

Preparation by Hydrolysis of Aerosols and Colour Properties of Cr-Doped and Co-Doped Zircon Powders

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Abstract

Cr-doped and Co-doped zircon powders consisting of spherical particles with broad size distribution (0.1–5 μm) and different M/Zr atomic ratios (M = Cr or Co) were prepared by hydrolysis of aerosols generated from mixtures of silicon and zirconium alkoxides and ethanolic solutions of the corresponding metal salt. The thermal evolution of these powders was studied up to zircon crystallisation and the colour properties of the resulting pigments were evaluated and related to the nature and localisation of the chromophore in the zircon matrix. The effects of the addition of a flux agent (NaF) on the colour properties of the pigments was also investigated. It was found that green Cr-doped pigments can only be obtained by heating the starting powders at 1300°C in the presence of NaF, since in the absence of the flux, the whole amount of the Cr ions was volatilised during zircon formation (1500°C). This colour was mainly due to Cr³⁺ ions located out of the zircon lattice, probably forming a sodium chromium (III) silicate. In Co doped zircon, the addition of NaF had no influence on the temperature of zircon formation (1100°C), although it affected the colour properties of the resulting pigments. Thus, the colour observed in the absence and the presence of the flux was green and blue, respectively. Although the only Co phase detected in both cases was Co₂SiO₄, the green colour was tentatively attributed to the presence of a small

amount of unreacted CoO, whereas the blue one, to the formation of a certain amount of a sodium cobalt (II) silicate. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

Zircon (ZrSiO₄) is one of the preferred host matrices for the preparation of ceramic pigments due to its high thermal and chemical stability which confer to the latter a superior resistance to dissolution during firing.¹ Nowadays, the only commercially produced zircon based pigments are the vanadium turquoise blue, the iron pink coral and the praseodymium yellow.² However, the introduction of other doping cation such as chromium^{3–5} and cobalt³ has been suggested to obtain different colours^{3,5} or to improve the stability of the corresponding pure metal oxide pigments.⁴

The traditional method for preparing ceramic pigments involves the initial milling of the mixture of the component precursors for homogenisation, the calcination of this mixture at high temperature to develop the desired phases and colours and a further grinding process to reduce and homogenise particle size.⁶ In some cases, a mineralising agent (alkaline halide) is added to the components mixture to reduce the temperature of pigment formation. We have recently shown that this procedure can be simplified by eliminating grinding if the doping cation is incorporated to the ceramic matrix through the hydrolysis of liquid aerosols.^{7–9}

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In general, this method consists of the generation of liquid droplets containing the appropriate precursors and their further hydrolysis to form solid particles in which all components are intimately mixed. An additional advantage of the process is its continuous character which makes it suitable for large scale production.

This paper deals with the preparation by hydrolysis of aerosols of Cr-doped and Co-doped zircon powders consisting of amorphous spherical particles of broad size distribution. The thermal evolution of these powders is studied up to zircon formation. In some experiments (NaF), as a flux agent is added to the as prepared powders prior to calcination to evaluate its effects on the process of formation and properties of the pigments. The influence of the doping cation content in the starting powders on the colour properties is also investigated. Finally, the nature and localisation of the chromophore in the zircon matrix are also analysed to determine the origin of the pigments colours, which to our knowledge, has not yet been studied in the case of Co-doped zircon, whereas it remains unclear in the case of Cr-doped zircon.^{3,5,10}

2 Experimental

2.1 Powders preparation

The preparation of M-doped zircon (M = Co or Cr) powders was carried out by hydrolysis of liquid aerosols, using a procedure similar to that previously reported to obtain vanadium doped zircon, with some slight modifications.⁷ Essentially, this method consists of the hydrolysis of an aerosol generated from a mixture of the appropriate liquid precursors, which, in principle, should have sufficiently high hydrolysis rate to produce the corresponding solid oxide particles in a very short reaction time.¹¹ Following these criteria, we selected silicon ethoxide (TEOS, Fluka, 98%) and zirconium propoxide (Aldrich, technical grade) as starting precursors for silicon and zirconium, respectively. Proper amounts of these compounds (Si/Zr atomic ratio = 1) were mixed under stirring and the resulting mixture was partially hydrolysed for 24 h in ambient conditions (20°C and 60% relative humidity) to avoid the important lack of stoichiometry (Si/Zr < 1) that would be produced in the resulting powders as a consequence of the incomplete hydrolysis of TEOS.¹² Highly hydrolysable Cr (III) or Co (II) compounds were not found commercially available. However, the incorporation of Co (II) or Cr (III) to the ceramic matrix could be carried out by encapsulating a Cr (III) ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Aldrich, 99%) or Co (II)

($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, Aldrich, 99%) salt in the solid particles simultaneously to the process of hydrolysis of the alkoxide mixture. For this purpose, the metal salt was dissolved in absolute ethanol in the desired concentration and an aliquot (2 cm³) of this solution was added to the prehydrolysed alkoxide mixture (31 cm³). The aerosol was then generated by nebulisation using a glass nozzle and nitrogen at a constant pressure (0.3 Kg cm⁻²) as a carrier gas. The hydrolysis of the droplets was carried out at room temperature with water vapours brought into contact with the aerosol stream by bubbling nitrogen at constant flow rate (2 l min⁻¹) through a water container. The resulting particles were collected with a system of nylon sieves. An schematic diagram of the apparatus used for the whole process can be found in Ref. 12.

The Co or Cr contents of the so produced powders were varied in order to analyse their effects on the optical properties of the pigments. The as-prepared samples were calcined for 8 h at the desired temperatures in platinum crucibles. The furnace was heated at heating rate of 10°C min⁻¹. In some experiments, a certain amount of NaF (NaF/ZrSiO₄ mole ratio = 20%) was admixed to the powders before calcination. This mixture was gently ground in an agate mortar for homogenisation.

2.2 Characterisation and measurements

The particle size and shape of the powders were examined by scanning (SEM, JEOL JSM5400) electron microscopy.

The composition of the solids (Zr/Si ratio and Co or Cr content) was determined by plasma emission (ICP, Perkin Elmer, Model 5500). For such a purpose, 100 mg of sample were first fused at 1100°C with a NaKCO₃:Na₂B₄O₇ mixture and then extracted with a HCl solution.

The different phases present in the solids were identified by X-ray diffraction (Siemens D501). The infrared spectra of the samples diluted in KBr were recorded in a Nicolet 20SXC spectrophotometer.

The unit cell parameters of the powders were measured by Rietveld analysis of the X-ray diffraction data following the procedure described in Ref. 8. In all experiments a silicon standard (20% by weight) was mechanically mixed with the pigment. The crystallographic data for zircon and silicon were taken from Refs 13 and 14, respectively.

Differential thermal (DTA) and thermogravimetric (TGA) analyses (Setaram 92-16.18) were carried out in air at a heating rate of 10°C min⁻¹.

X-band ESR spectra were obtained at temperatures from room (RT) to liquid nitrogen (LNT) temperature with a Varian E-112 spectrometer.

Magnetic field values were determined with a NMR gaussmeter. The diphenylpicrylhydrazyl (DPPH) signal was used to measure the microwave frequency.

XPS spectra were obtained with a VG Escalab 210 model using the MgK α excitation source. Calibration of the spectra was done at the C1s peak of surface contamination taken at 284.6 eV. Atomic percentages of the elements were calculated from the peaks areas after background subtraction (Shirley background). The areas were referred to the sensitivity factors of the elements as supplied by the instrument manufacturers.

The colour of the pigments was determined according to the Commission Internationale de l'Éclairage (CIE) by using *Lab* parameters.¹⁵ 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. For measurements, 40 mg of pigment were dispersed in doubly distilled water and filtered through 0.22 μm Millipore filters, resulting in a thin layer with a density of 6 mg cm⁻¹. This amount was sufficient to avoid substrate effects on colour measurements. After drying, the reflectance spectrum of the pigment layer was recorded (Varian 2300) from 780 to 360 nm using a BaSO₄ plate as a reference standard, and the *Lab* parameters determined for a standard illuminant, C.

3 Results and Discussion

3.1 Cr-doped zircon

Two Cr-doped zircon samples (Cr-A and Cr-B) with different Cr content (Table 1) were prepared in order to investigate the effects of composition on the colour properties of the pigments. It should be noted that the Cr/Zr atomic ratio of sample Cr-A (0.091, Table 1) represents the maximum amount of Cr that could be incorporated to the ceramic matrix by using the above described procedure. Attempts to increase this ratio by the addition of higher amounts of the chromium salt to the starting alkoxides mixture were unsuccessful due to the

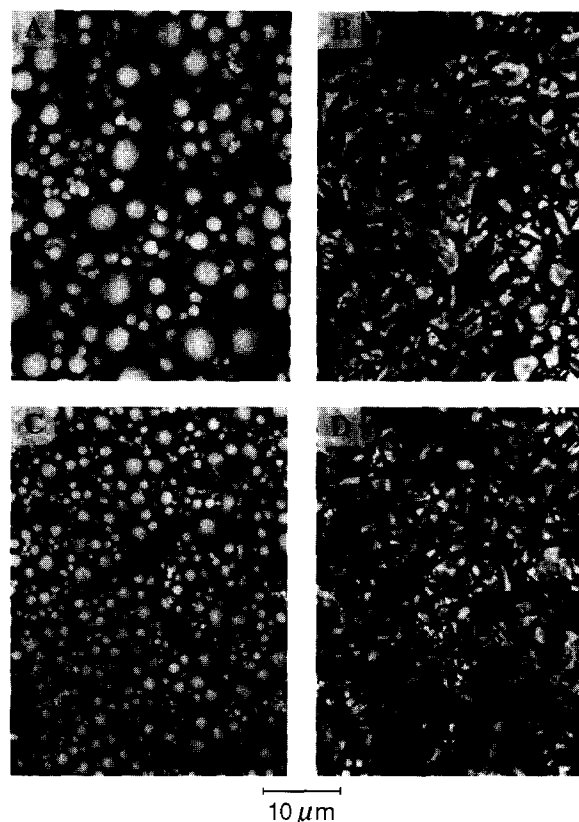


Fig. 1. Scanning electron micrographs of sample Cr-A as-prepared (A) and after heating at 1300°C in the presence of NaF (B), and sample Co-A after heating at 1100°C in the absence (C) and the presence (D) of NaF.

instantaneous hydrolysis of the latter produced as a consequence of the high water amount, coming from the Cr hydrated salt added under these conditions.

The as-prepared Cr-doped zircon particles were amorphous to X-ray diffraction, showing spherical shape and sizes ranging from 0.1 to 5 μm as illustrated in Fig. 1(A) (sample Cr-A). The infrared spectrum of this sample (Fig. 2) displayed strong bands at 1000 and 450 cm⁻¹ mainly due to Si–O and Zr–O vibrations, respectively.¹² Additional vibrations observed at 1385 and 1355 cm⁻¹ indicated the presence of nitrate anions in the particles,¹⁶ which also contained adsorbed water as evidenced by intense bands at 1635 and 3400 cm⁻¹ (the latter is not shown in the figure).

Table 1. Composition (Si/Zr and Cr/Zr atomic ratios) of the Cr-doped zircon samples as-prepared and after heating at different temperatures in the presence or the absence of NaF, measured by ICP. The composition obtained from the XPS spectra of sample Cr-A heated at 1300°C in the presence of NaF is also included

Samples	Temperature °C	(Si/Zr) _{ICP} (atomic)	(Cr/Zr) _{ICP} (atomic)	(Si/Zr) _{XPS} (atomic)	(Cr/Zr) _{XPS} (atomic)	(Na/Zr) _{XPS} (atomic)
Cr-A	As-prepared	0.93	0.091			
Cr-A	1100	0.92	0.061			
Cr-A	1300	0.93	0.050			
Cr-A	1500	0.96	Not detected			
Cr-A + NaF	1300	0.94	0.075	2.27	0.095	0.33
Cr-B	As-prepared	0.93	0.058			
Cr-B + NaF	1300	0.98	0.040			

The thermal behaviour of the two prepared Cr-zircon samples was similar. The characterisation data hereafter presented corresponds to sample Cr-A chosen as a representative example. Differential thermal analysis of this sample (Fig. 3) showed an endothermic peak centred at 100°C followed by three exothermic ones at 180 and 275 and 940°C.

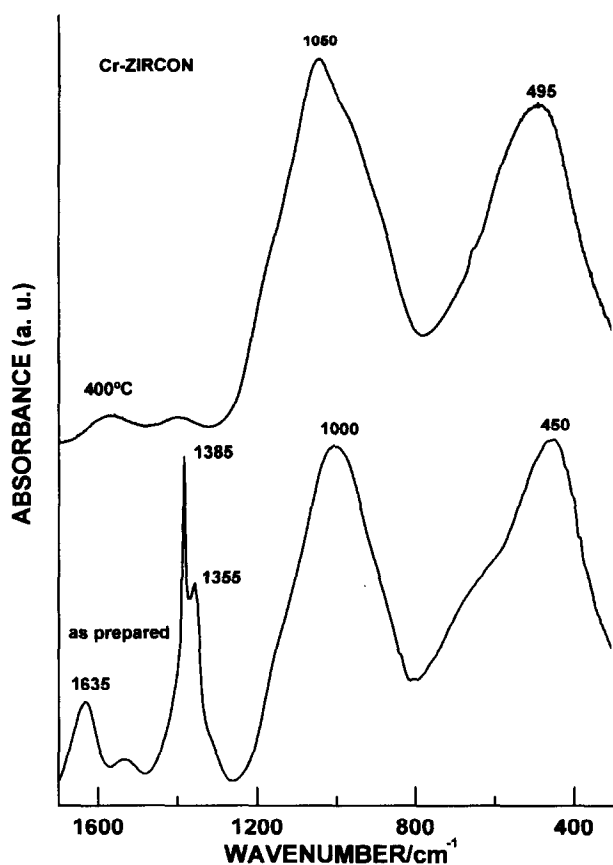


Fig. 2. Infrared spectra of sample Cr-A as-prepared and after heating at 400°C.

The endothermic effect is due to the release of adsorbed water and probably of adsorbed alcohols produced as a by-product of the alkoxides hydrolysis. The exothermic peaks at 180 and 275°C are mainly attributed to the decomposition of the nitrate anions, as indicated by the absence of the bands at 1385 and 1355 cm^{-1} in the infrared spectrum of the sample heated at 400°C (Fig. 2). The weight loss detected by TGA between 20 and 400°C corresponding to the above processes was $\sim 27\%$ (Fig. 3). According to X-ray diffraction (Fig. 4), the last exothermic effect (940°C) can be associated to the crystallisation of metastable cubic ($c\text{-ZrO}_2$) or metastable tetragonal ($t\text{-ZrO}_2$) zirconia. The observed broad peaks, indicative of small crystallite size, preclude the clear identification of these phases, which may show similar X-ray diffraction patterns^{17,18} under these conditions. This process was accompanied by a slight weight loss (1%) (Fig. 3), which has been also observed for undoped zircon gels and attributed to the release of residual carbonaceous species coming from the adsorbed alcohols still retained in the sample.¹⁹ It should be noted that a small and continuous weight loss was also observed up to 1400°C (Fig. 3) due to the volatilisation of Cr, probably as Cr_2O_3 , as suggested by the chemical analyses of the sample (Table 1) heated at increasing temperatures (1100–1500°C).

The X-ray diffraction patterns of sample Cr-A heated at different temperatures are shown in Fig. 4. As observed, metastable $c\text{-ZrO}_2$ (or $t\text{-ZrO}_2$) partially transformed into the monoclinic phase ($m\text{-ZrO}_2$) on calcination at 1100°C, at which temperature the crystallisation of cristobalite was also detected. Although the formation of zircon started

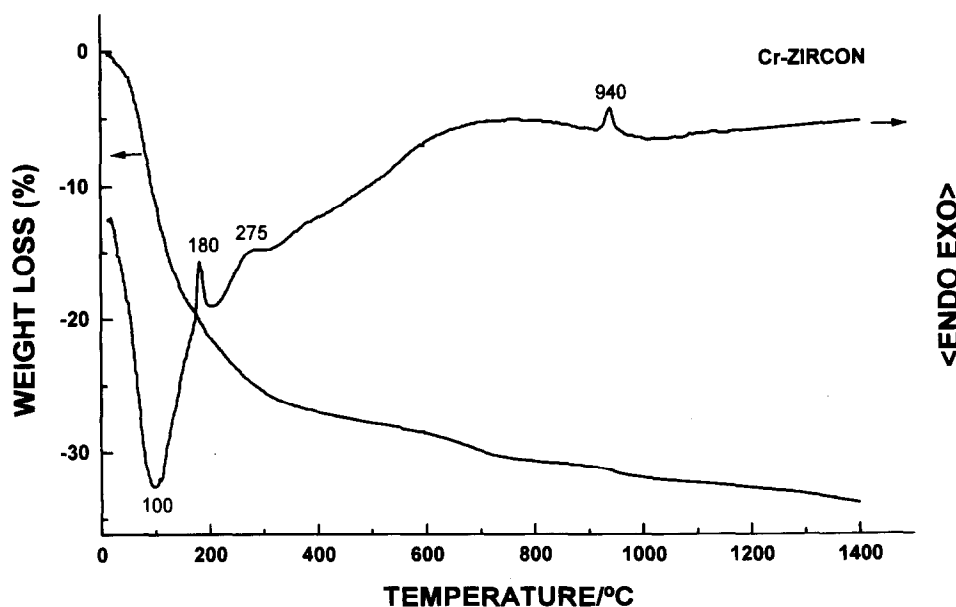


Fig. 3. Differential thermal and thermogravimetric analyses for sample Cr-A.

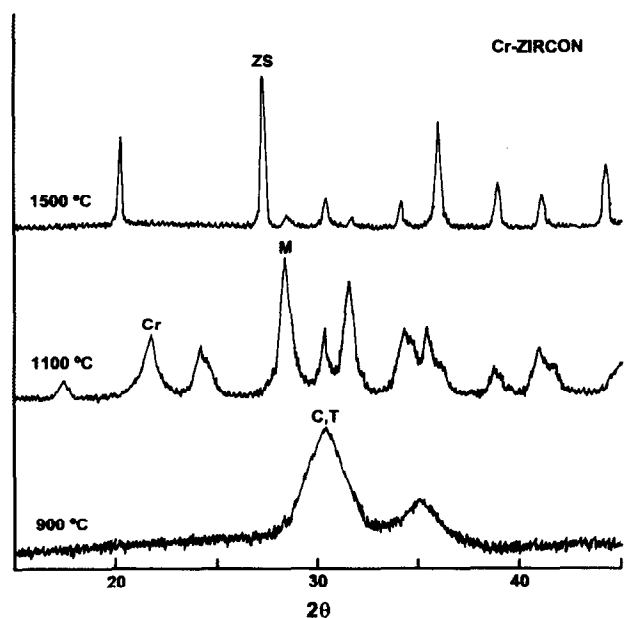


Fig. 4. X-ray diffraction patterns obtained for sample Cr-A after heating at different temperatures. Symbols designating different kinds of phases: ZS=zircon, Cr=cristobalite, M=monoclinic zirconia, T=tetragonal zirconia and C=cubic

at 1400°C (not shown in Fig. 4), a prolonged heating (24 h) at 1500°C was required to complete this process (Fig. 4). After this treatment, weak peaks of t-ZrO₂ and m-ZrO₂ were still observed in the pattern as expected from the slight excess of ZrO₂ present in this sample (Si/Zr ratio=0.96, Table 1).

As stated above, the amount of Cr present in sample Cr-A continuously decreased on calcination (Table 1). The chemical analysis of the sample after zircon formation (1500°C) showed the total volatilisation of Cr and consequently, the sample presented a white colour. In order to decrease the temperature of zircon formation and minimise the Cr losses, NaF was added to sample Cr-A before calcination. In effect, as manifested by X-ray diffraction, all structural changes took place at lower temperature in the presence of the flux agent (Fig. 5). Thus, the crystallisation of metastable c-ZrO₂ (or t-ZrO₂) was observed at 900°C, whereas zircon formation started at 1100°C, being completed at 1300°C. It should be noted that in these conditions, the X-ray diffraction pattern also showed a certain amount of t-ZrO₂ and m-ZrO₂, which was higher than that observed after zircon formation in the sample prepared in the absence of the flux, although the Si/Zr ratio was not modified by this treatment (Table 1). The addition of NaF also affected the morphological characteristics of the particles which lost their spherical shape, keeping their size < 10 μm [Fig. 1(B)].

The Cr/Zr ratio measured for sample Cr-A after calcination at 1300°C in the presence of NaF was 0.075 (Table 1). The *Lab* parameters of this sample ($L=62.7$, $a=-8.4$ and $b=9.3$) (Table 2)

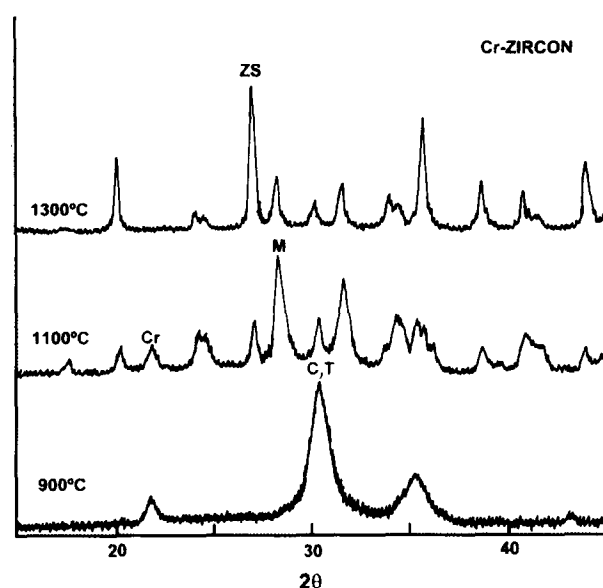


Fig. 5. X-ray diffraction patterns obtained for sample Cr-A after heating at different temperatures in the presence of NaF. Symbols designating different kinds of phases: ZS=zircon, Cr=cristobalite, M=monoclinic zirconia, T=tetragonal zirconia and C=cubic zirconia.

corresponded to a green colour, in agreement with that previously observed for samples prepared by the sol-gel process.³⁻⁵ The decrease of the Cr/Zr ratio in the pigments to 0.04 by decreasing the initial value to 0.058, using the same calcination conditions (sample Cr-B, Table 1), gave rise to a decrease in colour strength (*L* increased and *a* and *b* shifted toward 0) (Table 2).

As previously mentioned, the origin of the green colour of Cr doped zircon pigments, which is obviously related to the nature and localisation of the chromophore in the zircon matrix, has not yet been clarified. Thus, it has been concluded, from different X-ray studies (not including the determination of the unit cell parameters of zircon) carried out on powdered samples prepared by the traditional ceramic procedure and using different fluxes, that the Cr species form a solid solution with the zircon lattice, although no data are offered in this work to identify the Cr valence.⁵ It has been also reported that the hypothesis of a replacement of Si⁴⁺ with Cr⁴⁺ is acceptable from the interpretation of the absorption spectrum in the uv-visible region of Cr-doped zircon single crystals.¹⁰ Finally,

Table 2. *Lab* parameters and colour of the Cr-doped and Co-doped zircon samples heated at different temperatures in the absence or the presence of NaF

Sample	Temperature	<i>L</i>	<i>a</i>	<i>b</i>	Colour
Cr-A + NaF	1300°C	62.7	-8.4	9.3	Green
Cr-B + NaF	1300°C	65.7	-6.2	7.8	Green
Co-A	1100°C	58.7	-1.5	9.6	Green
Co-B	1100°C	58	-2.1	10.2	Green
Co-A + NaF	1100°C	56.7	0.9	-7.0	Blue

the presence of Cr^{2+} species in Cr-doped zircon powders has also been suggested on the basis of their absorption spectrum.³

In order to determine the valence of Cr in our pigments, the ESR spectrum of sample Cr-A heated at 1300°C in the presence of NaF was measured at RT and at LNT. In both cases, the obtained spectrum (Fig. 6) consisted of a relatively narrow and asymmetric line at $g=1.984$, a broad signal around $g=2$ extending towards the low field side and an intense broad line at very low fields. It should be noted that the very weak signal at $g=4.4$ can be attributed to the presence of very small amount of Fe^{3+} impurities. The broad bands are a consequence of the strong dipolar interaction between highly concentrated paramagnetic entities. Following previous studies carried out on Cr^{3+} in disordered systems,²⁰ these signals can be ascribed to Cr^{3+} ions, some of which ($g=2$) being in a coupled situation. The narrow resonance at $g=1.98$ can be also attributed to Cr^{3+} ions but isolated in slightly distorted octahedral sites. It should be noted that, as shown by the relative intensity of ESR bands, the amount Cr^{3+} cations in the isolated positions is very small.

Several experiments were then conducted to investigate the localisation of the Cr^{3+} ions in the zircon matrix. We found that the unit cell parameters of zircon measured for Cr-A sample heated at 1300°C in the presence of NaF were not altered with respect to those of pure zircon, indicating that the Cr cations must be located out of the zircon lattice forming a different phase, which does not seem to consist of Cr_2O_3 as suggested by the important discrepancies observed between the ESR

spectra of the latter and the Cr-doped zircon sample (Fig. 6). To gain information about the distribution of the Cr species in the Cr-doped zircon particles, the same Cr-doped zircon sample was examined by XPS spectroscopy. As expected, the obtained spectrum (data not shown) showed bands corresponding²¹ to Si (102.2 eV), Zr (182.6 and 184.9 eV), O (531 eV) and Cr (576.4 and 586.1 eV). The Cr bands, associated to the $2p_{3/2}$ (576.4 eV) and $2p_{1/2}$ levels (586.1 eV), are consistent with Cr^{3+} ions in agreement with the ESR spectrum of the sample. The Cr/Zr atomic ratio resulting from the intensity of the XPS bands ($\text{Cr/Zr}=0.095$) was slightly higher than that measured by ICP for the same sample ($\text{Cr/Zr}=0.075$) (Table 1) indicating a certain enrichment of Cr^{3+} in the particles outer layers. It should be noted that the XPS spectrum also displayed a band at 1071 eV due to the 1s level of Na, which was added as NaF. This finding along with the Si/Zr atomic ratio calculated from this spectrum, much higher ($\text{Si/Zr}=2.27$) than that determined by ICP ($\text{Si/Zr}=0.94$), suggest the presence of a sodium silicate in the particles outer layers which would explain the decrease in zircon yield observed when adding NaF (Fig. 4 and Fig. 5). In agreement with such an explanation is the slight shift of the Si2p XPS band (102.2 eV), with respect to its position in undoped zircon (101.8 eV), and its broadening [Fig. 7(A)] which indicates a more heterogeneous Si environment. Although the used characterisation techniques do not allow to identify the nature of this sodium silicate, it could consist of a sodium chromium (III) silicate such as NaCrSiO_4 which is known to be formed above 1000°C ²² and shows a green colour

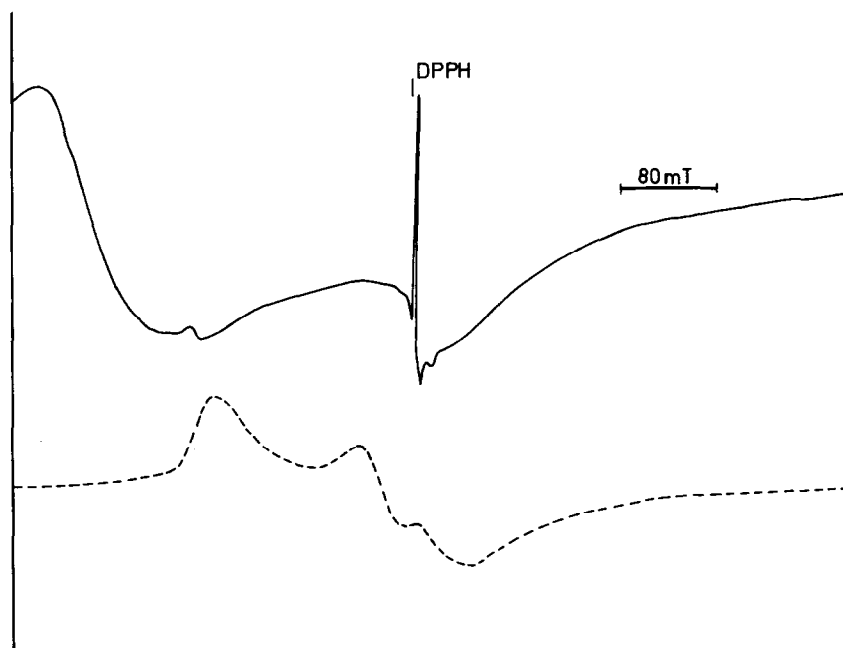


Fig. 6. ESR spectra obtained at 300 K for sample Cr-A heated at 1300°C in the presence of NaF (—) and for Cr_2O_3 (---).

as the Cr doped zircon sample. It should be noted that this Cr phase would not be detected in the X-ray diffraction pattern of our sample since its main peaks²² overlap with other zircon¹³ and zirconia^{18,23} reflections.

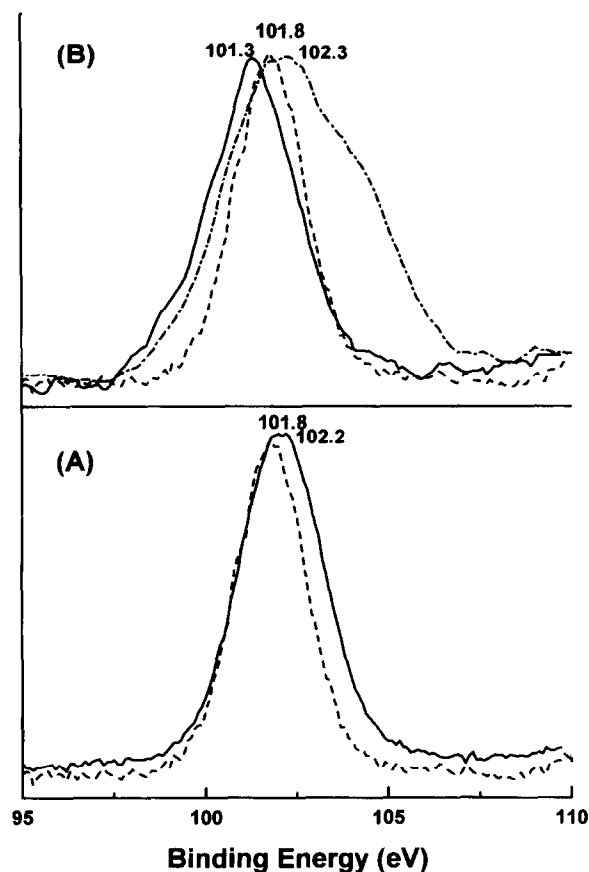


Fig. 7. Normalised Si_{2p} bands observed in the XPS spectra of: (A) sample Cr-A heated at 1300°C in the presence of NaF (—) and undoped zircon (---), (B) sample Co-A heated at 1100°C in the absence (—) and the presence of NaF (-·-·-), and undoped zircon (---).

3.2 Co-doped zircon

The composition of the Co-doped zircon samples (Co-A and Co-B) is shown in Table 3. In this case, the maximum Co amount incorporated to the zircon matrix (sample Co-A) was higher ($\text{Co}/\text{Zr}=0.127$) than that in Cr doped samples ($\text{Cr}/\text{Zr}=0.091$, Table 1), in agreement with the lower amount of hydration water contained in the starting Co salt.

As expected, the as-prepared Co doped zircon particles were also amorphous and presented the same shape and size distribution than those of the Cr doped samples [Fig. 1(A)], since they were prepared under similar experimental conditions. Their infrared spectrum displayed similar bands to that of sample Cr-A (Fig. 2) except those corresponding to the nitrate anions (1385 and 1355 cm^{-1}).

The DTA curve of sample Co-A (Fig. 8) showed two endothermic effects (135 and 900°C) and three exothermic ones (755 , 875 and 1050°C). The strong endothermic peak at 135°C which was accompanied by a weight loss of 27% (from 25 to 500°C) (Fig. 8), is mainly due to the release of water and adsorbed alcohols. On the basis of DTA, TGA and X-ray diffraction analyses conducted on $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (data not shown), this weight loss could also have a small contribution from the elimination of chlorine generated in the decomposition of the Co salt to form Co_3O_4 . Such analyses also suggested that the weak exothermic peak at 875°C and the weak endothermic one at 900°C observed for sample Co-A can be attributed to the reduction of Co_3O_4 to CoO , although these cobalt oxide phases were not observed by X-ray diffraction in our sample probably due to its low Co content. The weight loss (1.5%) detected at 900°C

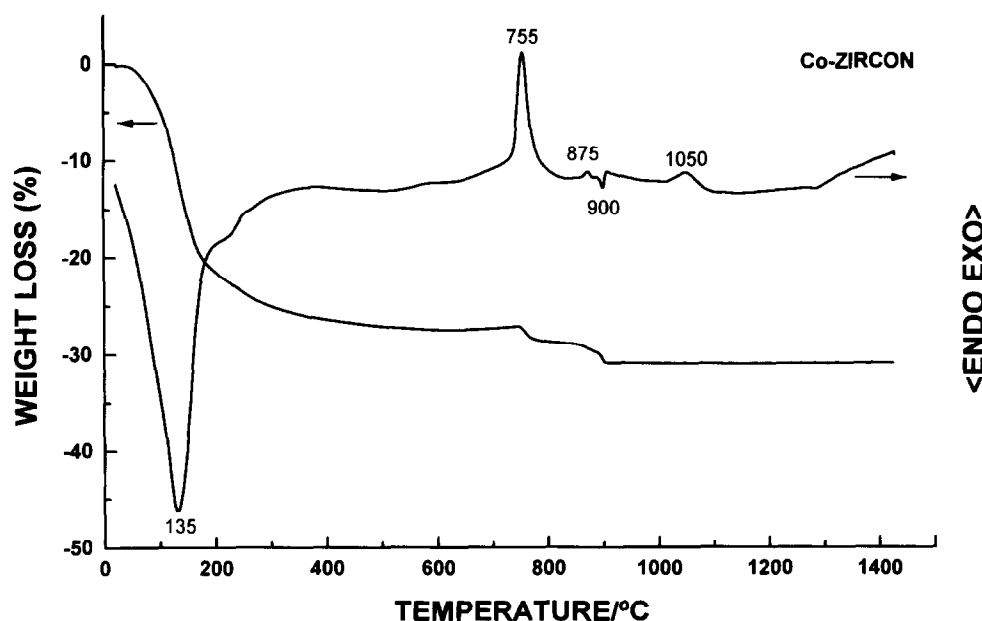


Fig. 8. Differential thermal and thermogravimetric analyses for sample Co-A.

would be in agreement with such an assignment. The exothermic effects at 755 and 1050°C correspond to the crystallisation of zirconia and zircon, respectively, as indicated by X-ray diffraction (Fig. 9). Thus, the sample remained amorphous after heating up to 700°C, whereas at 800°C, the observed pattern was consistent with metastable c-ZrO₂ or t-ZrO₂ with low crystallinity. It should be noted the crystallisation of zirconia occurred at lower temperature in this sample than in Cr doped (940°C, Fig. 3) or undoped zircon (905°C)¹² samples. This catalytic effect can be associated to the formation of a solid solution between some Co²⁺ ions and the c-ZrO₂ lattice, which as previously reported,²⁴ may take place at about 700°C. The onset of zircon formation was detected after calcination at 950°C (Fig. 8), at which temperature, the presence of metastable t-ZrO₂ was clearly indicated by the splitting of the X-ray diffraction peak at 2θ~35°. The complete formation of zircon was accomplished on calcination at 1100°C, after which

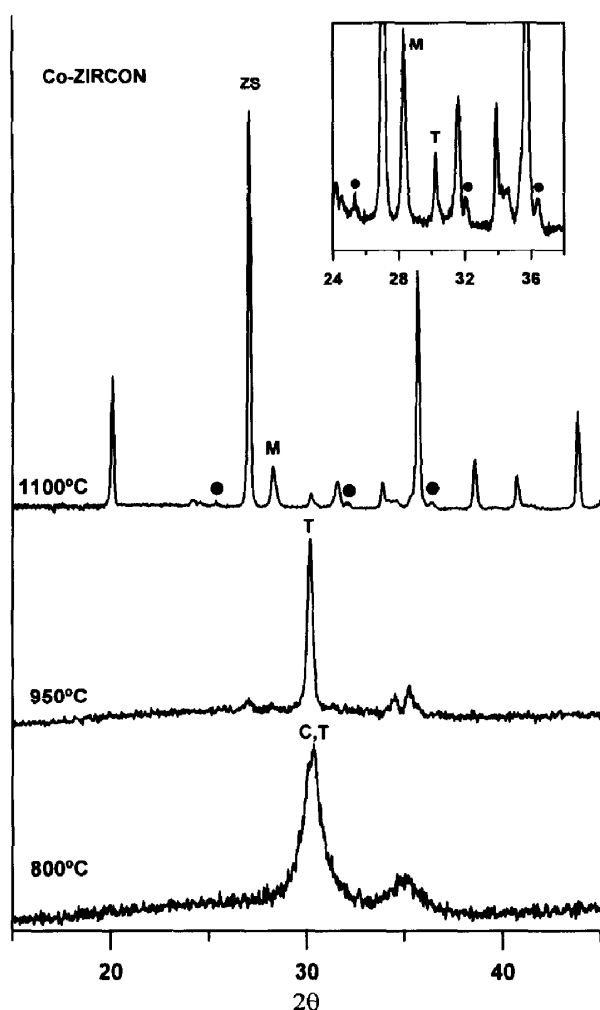


Fig. 9. X-ray diffraction patterns obtained for sample Co-A after heating at different temperatures. Symbols designating different kinds of phases: ZS = zircon, M = monoclinic zirconia, T = tetragonal zirconia, C = cubic zirconia and (●) Co₂SiO₄. The inset corresponds to a magnified region of the pattern of the sample heated at 1100°C for a better observation of the Co₂SiO₄ peaks.

the X-ray diffraction pattern of the sample also showed an excess of zirconia (tetragonal and monoclinic), as expected from the sample composition (Table 3), and very weak peaks that could be identified as Co₂SiO₄.²⁵ This treatment did not produce changes in particle shape, although a certain shrinkage (particle diameter ≤ 3.5 μm) was detected [Fig. 1(C)] as a consequence of the weight losses showed by TGA (Fig. 8). The process of zircon formation was also accelerated in this sample as compared with undoped zircon and Cr-doped samples (1500°C). This finding could be related to the presence of defects generated in the previously formed Co²⁺/c-ZrO₂ solid solution which would favour the diffusion process required for zircon formation,¹⁹ as it was suggested in the case of Fe doped zircon samples.²⁶ No further significant changes were detected by X-ray diffraction after heating sample Co-A at > 1100°C. This thermal behaviour was similar to that observed for sample Co-B, except that the exothermic peak due to the crystallisation of metastable zirconia appeared at higher temperature (815°C) in the latter in agreement with its lower Co content. In both samples, Co-A and Co-B, the Co content was not significantly modified with respect to the initial values after zircon formation (1100°C) (Table 3).

The *Lab* parameters of the Co doped zircon samples heated at 1100°C (Table 2) corresponded to a green colour with a different hue (higher *a* value) to that of Cr doped samples. The variation of the colour intensity (*L*) and hue (*a* and *b*) observed after changing the Co content from Co/Zr = 0.117 (sample Co-A) to Co/Zr = 0.063 (sample Co-B) was negligible.

Sample Co-A was also calcined in the presence of NaF to investigate the influence of this flux agent on the colour properties of Co-doped zircon pigments. X-ray diffraction (Fig. 10) showed that the addition of NaF slightly advanced the beginning of zircon formation (900°C), although it did not affect the temperature required to complete this process (1100°C). After zircon formation, a small amount of Co₂SiO₄ and an excess of unreacted zirconia higher than in the absence of NaF, were also detected. As expected, the particles lost their spherical shape when heated at 1100°C in the presence of the flux [Fig. 1(D)].

The colour observed for sample Co-A heated at 1100°C in the presence of NaF was different (blue) from that of the same sample heated in the absence of this flux (green) (Table 2), although the only Co phase identified by X-ray diffraction in both cases was Co₂SiO₄ (Figs 9 and 10), which is well known to show a pink violet colour. This seems to suggest the presence of additional Co phases in the pigments, which do not include any kind of solid

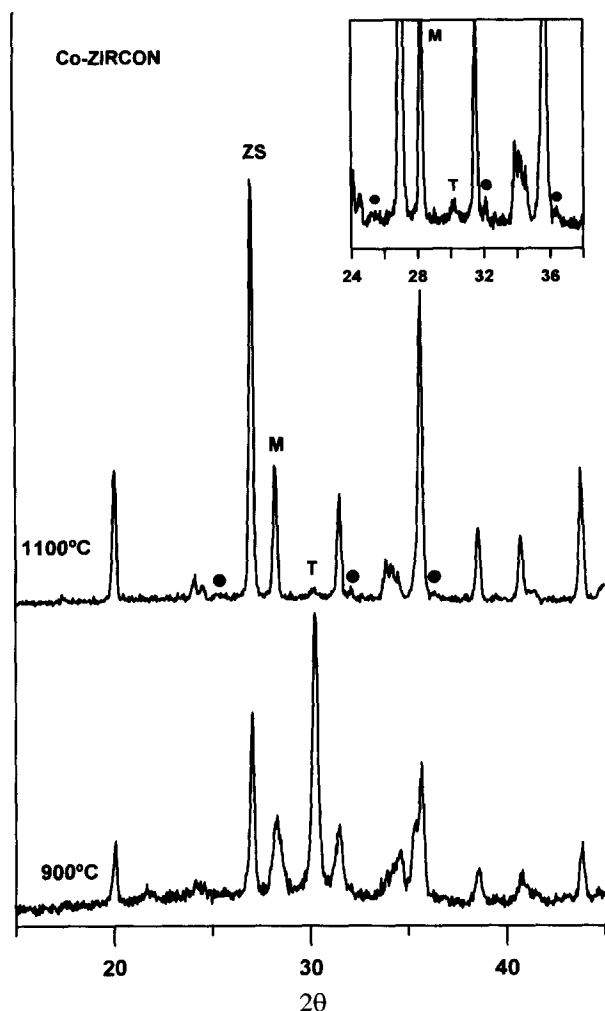


Fig. 10. X-ray diffraction patterns obtained for sample Co-A after heating at different temperatures in the presence of NaF. Symbols designating different kinds of phases: ZS = zircon, M = monoclinic zirconia, T = tetragonal zirconia, C = cubic zirconia and (●) Co_2SiO_4 . The inset corresponds to a magnified region of the pattern of the sample heated at 1100°C for a better observation of the Co_2SiO_4 peaks.

solutions between Co ions and the zircon lattice, since the unit cell parameters of zircon measured for sample Co-A heated at 1100°C either in the absence or in the presence of NaF showed similar values to those of undoped zircon. As expected from the presence of Co_2SiO_4 , the XPS spectrum of these two samples showed that the Si2p band was broader and shifted with respect to the same band in undoped zircon [Fig. 7(B)]. However, this

increase in band broadening was much higher in the sample prepared in the presence of the flux (blue), being even higher than in the Cr doped sample [Fig. 7(A)]. This behaviour indicates that the Si environment is more heterogeneous in the blue sample which along with the presence of Na detected by XPS (band at 1071 eV) and the lower zircon yield obtained in this case, could suggest the formation of a sodium cobalt (II) silicate, probably consisting of $\text{Na}_2\text{CoSiO}_4$, since this phase is blue²⁷ as the Co-doped zircon pigment. Notice that this sodium cobalt silicate could not be detected in our case by X-ray diffraction since their main d-spacing²⁷ is very close to those of some Co_2SiO_4 ²⁴ and t-ZrO_2 ¹⁸ peaks. In the case of the sample prepared in the absence of the flux, the green colour is tentatively associated to the presence of a small amount of unreacted CoO on the basis of the similitude of colour that this phase²⁸ and the pigment present. Finally, the Co/Zr ratio resulting from the intensity of the corresponding XPS bands for both samples were much higher than those obtained from ICP (Table 3) indicating that the Co phases are preferentially located in the outer layers of the Co doped zircon particles.

4 Summary

Cr-doped and Co-doped zircon powders consisting of spherical particles with broad size distribution ($0.1\text{--}5\ \mu\text{m}$) and different M/Zr atomic ratio (M = Cr or Co) have been prepared by hydrolysis of aerosols generated from mixtures of silicon and zirconium alkoxide and ethanolic solutions of chromium nitrate or cobalt chloride. These powders were calcined up to zircon crystallisation, which took place at 1500°C in Cr doped samples and at 1100°C in Co-doped samples. This catalytic effect of Co on zircon crystallisation was attributed to the previous formation of a solid solution between Co^{2+} and zirconia which would generate defects thus favouring the required diffusion process. It was also found that in Cr-doped samples, the whole amount of the Cr ions was volatilised during zircon formation (1500°C). The addition of

Table 3. Composition (Si/Zr and Co/Zr atomic ratios) of the Co-doped zircon samples as-prepared and after heating at 1100°C in the absence or the presence of NaF, measured by ICP. The composition obtained from the XPS spectra of sample Co-A heated at 1100°C in the presence or the absence of NaF, is also included

Samples	Treatment	(Si/Zr) _{ICP} (atomic)	(Co/Zr) _{ICP} (atomic)	(Si/Zr) _{XPS} (atomic)	(Co/Zr) _{XPS} (atomic)	(Na/Zr) _{XPS} (atomic)
Co-A	As-prepared	0.85	0.127			
Co-A	1100°C	0.85	0.117	1.12	0.19	
Co-A	NaF, 1100°C	0.87	0.108	2.27	0.38	1.0
Co-B	As-prepared	0.85	0.064			
Co-B	1100°C	0.84	0.063			
Co-B	NaF, 1100°C	0.88	0.060			

NaF to these powders lowered the temperature of zircon crystallisation to 1300°C, which considerably reduced the Cr losses. As a result, green pigments were obtained in which the colour was mainly due to Cr³⁺ ions located out of the zircon lattice, probably forming a sodium chromium (III) silicate. In Co-doped zircon powders, the addition of the flux had no effect on the temperature required for zircon formation (1100°C), however, it had influence on the resulting colour. Thus, although the only Co phase detected by X-ray diffraction either in the presence or the absence of NaF was cobalt silicate (Co₂SiO₄), in the absence of the flux, green pigments were obtained whereas in the presence of NaF a blue colour resulted. The green colour was attributed to the presence of a small amount of unreacted CoO, while the blue one was probably due to the formation of a small amount of a sodium cobalt (II) silicate.

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