCaAlO <sub>4</sub> ) molar ratio	(Ca/Y) atomic ratio	(Al/Y) atomic ratio
R1	Nominal	0.05	1.1	1.0
	Experimental	0.05	1.17	0.91
R2	Nominal	0.08	1.1	1.0
	Experimental	0.08	1.08	0.88
R3	Nominal	0.11	1.1	1.0
	Experimental	0.11	1.10	0.91

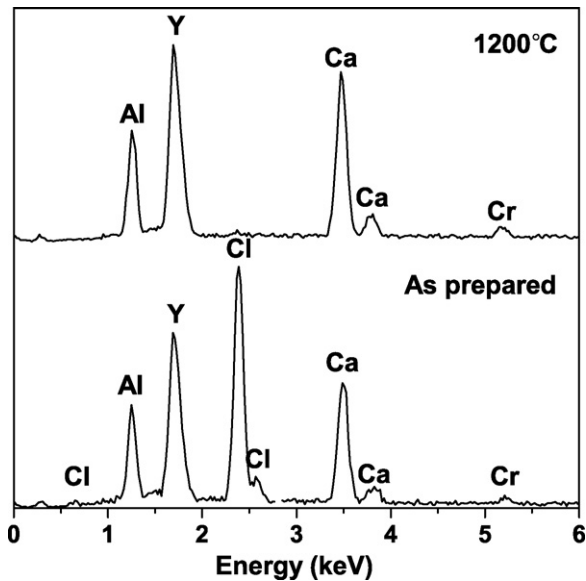


Fig. 1. EDX analyses of sample R1, as prepared and after heating at 1200 °C.

the spectrum probably indicating the incomplete decomposition of the precursors during the pyrolysis process. This peak disappeared after sample calcination at 1200 °C (Fig. 1).

All samples, as prepared, consisted of spherical particles with broad size distribution with diameters  $< 2 \mu\text{m}$  as illustrated in Fig. 2A for sample R1, which has been chosen as a representative example. The TEM micrograph (Fig. 2B) shows that most of the spheres are dense, revealing the volumetric precipitation of the precursors during the solvent evaporation process.<sup>19</sup> According to X-ray diffraction (data not shown), the particles were amorphous; for this reason, they were further calcined at increasing temperatures up to the development of the desired crystalline phase.

X-ray diffraction (Fig. 3) revealed that the calcination of sample R1 at 1000 °C, resulted in the crystallization of a mixture of phases,  $\text{CaYAIO}_4$  (JCPDS card no. 1-081-0742) and  $\text{CaYAl}_3\text{O}_7$

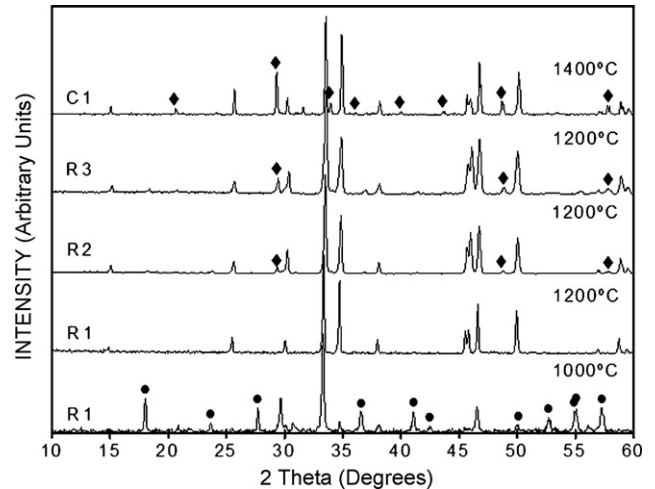


Fig. 3. X-ray diffraction patterns of the Cr-doped  $\text{CaYAIO}_4$  samples prepared by pyrolysis of aerosols (R1, R2 and R3) and by the ceramic procedure (C1) after heating at different temperatures. Symbols: (◆)  $\text{Y}_2\text{O}_3$ ; (●)  $\text{CaYAl}_3\text{O}_7$ . The non-labelled peaks correspond to  $\text{CaYAIO}_4$ .

(JCPDS card no. 49-0605). The latter disappeared after heating at 1200 °C leaving  $\text{CaYAIO}_4$  as the only detectable phase. Similar thermal behaviour was observed for samples R2 and R3. The only noticeable difference was that a small amount of  $\text{Y}_2\text{O}_3$  (JCPDS card no. 41-1105) was still detected after calcination, which increased with the chromium content (Fig. 3). The origin of this behaviour will be further addressed.

It should be noted that for the sample prepared by the ceramic procedure,  $\text{CaYAIO}_4$  was not completely formed (an important amount of unreacted  $\text{Y}_2\text{O}_3$  still remained) even after calcinations at higher temperature (1400 °C) (Fig. 3), in agreement with previous works which indicated that for the completion of such process, the addition of mineralizers was needed.<sup>11</sup> The higher reactivity of the pyrolysis-derived samples can be explained by the high degree of chemical homogeneity of the so prepared particles that favours the diffusion process required for crystallization.

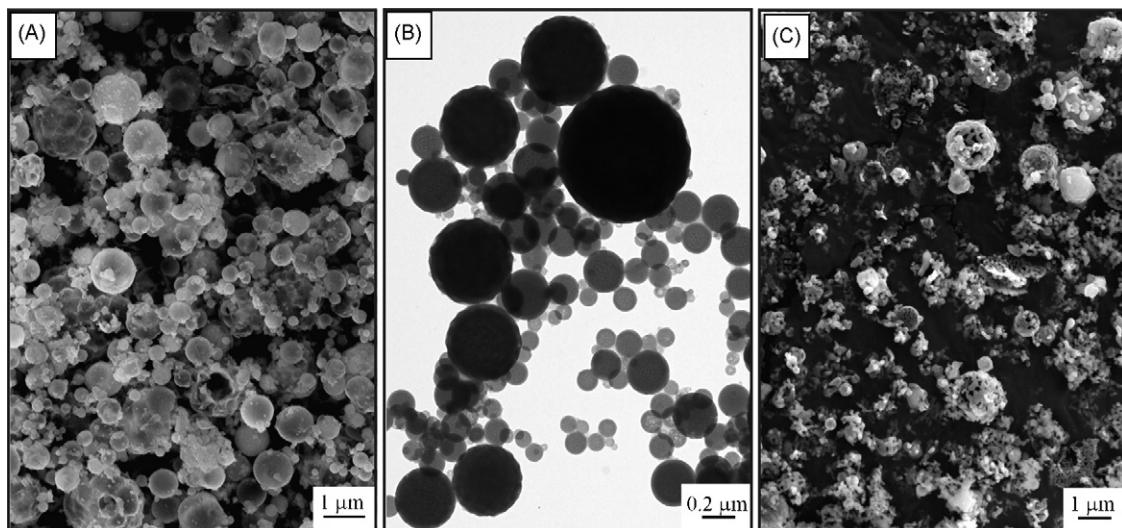


Fig. 2. SEM (A) and TEM (B) micrographs of sample R1 as prepared, and SEM (C) micrograph of the same sample calcined at 1200 °C (C).

Table 2

Reticular parameters measured for samples R1, R2 and R3 and for a  $\text{CaYAlO}_4$  blank heated at  $1200^\circ\text{C}$ .

Sample	$a=b$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )
$\text{CaYAlO}_4$	$3.6463 \pm 0.0006$	$11.8758 \pm 0.0018$	$157.894 \pm 0.076$
R1	$3.6493 \pm 0.0003$	$11.8732 \pm 0.0009$	$158.120 \pm 0.038$
R2	$3.6524 \pm 0.0003$	$11.8671 \pm 0.0010$	$158.307 \pm 0.040$
R3	$3.6591 \pm 0.0009$	$11.8665 \pm 0.0025$	$158.880 \pm 0.110$

The unit cell parameters measured for the calcined doped samples are shown in Table 2 along with those for undoped  $\text{CaYAlO}_4$ . A unit cell expansion was observed in all cases, which was more evident as the Cr amount increased, implying the formation of a solid solution by substitution of  $\text{Al}^{3+}$  (ionic radius =  $0.535 \text{ \AA}$ ) by larger  $\text{Cr}^{3+}$  ( $0.615 \text{ \AA}$ ) cations in the sixfold coordination site.<sup>11,20</sup> It was also observed that whereas the values of  $a$  increased with Cr content, those of  $c$  decreased. Such unusual variation is in agreement with previous reports in which it was associated to the simultaneous distortion of both the  $(\text{Al,Cr})\text{O}_6$  octahedra and the  $(\text{Y,Ca})\text{O}$  polyhedra induced by the incorporation of  $\text{Cr}^{3+}$ .<sup>9,10,21</sup>

Finally, no appreciable changes in particle size and shape (Fig. 2C) were observed after heating at  $1200^\circ\text{C}$ , but certain sintering process took place during this treatment. Therefore, the obtained grains were sufficiently small ( $<5 \mu\text{m}$ ) for their direct application in ceramic glazes<sup>22,23</sup> without the usual preliminary grinding required in the traditional preparation of pigments.

### 3.2. Optical properties

The UV–visible spectra recorded for the Cr-doped  $\text{CaYAlO}_4$  samples are presented in Fig. 4. All spectra exhibited similar features, irrespective of the Cr content, which can be summarised as follows: (a) in the ultraviolet region, an intense sharp band is observed, which does not affect to the final colour and therefore will not be discussed; (b) the visible region is dominated by a broad band centred at about  $430 \text{ nm}$ , although other two very weak bands at  $\sim 640$  and  $\sim 710 \text{ nm}$  are also present together with a shoulder at  $\sim 540 \text{ nm}$ ; and (c) the NIR region exhibits a weak and very broad band from  $900 \text{ nm}$  to  $1400 \text{ nm}$ .

The bands at  $430 \text{ nm}$  and  $540 \text{ nm}$  could be attributed to the  $^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}$  ( $^4\text{F}$ ) and  $^4\text{A}_{2g}$  ( $^4\text{F}$ )  $\rightarrow ^4\text{T}_{2g}$  ( $^4\text{F}$ ) electronic transitions of  $\text{Cr}^{3+}$  in the octahedral sites of  $\text{Al}^{3+}$ , respectively.<sup>24–29</sup> The weak bands  $\sim 640$  and at  $\sim 710 \text{ nm}$  could be originated by the spin-forbidden transitions of  $\text{Cr}^{3+}$ .<sup>16,25,26,31,32</sup> Finally, the extended absorption in the NIR region, which does not exist for the undoped  $\text{YCaAlO}_4$  sample, is similar to that found for other Cr-doped pigment systems such as  $\text{CaSnSiO}_5$ ,<sup>14</sup>  $\text{CaTiSiO}_5$ ,<sup>16,31</sup> and stannate and titanite pyrochlores.<sup>35</sup> In these cases, it was ascribed to  $\text{Cr}^{4+}$  either in octahedral or in tetrahedral coordination. The presence of  $\text{Cr}^{4+}$  in our samples would be in agreement with a previous report by Zvereva et al.<sup>9</sup> who detected through magnetic measurements a partial oxidation of  $\text{Cr}^{3+}$  to  $\text{Cr}^{4+}$  in Cr-doped  $\text{YCaAlO}_4$  samples accompanied by a substitution of  $\text{Y}^{3+}$  by  $\text{Ca}^{2+}$  in the  $\text{YCaAlO}_4$  lattice to maintain electroneutrality. This interpretation would explain the presence of a certain

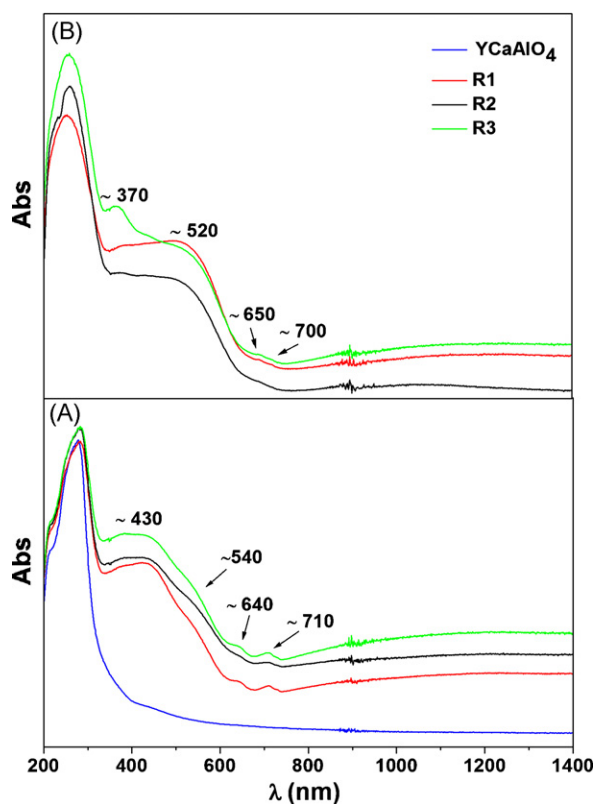


Fig. 4. UV–vis spectra for (A) samples R1, R2 and R3 and an undoped  $\text{YCaAlO}_4$  sample heated at  $1200^\circ\text{C}$  for 4 h; (B) samples R1, R2, and R3 applied in glazes.

amount of unreacted yttria in our pigments, which increased as the Cr content increased (Fig. 3). Since in the  $\text{YCaAlO}_4$  structure there are no tetrahedral sites occupied by Y, Al or Ca cations, the  $\text{Cr}^{4+}$  ions might be situated in interstitial sites or in the octahedral Al sites.

All pigments exhibit orange shades as indicated by the  $L^*a^*b^*$  parameters measured on the powdered samples, shown in Table 3, in which a decrease of  $L^*$ ,  $a^*$  and  $b^*$  can be also observed as increasing the Cr content that resulted in a colour change from orange to brownish. Accordingly, it can be concluded that sample R1 (Cr/ $\text{CaYAlO}_4$  molar ratio = 0.05) is the optimum pigment obtained by spray pyrolysis procedure as it exhibits the reddest shade with the lowest Cr content. It should be also emphasized that the colour developed is better than that those reported by Olazcuaga et al.<sup>11</sup> for pigments with chromium content of 8% and synthesised by the ceramic procedure.

In order to assess the applicability of the synthesised samples as ceramic pigments, they were incorporated into transparent commercial glazes. First of all, it must be mentioned that no defects were found in all decorated tiles. Secondly, unexpected

Table 3

Colour coordinates of the Cr-doped  $\text{CaYAlO}_4$  pigments calcined at  $1200^\circ\text{C}$  in powder form and after their incorporation in glazes.

Sample	$L^*$ <sub>powder/glaze</sub>	$a^*$ <sub>powder/glaze</sub>	$b^*$ <sub>powder/glaze</sub>	Colour <sub>powder/glaze</sub>
R1	58.9/64.0	12.7/15.4	23.6/11.0	Orange/pink
R2	48.8/59.3	10.6/14.8	15.7/10.2	Light brown/pink
R3	45.4/58.3	11.3/13.9	13.1/10.0	Light brown/pink

increase of the red component  $a^*$  and a decrease of the yellow parameter  $b^*$  were observed in all tiles, resulting in an attractive pink coloration (Table 3). To explain such behaviour, the UV–visible spectra of the glazed tiles were also recorded. As it can be seen in Fig. 4B, the spin-forbidden bands of  $\text{Cr}^{3+}$  at 650–700 nm were much less intense than in the powdered pigments (Fig. 4A). In addition, the broad adsorption in the NIR region related to  $\text{Cr}^{4+}$  was still present and the main absorption band shifted from 430 nm (powdered pigments) to 520 nm (glazes). These features, along with the absorption effect centred at 370 nm, have been already observed for other Cr pigments (e.g. malayaite) and attributed to  $\text{Cr}^{4+}$  in octahedral coordination.<sup>15,33–35</sup> These findings seem to indicate that most  $\text{Cr}^{3+}$  cations might be oxidized to  $\text{Cr}^{4+}$  when the pigments are processed with the ceramic frits. Finally, the sharp band detected at  $\sim 520$  nm is analogous to that developed by Cr-doped  $\text{YAlO}_3$ , whose origin is still unclear.<sup>2,26</sup>

#### 4. Conclusions

Cr-doped  $\text{YCaAlO}_4$  red–orange pigments have been synthesised by spray pyrolysis at lower temperature (1200 °C) than that involved in the traditional ceramic method ( $\geq 1400$  °C), not requiring the addition of fluxing agents, which is highly desirable from the environmental point of view. The pigments so synthesised consist of spherical particles with broad size distribution and maximum diameter  $\leq 5$   $\mu\text{m}$ , which are sufficiently small for their direct application in glazes without preliminary grinding. The observed hues were mainly due to  $\text{Cr}^{3+}$  ions at the octahedral sites of the  $\text{YCaAlO}_4$  lattice, although a certain amount of  $\text{Cr}^{4+}$  seems to be also present. The optimum pigment, having the reddest shade with the lowest Cr content, corresponds to a chromium content of 5% (expressed as the Cr/ $\text{YCaAlO}_4$  molar ratio). Its colour is better than that previously reported for samples prepared by the ceramic procedure in the presence of fluxes. The applicability of these materials in industrial glazes was successfully demonstrated, as glazes free of defects can be prepared with commercial transparent frits. A change from orange to pink shades was detected after glaze firing, which is mainly attributed to the oxidation of  $\text{Cr}^{3+}$  to  $\text{Cr}^{4+}$  in the octahedral sites of the  $\text{YCaAlO}_4$  lattice, with correspondent blue-shift of optical bands.

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