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Towards more ecological ceramic pigments: Study of the influence of glass composition on the colour stability of a pink chromium-doped ceramic pigment

Mónica Martos *, Marta Martínez, Eloisa Cordoncillo, Purificación Escribano

Departament of Inorganic and Organic Chemistry, Universitat Jaume I, Campus Riu Sec, 12071 Castellón, Spain

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Abstract

This paper describes the study of a pink ceramic pigment based on the optical properties of Cr-doped structures, having into account environmental considerations. The research is focused on the optimisation of the synthesis parameters in order to minimise the amount of pollutant Cr(VI) in the washing liquids and enhance chromatic coordinates. In a first stage, the $Al_{2-x}Cr_xO_3$ solid solution was studied. Nevertheless, the observation that ZnO was required in the frit to stabilise the pink colour after glazing made us to conduct the research towards the optimisation of the $ZnAl_{2-x}Cr_xO_4$ system. X-ray diffraction (XRD) indicates a solid solution formation based on the gahnite structure; moreover, no Cr(VI) and B contents were found in the analysis of the washing liquids. Thus, this research enabled us to produce a pink pigment with low environmental impact and good chromatic coordinates. Further study of the pigment applied in a glaze showed evidence of the importance of the glaze composition for the colour development and stability of the ceramic pigments.

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Keywords: Pigments; Powders-solid state reaction; Spinel; Al_2O_3

1. Introduction

Inorganic pigments are traditionally based on transition metal compounds.[1] Nevertheless, due to the high toxicity of these elements, research on ceramic pigments has lately been dedicated to improve traditional coloured systems from an environmental point of view and maintaining their colouring properties and technological requirements. Attempting to achieve zero emissions and waste, as well as a reduction of energy costs, a good understanding of the reaction mechanisms depending on the chemical composition is required. Moreover, the product performance must meet the growing social demands with regard to safety, sustainability and minimal environmental impact.

Doping a structure using metal species is one of the most frequently adopted practices to induce modifications, not only in its structural characteristics, but also in its composition and reactivity. The chromatic features of a pigment depend on the crystalline field around the chromophore ions which is a complex function of lattice accommodation and metal ion valence-dimensions.[2] Among different types of doping ions, Cr^{3+} is one of the most popular elements due to its optical and technological properties as a consequence of its electronic structure. For instance, it has been widely used in the development of solid-state lasers.[3] Furthermore, the host matrix influences the strength of the crystal field surrounding the Cr(III) ions, leading to a large chromatic variety from green to red-pink colours upon low and high crystal field conditions, respectively.[4]

By other hand, synthesis conditions can affect the oxidation states (II–VI) of chromium ions which generate different properties, stabilities and colourations. Chromium is commonly found in the environment as trivalent and hexavalent ions. Cr(III) is an essential nutrient required by the human body to promote the action of insulin, but high doses of this ion and long term exposure to it can affect the body's immune system. Although Cr(III) is unable to enter into cells, Cr(VI) can enter thorough cell membranes and is then reduced to Cr(III) which causes

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* Corresponding author. Tel.: +34 964728247; fax: +34 964728214.
E-mail addresses: mmartos@qio.uji.es (M. Martos), Marta.Martinez@qio.uji.es (M. Martínez), cordonci@qio.uji.es (E. Cordoncillo), escriban@qio.uji.es (P. Escribano).

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reactions that contribute to the toxicity of Cr(VI)-containing compounds.[5] Oxidation from Cr(III) to Cr(VI) takes place spontaneously when the material is thermally treated. Therefore, one of the most important motivations of this work is to prevent the appearance of carcinogenic Cr(VI) in the washing liquids during the industrial production.[6]

As it has been mentioned, one way to obtain red hues is by intensifying Cr(III) crystal field. This is the case of the natural ruby, which is the red variety of corundum, the second hardest natural mineral. This coloration is caused by traces of chromium (0.05% wt) substituting Al(III) ions in a corundum structure (α-Al_2O_3). In this structure, electronic transitions between d-electron orbitals in the chromium ions are shifted to high energy, thus producing red tonality.[7] As the chromium concentration on ruby is increased, the ligand field becomes weaker and therefore a change from red to green occurs. Indeed, the Cr_2O_3 and Al_2O_3 oxides can form a complete range of substitutional solid solutions between the solidus temperatures ∼2100 and ∼950 °C.[8]

Besides the corundum structure, the spinel family is a group which develops a great variety of colours by doping with different chromophore ions and, as a result, it is probably the most used pigment structure. In particular, $ZnAl_2O_4$ spinel (gahnite) presents a good optical quality provided by the very small size of spinel nanocrystalites formed during the thermal treatment, where Cr ions tend to be situated.[9] In fact, $Zn(Al,Cr)_2O_4$ system corresponds to a pink pigment included in Group XIII of the DCMA classification.[10]

The synthesis of ceramic pigments by traditional solid-state route is based on an interdiffusion reaction between the reagents. The high temperatures and reaction times involved in this processes require the use of certain additives (known as mineralisers) in order to improve the slow inter-diffusion processes of solid-state reactions. Among the mineralisers, boron is typically used as a flux agent to encourage fluidity and homogeneity during thermal treatment. Boron is known to be an essential micronutrient; however, the range between deficiency and excess uptake (toxicity) in plants is small, rising up environmental and health problems. In fact, irrigation water with high boron contents is one of the main sources of pollution for agriculture.[11]

Keeping all these aspects in mind, the aim of the current research is to optimise a pink pigment based on Cr-doped system from a toxicological and ecological point of view, in particular to incorporate the whole quantity of the initial chromium ions in the host lattice avoiding its possible segregation during washing and ulterior oxidation as toxic Cr(VI) species.

The specific objectives were to optimise the synthesis conditions studying the best mineraliser as well as the chromium content in the structures in order to minimize the segregation of toxic Cr(VI) ions in the washing liquids without decreasing the pigmenting properties. In the first stage, the development of the best pink colour in function of the quantity of chromium in the $Al_{2-x}Cr_xO_3$ system was studied. However, since the pink colour turned out to be unstable in the glaze unless ZnO was present in the composition of the frit, the following study was redirected towards the Cr-doped $ZnAl_2O_4$ system.

2. Experimental

2.1. Sample preparation

The different compositions studied in this paper were prepared using traditional ceramic pigment synthesis methodology. The precursors were the corresponding chemically pure oxides: Al_2O_3, Cr_2O_3 and ZnO; and the additives chosen as mineralisers were LiF, $LiBO_2$ and H_3BO_3. These particular additives were chosen due to their low melting points, and also taking into account the results obtained in a previous work based on the study of the greenish $Cr_{2-x}Al_xO_3$.[12]

Precursors were mixed in acetone in a laboratory planetary ball mill for 20 min. After drying, samples were fired in a Nabertherm electric furnace at a heating rate of 10 °C/min at 1000, 1100, 1200 and 1300 °C and were held at each final temperature for 2 h. To refine and homogenise the particle size after firing, the resulting products were ground in an agate mill with acetone.

To verify the compositional stability of the compounds obtained as ceramic colorants, 3% (w/w) of the calcined samples was glazed using two different industrial frits. The thermal treatment used corresponds to a standard industrial ceramic tile firing cycle, and consisted of five steps: heating to 800 °C in 18 min, followed by heating from 800 to 1080 °C in 17 min, 5 min hold at 1080 °C, followed by cooling to 600 °C in 20 min, and finally cooling to room temperature in 15 min.

In a first stage, a study of the influence of the mineralisers on the temperature and reaction time, and also in the chromium segregation was performed. The mineralisers were incorporated in 2 wt% additions. The samples prepared are listed in Table 1.

After establishing the mineraliser and the firing temperature at which pink pigment presents the best colouration and the lowest chromium segregation, we proceed to perform the following studies under the same conditions. In this case, the best mineraliser effect was afforded with $LiBO_2$. According to the DCMA classification, there is a pink pigment based on the $Al_{2-x}Cr_xO_3$ stoichiometry (DCMA 3-03-5). Firstly, in this work we studied the effect of chromium concentration on pigment colour. It is known that to produce a pink colour pigment, the Al_2O_3 content needs to exceed that of Cr_2O_3. Thus, the compositions were prepared containing low concentrations of chromium ($x = 0.0125$, 0.025, 0.050, 0.075, 0.10, 0.20 and 0.30).

Since the development of the pink colour requires the presence of ZnO, the spinel $ZnAl_2O_4$ was chosen as host hue to introduce Cr(III) ions substituting Al(III) ions in octahedral positions. Therefore, several compositions based on $ZnAl_{2-x}Cr_xO_4$

Table 1
Study of mineralisers for composition $Al_{1.55}Cr_{0.45}O_3$

Samples	$Al_{1.55}Cr_{0.45}O_3$ mineralisers
R1SM	–
R1M1	2% $LiBO_2$
R1M2	2% H_3BO_3
R1M3	2% LiF
R1M(2 + 3)	2% LiF + H_3BO_3 (1:1 mixture)

($0.1 \leq x \leq 0.9$) stoichiometry were prepared in order to optimise the composition of the ceramic pigment from both an optical and environmental point of view. Due to the fact that the eutectic point of the ZnO–Al_2O_3 system is at ∼1700 °C (82.5 mol% ZnO),[13] $LiBO_2$ was added as mineraliser to improve the synthetic process allowing a faster crystallization and a more homogeneous reaction of the components.

2.2. *Characterization techniques*

Phase analysis of the fired samples was performed by X-ray powder diffraction (XRD) with a SIEMENS D5000 diffractometer with Cu Kα radiation. Data was collected through step by step-scanning, from 20° to 70° 2θ with a step size of 0.05° 2θ and 5 s, counting time at each step. The goniometer was controlled by the "SIEMENS DIFFRACT plus" software, which also determined diffraction peak positions and intensities. The instrument was calibrated using an external Si standard. In some fired samples, structure refinement was carried out using the WinXPow program with the data obtained in the 10–110° 2θ range, using a step size of 0.02° 2θ and 10 s for each step.

UV–vis spectroscopy and a colorimetric study were performed with a CARY 500 SCAN VARIAN spectrophotometer. The diffuse reflectance spectra (DRS) were obtained using an integrating sphere and $BaSO_4$ as a reference. The $L^*a^*b^*$ were compared to those of a pink pigment used in the ceramic industry, referenced STD. CIELAB colour parameters were determined by coupling an analytical software used for colour measurements to the VARIAN UV/Visible spectrophotometer. The data was registered from 380 to 700 nm using a PTFE blank as reflecting standard and a D65 standard illuminant. In the CIELAB system, L^* is the lightness axis [black (0) to white (100)], a^* is the green (<0) to red (>0), and b^* is the blue (<0) to yellow (>0) axis.[14,15]

The study of Cr(VI) content in the washing liquids of the samples was carried out using the colorimetric method as recommended by the EPA (Environmental Protection Agency).[16] Thus, a 0.3 g fired sample was subjected to successive washings with hot 0.3 M HNO_3 until 50 mL of solution was obtained. Measurements were conducted on the spectrophotometer used for CIELAB measurements at 540 nm.

Since it is known that boron have some negative environmental effects and, by other hand, it was added in the synthesis for its mineralizing effect, its content in the washing liquids was also analysed. The boron content was determined by a Hewlett Packard 4500 induced coupled plasma mass spectrometer (ICP-MS).

The chemical composition of the industrial frits was determined by X-ray fluorescence (XRF) using a SIEMENS SRS 3000 wavelength dispersive XRF spectrophotometer.

3. Results and discussion

3.1. *$Al_{2-x}Cr_xO_3$ solid solution*

Initially, in order to determine the best mineraliser which reduces Cr(VI) segregation in washing liquids without decreasing the pigmenting properties, an initial study on the $Al_{2-x}Cr_xO_3$ composition was performed. According to Fig. 1 taken from Ref. 15, this study was carried out on the $Al_{1.55}Cr_{0.45}O_3$ stoichiometry (78% mol Al_2O_3–22% mol Cr_2O_3), which corresponds to the limit between the green and red colouration.

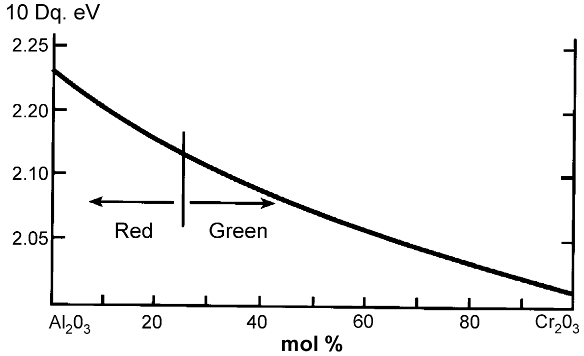

Fig. 1. Variation of the ligand field and the colour in the Cr_2O_3–Al_2O_3 solid solutions.

XRD patterns of the different samples revealed the formation of the Al_2O_3 (corundum) phase (JCPDS 71-1128) as a single phase in all the compositions, with and without the addition of the mineralisers (not shown).

Fig. 2 depicts the Cr(VI) content in the washing liquids. It can be observed that compositions R1M1, R1M2 and R1M(2 + 3), fired at 1200 and 1300 °C for 2 h, segregate less Cr(VI) during washing.

To evaluate the chromatic properties of the ceramic pigments, the values of CIELAB chromatic coordinates of the samples were determined before and after glazing because it is well-known that not all the ceramic pigments exhibit the same colour features after glazing. The main reason deals with possible reactions between the pigments and some of the components of the glaze. The colorimetric study performed on both the powdered samples and the samples after glazing showed that in both cases the best pink colour (the highest a^* and the lowest b^* values) was obtained for the R1M1 composition. Taking into account that the temperatures with less chromium segregation were 1200 and 1300 °C, Fig. 3 illustrates the values of the CIELAB coordinates

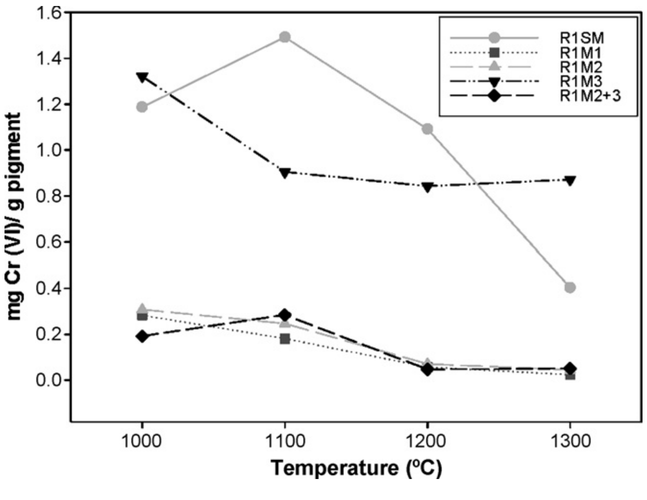

Fig. 2. Cr(VI) segregation in the washing liquids of composition $Al_{1.55}Cr_{0.45}O_3$ (R1) with and without different mineralisers.

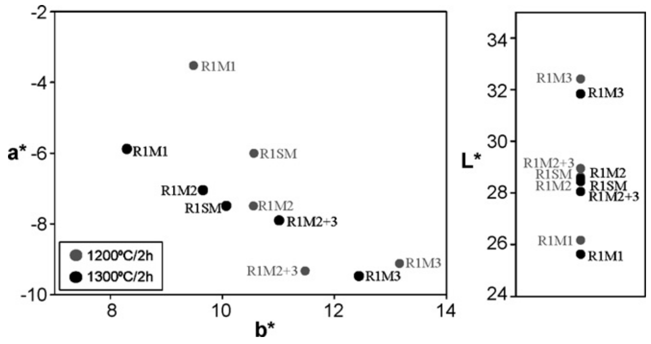

Fig. 3. CIELAB colorimetric coordinates of composition $Al_{1.55}Cr_{0.45}O_3$ (R1) with and without different mineralisers fired at 1200 °C/2 h and 1300 °C/2 h after glazing.

corresponding to the glazed samples with and without mineralisers, fired at these firing temperatures. The highest a^* was achieved after calcining at 1200 °C. As a result, the following studies were carried out at this synthesis temperature.

In brief, the results obtained by XRD, colorimetry and analysis of Cr(VI) in the washing liquids suggested that $LiBO_2$ is the best additive for synthesizing this solid solution. As has been indicated in previous reports,[12] the effect of boron compounds in ceramic pigment synthesis could stem from the fact that the B_2O_3 formed from $LiBO_2$ during firing has a particularly useful effect in shortening melting and refining time (removal of gas bubbles). For this reason, since boron favours the ion incorporation into the solid solution, the quantity of Cr(III) that diffuses inside increases and the oxidation of Cr(III) to Cr(VI) is prevented (given the atmosphere in which the calcinations are conducted).

Once the best mineraliser was identified, a study to optimise the chromium content was performed in the $Al_{2-x}Cr_xO_3$ system ($x = 0.0125, 0.025, 0.050, 0.075, 0.10, 0.20$ and 0.30). The XRD spectra of all samples (not shown) exhibited peaks associated to the corundum structure (JCPDS 71-1123) as a single phase. The formation of the different solid solutions is supported by the shift observed for the peak positions towards lower 2θ values.

Although the effect of a solid solution formation between aluminium and chromium in the corundum structure have been studied before[17] we have obtained the cell parameters of the corundum lattice for the non-doped and doped ($x = 0.025$, 0.050 and 0.075) samples fired at 1200 °C/2 h from the refinement of the XRD patterns using the WinXPow program (Table 2). It can be observed that when x increases, the a and c parameters also increase. This expansion of the lattice corresponds to the substitution of Al ions in their atomic positions by Cr ions, since, according to Shannon and Prewitt data,[18] the atomic radii for Cr(III) and Al(III), both in octahedral coordination, are 75.5 pm and 67.5 pm, respectively. Hence, due to the larger lattice plane d-spacing existing in the Cr_2O_3 structure, an increase in the parameters with the substitution occurs. This therefore confirms the formation of the expected solid solution in our working conditions.

Table 2
Corundum unit cell parameters in $Al_{2-x}Cr_xO_3$ ($x = 0.025$ and 0.075)

	$a \pm 0.0001$	$c \pm 0.0001$
Al_2O_3	4.7342	12.9176
$Al_{1.975}Cr_{0.025}O_3$	4.7533	12.9761
$Al_{1.975}Cr_{0.050}O_3$	4.7627	13.0003
$Al_{1.925}Cr_{0.075}O_3$	4.7670	13.0090

Table 3
CIELAB colour parameters of composition $Al_{1.925}Cr_{0.075}O_3$ (R1) after glazing with two different frits (±1%, according to the instrument specifications)

Frit	L^*	a^*	b^*
F1	70.3	8.9	8.2
F2	67.6	4.9	19.9

Analysis of Cr(VI) content in the washing liquids indicated that there is a small segregation of this ion in the samples studied, but below the permitted limits in European legislation for Cr(VI) in water emissions (0.2–0.5 ppm).

The CIELAB chromatic coordinates measurements of the different samples showed that the composition with $x = 0.075$ calcined at 1200 °C for 2 h exhibited the best pink values. After optimising the stoichimetry, this pigment was tested (3% w/w) in two different industrial frits, and their chromatic coordinates are detailed in Table 3.

It can be observed that after glazing with the frit F1, the pink colour proved to be stable. However, in the case of the frit F2 there was a loss of coloration. By comparing the chemical composition of both frits in order to ascertain the possible effects of the frits, we realised that the main difference between them was the presence or absence of ZnO in their compositions. As a conclusion, this study showed that ZnO in the composition of the frit favours obtaining the pink colour; meanwhile, when there was no ZnO in the frit, the pink colour did not develop. These facts could indicate that the formation of a zinc aluminium oxide spinel doped with chromium is responsible for the existence of the pink colouring. Indeed, the formation of this structure that causes pink coloration corresponds to another pink ceramic pigment in the DCMA classification based on the $Zn(Al,Cr)_2O_4$ structure.[10] In order to go deeper into this subject and verify the origin of the colour, a study of the $ZnAl_{2-x}Cr_xO_4$ system was performed.

3.2. $ZnAl_{2-x}Cr_xO_4$ solid solution

Fig. 4 illustrates the XRD patterns of the compositions synthesised for the $ZnAl_{2-x}Cr_xO_4$ solid solution calcined at 1200 °C/2h. The diffractograms showed that zinc aluminate structure (JCPDS 82-1043) was formed as a single phase. In these samples, Cr ions seem to be completely incorporated into the spinel lattice. Diffusion processes in the $ZnO–Cr_2O_3–Al_2O_3$ system give raise to a $Cr:ZnAl_2O_4$ solid solution, which is supported by the shift observed in peak positions of the gahnite phase towards lower 2θ values according to the d-spacing with the Cr substitution. As has been mentioned previously, these results are in agreement with the atomic radii for Cr(III) and Al(III), both in octahedral coordination. Thus, when the quan-

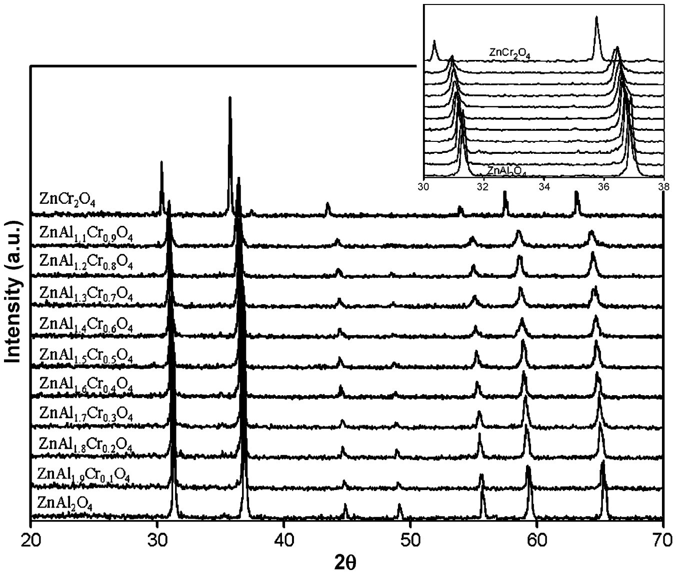

Fig. 4. XRD for the compositions $ZnAl_{2-x}Cr_xO_4$ fired at 1200 °C/2h.

tity of Cr_2O_3 increases, the 2θ peak position decreases and shifts closer to the $ZnCr_2O_4$ structure.

Table 4 indicates the cell parameters of the cubic spinel in the $ZnAl_{2-x}Cr_xO_4$ system. A continuous increase of this value can be observed when the amount of dopant increases.

Analysis of Cr(VI) in the washing liquids of the all samples prepared with the addition of mineraliser indicated that no Cr(VI) ions were present in the washing liquids. This fact corroborates the formation of a solid solution with all chromium ions introduced in the spinel structure. Boron segregation analysis showed that the values obtained were lower than the permitted quantities in European legislation for B segregation (2–10 ppm).

The colorimetric study performed on the powdered samples is depicted in Fig. 5, where the variation of the colorimetric coordinates against the x value is presented. The chromatic coordinates of a commercial pink pigment (dotted line, standard: std) is included as a reference of the typical coloration used in industry.

As a result of the XRD study, colorimetry and analysis of Cr(VI) in the washing liquids, it was concluded that the sample $ZnAl_{1.8}Cr_{0.2}O_4$ ($x = 0.2$) exhibited the best optical properties, very similar to the STD ones.

Table 4
Gahnite unit cell parameters in $ZnAl_{2-x}Cr_xO_4$ ($x = 0 - 0.9$)

x	$a \pm 0.0001$
0.0	8.0742
0.1	8.0893
0.2	8.1038
0.3	8.1131
0.4	8.1299
0.5	8.1385
0.6	8.1476
0.7	8.1587
0.8	8.1718
0.9	8.1805

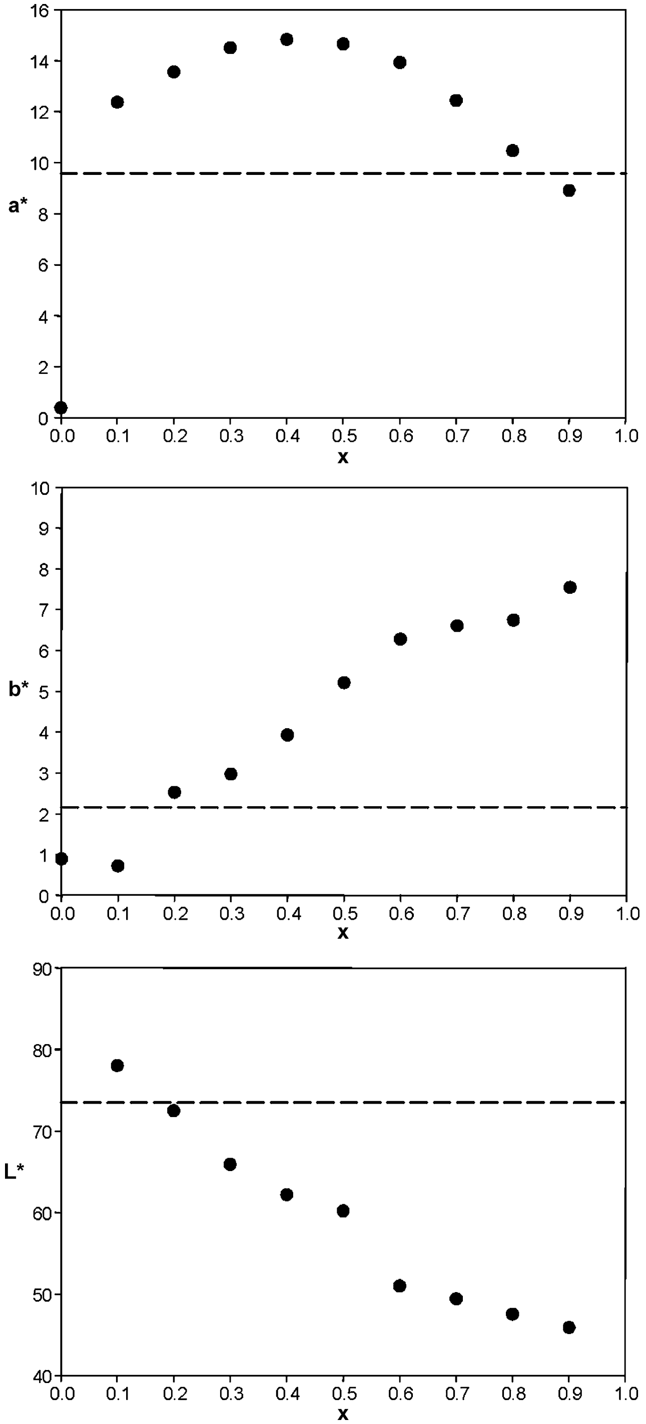

Fig. 5. CIELAB colour parameters of the compositions $ZnAl_{2-x}Cr_xO_4$: (a) a^*, (b) b^* and (c) L^* (standard: dotted line).

In order to know the quantity of Cr(III) in the solid solution, a representation of the $ZnAl_{2-x}Cr_xO_4$ cell parameter versus x was performed, Fig. 6. It can be observed that the values fit well with a linear regression ($r^2 = 0.9951$), in agreement to Vegard's law. From the coefficients of the linear equation, the real Cr-content of the optimised solid solution ($x = 0.2$) was recalculated, giving an x value of 0.2043, very close to the theoretical stoichiometry proposed.

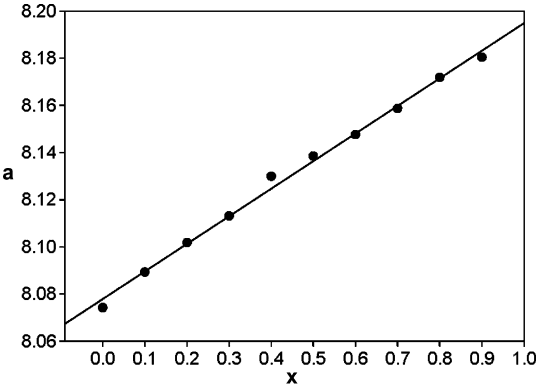

Fig. 6. Linear regression of $ZnAl_{2-x}Cr_xO_4$ cell parameter vs. x.

After establishing the composition and conditions which best matched the set objectives, $ZnAl_{1.8}Cr_{0.2}O_4$ ($x = 0.2$) was analyzed by UV–vis spectroscopy diffuse reflectance in order to study the surroundings of the Cr(III) chromophor. The spectrum is presented in Fig. 7. It has been deconvoluted by means of a Gaussian decomposition in three bands located at 542, 431 and 391 nm that can be related to d–d electronic transitions of the Cr(III).

The theory of the ligand field [19] for a Cr(III) ion in an octahedral environment predicts the existence of three absorption bands. The energies of the first two electronic spin allowed transitions, $^4A_{2g} \rightarrow {}^4T_{1g}$ (F) and $^4A_{2g} \rightarrow {}^4T_{2g}$ (F), correspond to visible light energies. There is a third spin allowed transition from $^4A_{2g}$ to $^4T_{1g}$ (P) whose energy corresponds to ultraviolet light that does not affect the colour. Depending on the ligand field created by the oxide ions, the position of these bands can be modified, resulting in a variation in the observed coloration.

In fact, the absorption bands of pure Cr_2O_3 appear at 580 and 405 nm, respectively. We can observe in Fig. 7 that these two absorption bands for the sample measured appear at wavelength values lower than the Cr_2O_3 ones. This shift can be attributed to an increase in the intensity of the ligand field due to the decrease of the Cr-O distances produced by the substitution of Al(III) by Cr(III) in the spinel structure, and therefore, because of the higher intensity of crystalline field around the Cr(III) ions than in Cr_2O_3 system. The larger size of chromium ions compared to aluminium ones produces this effect, given that the chromium species are situated in a more compressed environment. In the spectrum, the pink shade is associated with the absorption centred at 542 nm, which explains the existence of this coloration.

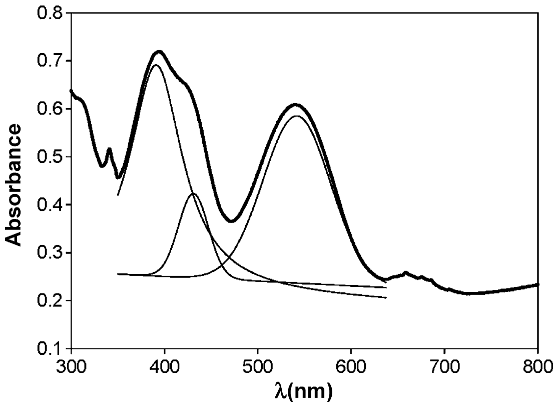

Fig. 7. UV–vis spectrum of the $ZnAl_{1.8}Cr_{0.2}O_4$ sample.

Table 5
Chromatic coordinates of $ZnAl_{1.8}Cr_{0.2}O_4$ pigment after glazing in two frits (F1) with ZnO and (F2) without ZnO (±1%, according to the instrument specifications)

Frit	*L**	*a**	*b**
F1	75.9	12.4	11.1
F2	66.4	13.3	17.8

Finally, in order to test both the strength of the pigmentation and the stability of the solid solution in a glaze, the colour was glazed with the same frits used in the $Al_2Cr_{2-x}O_3$ system (F1: with ZnO in its composition; and F2: in absence of ZnO). Table 5 lists the chromatic coordinates of the pigment after glazing.

It can be observed that, in both cases, pink colour is developed, although in the case of F1 the colour obtained had the best chromatic coordinates. This result confirms the requirement of the presence of ZnO in the frit to achieve a good level of stabilization in the pink colouring. Thus, it can be concluded that this pigment gives the best results in glazes with high ZnO content.

It is known that some elements, such as Pb and Zn, do not contribute any colour by themselves, but have a considerable influence on the colour produced by other ions. This requirement is explained by the ZnO behavior as an active flux in glazes in smaller amounts. However, in greater amounts, zinc oxide has the capacity to produce its own phases in glazes and generally promotes secondary crystalline phases which can involve the absorption of the colouring agents, producing the loss of stoichiometry in the ceramic pigment.[20,21] Therefore, in our system, the presence of a sufficient quantity of ZnO in the frit, together with a sufficient amount of Al_2O_3, produces the $ZnAl_2O_4$ spinel and compensates the possible dissolution of the pigment structure in the glaze, enhancing the pigmenting colour.

In brief, our results show evidence of the importance of glaze composition in colour development and stability of ceramic pigments.

4. Conclusion

In summary, the optimisation of a pink pigment based on Cr-doped system from a toxicological and ecological point of view is reported. The whole research was focused on the optimisation of the synthesis parameters in order to minimise the amount of pollutant Cr(VI) in the washing liquids without decreasing its pigmenting properties. Due to the low interdiffusion processes involved in a solid-state reaction, the addition of a mineraliser was needed. $LiBO_2$ resulted to be the best additive improving the synthesis conditions, leading to obtain the best coloration and the lowest Cr(VI) segregation in washing water. After studying the coloration of the $Al_{2-x}Cr_xO_3$ solid solution, it was found that the presence of ZnO in the frits was a requirement for the stability of the pink colour after glazing. In view of this result, the research was redirected towards the study of the Cr-doped $ZnAl_2O_4$ system. XRD showed a solid solution formation based on the gahnite structure as unique phase. Colorimetric study and analysis of leached Cr(VI) in the washing liquids led to conclude that the optimal composition corresponds to the $ZnAl_{1.8}Cr_{0.2}O_4$ stoichiometry. Thus, this work has enabled to produce a pink pigment with low environmental impact and good chromatic coordinates, although, these results also have shown that an exhaustive study on the influence of the glaze composition is really required.

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