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Hydrothermal synthesis of Co-doped willemite powders with controlled particle size and shape

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Abstract

The preparation of uniform elongated (axial ratio ~2) particles with mean length from 0.2 to 4.5 μm of Co-doped willemite (Zn_2SiO_4) blue pigments is reported. The procedure is based on the hydrothermal treatment at 225 °C for 5 h of the dispersions obtained by the precipitation with ammonia of Zn(II) and Co(II) sulphate aqueous solutions containing Ludox silica. The pH and Co concentration of the starting dispersions were varied to analyse the effects of these parameters on particle size, shape and composition. The crystallochemical, morphological and colour changes produced by the thermal treatment up to 1200 °C of the hydrothermally prepared powders were also studied by mainly using scanning electron microscopy, thermogravimetric analysis and optical and X-ray photoelectron spectroscopies.

Keywords: Powders-chemical preparation; Colour; Optical properties; Silicates; Zn_2SiO_4; Pigments; Hydrothermal methods

1. Introduction

Cobalt-doped willemite (Zn_2SiO_4) solid solutions, in which the Co(II) cations occupy the tetrahedral positions of Zn(II), find applications in the ceramic industry as blue pigments suitable for colouring glazes.[1] It is well known that for this application it is very important to control not only the powders' composition but also their particle size and shape, since these morphological parameters may strongly affect the optical properties (absorption and scattering cross-sections) of the pigment as well as their chemical (degree of solubility in glaze) and colloidal (degree of particle agglomeration) behaviour during enamelling.[2] In general, cobalt-willemite pigments are prepared by the conventional solid state method which involves the mechanical mixture of the metal oxide precursors, their calcination at high temperatures (1300 °C) and a final milling process to reduce and homogenise particle size.[3,4] This procedure usually yields powders with heterogeneous composition (some unreacted phases are still detected after calcination),[3,4] which consist of particles with irregular shape and broad size distribution. The preparation of this pigment by calcination of precursors prepared by a non-conventional method such as the sol–gel process has also been reported,[5] although the obtained particles showed similar heterogeneities (in composition and morphology) to those synthesised by the traditional method.

It has been shown that the hydrothermal treatment at 225 °C of aqueous solution containing Zn(II) salts and colloidal silica, precipitated by the addition of ammonia before aging, yielded willemite (Zn_2SiO_4) powders with rather homogeneous particle sizes and various morphologies.[6] The aim of this work is to explore the applicability of this method for the preparation of Co-doped willemite pigments with controlled particle size and shape. For this purpose, the effects of the pH and Co content of the solution were systematically varied in order to investigate the effects of these parameters on the composition and morphological features of the resulting powders. The thermal stability of the so obtained pigments was also studied to get

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information on the extent of the Co-willemite solid solution formation.

2. Experimental

2.1. Powders preparation

The Co-doped willemite samples were prepared by hydrothermal treatment at 225 °C for 5 h of the dispersions resulting from the precipitation with ammonia (NH_4OH, Fluka, 28%) of aqueous solutions containing 0.1 mol dm^{-3} zinc sulphate ($ZnSO_4 \cdot 7H_2O$, Aldrich, 98%), 0.05 mol dm^{-3} Ludox silica (Aldrich, 34%) and the desired concentration of cobalt(II) sulphate ($CoSO_4 \cdot 7H_2O$, Merck, 99%). The amount of ammonia added for precipitation was systematically varied to analyse the effect of pH on particle size and shape. The Co(II) content was also varied to optimize the colour of the resulting pigments. After aging, the samples were cooled to room temperature, filtered through Millipore membranes and the precipitated washed several times with doubly distilled water for purification. Finally, the so obtained powders were dried at 50 °C before analyses.

The samples were calcined in platinum crucibles for 2 h at different temperatures, which were reached at a heating rate of 10 °C min^{-1}.

2.2. Characterization

The particle morphology of the powders was examined by scanning electron microscopy (SEM) (JEOL JSM5400). The composition of the solids (Co/Si and Zn/Si mol ratio) was analyzed by X-ray fluorescence (XRF) (Siemens SRS3000).

The crystalline phases present in the solids were identified by X-ray diffraction (XRD) (Siemens D501). Thermogravimetric (TGA) analyses (Seiko EXSTAR 6000) were carried out in air at a heating rate of 10 °C min^{-1}.

Information on the oxidation state and distribution of the Co species in the pigments particles was obtained from the X-ray photoelectron spectra (XPS) of the samples measured with a VG Escalab apparatus (Model 220, West Sussex, UK) using the Mg Kα 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.

Optical absorption spectra were obtained from diffuse reflectance measurements for the powdered samples performed using a Praying Mantis accessory for a Varian spectrophotometer (Model Cary 500) and using $BaSO_4$ as a diffuse reflectance standard. The absorption coefficient (k) was obtained from absolute reflectance values (R) using the Kubelka–Munk equation.[7,8]

The colour of the pigments was evaluated according to the Commission Internationale de l'Eclairage (CIE) through $L^*a^*b^*$ parameters.[9] In this system, L^* is the colour lightness ($L^* = 0$ for black and $L^* = 100$ for white), a^* is the green (−)/red (+) axis, and b^* is the blue (−)/yellow (+) axis. These parameters were measured for an illuminant D 65, using a Dr. Lange colorimeter (Model LUCI 100) and a white tile ceramic (chromaticity coordinates: $x = 0.315$, $y = 0.335$) as standard reference. Before measurements, the calcined samples were gently ground in an agate mortar.

3. Results and discussion

The first Co-doped willemite sample (sample A) was prepared with a Co/Si atomic ratio = 0.1 by adding an ammonia amount (NH_4OH/Zn(II) mol ratio = 3.9) within the range (from 1.7 to 4.9) previously reported to obtain undoped willemite,[6] which gave a pH value after ammonia addition of 7.7 (Table 1). Under these conditions, rather uniform ellipsoidal particles with length about 2–2.7 μm and axial ratio ∼2 were produced (Fig. 1a), which according with X-ray diffraction consisted of single phase willemite[10] (Fig. 2). Chemical analysis (Table 1) showed that the Zn/Si atomic ratio of these particles was very similar (1.93) to the nominal value (2) whereas their Co content was much lower (Co/Si atomic ratio = 0.02) than that of the starting solutions (Co/Si = 0.1), indicating that at this pH most Co remained in solution after aging. Such a Co amount conferred a light blue colour to the sample, whose $L^*a^*b^*$ parameters are included in Table 1.

In order to investigate the effect of pH on the Co content, size and shape of the formed particles as well as on their colour, several experiments were conducted in which the amount of added ammonia was increased resulting the pH values shown in Table 1. It was observed that the pH increase gave rise to a decrease of particle size (length = 0.2–0.3 μm) as illustrated in Fig. 1b, for the sample prepared at pH 9.4 (sample B), and to a slight decrease of the Zn/Si ratio of the solids (Table 1), which may be ascribed to the amphoteric character of zinc hydroxide.[11] It was also found that

Table 1
Experimental Zn/Si and Co/Si atomic ratios, colour and $L^*a^*b^*$ parameters for the Co-doped willemite powders obtained at different pH values by hydrothermal treatment at 225 °C from the same raw cobalt (Co/Si = 0.1) and Zn (Zn/Si = 2) contents

	pH	$(Zn/Si)_{exp}$	$(Co/Si)_{exp}$	Colour	L^*	a^*	b^*
Sample A	7.7	1.93	0.02	Blue	74.8	−0.9	−15.1
	8.7	1.90	0.05	Blue	71.9	−1.7	−19.7
Sample B	9.4	1.85	0.09	Blue	64.4	−4.0	−23.7
	10.2	1.80	0.09	Bluish grey	60.1	−4.1	−17.1

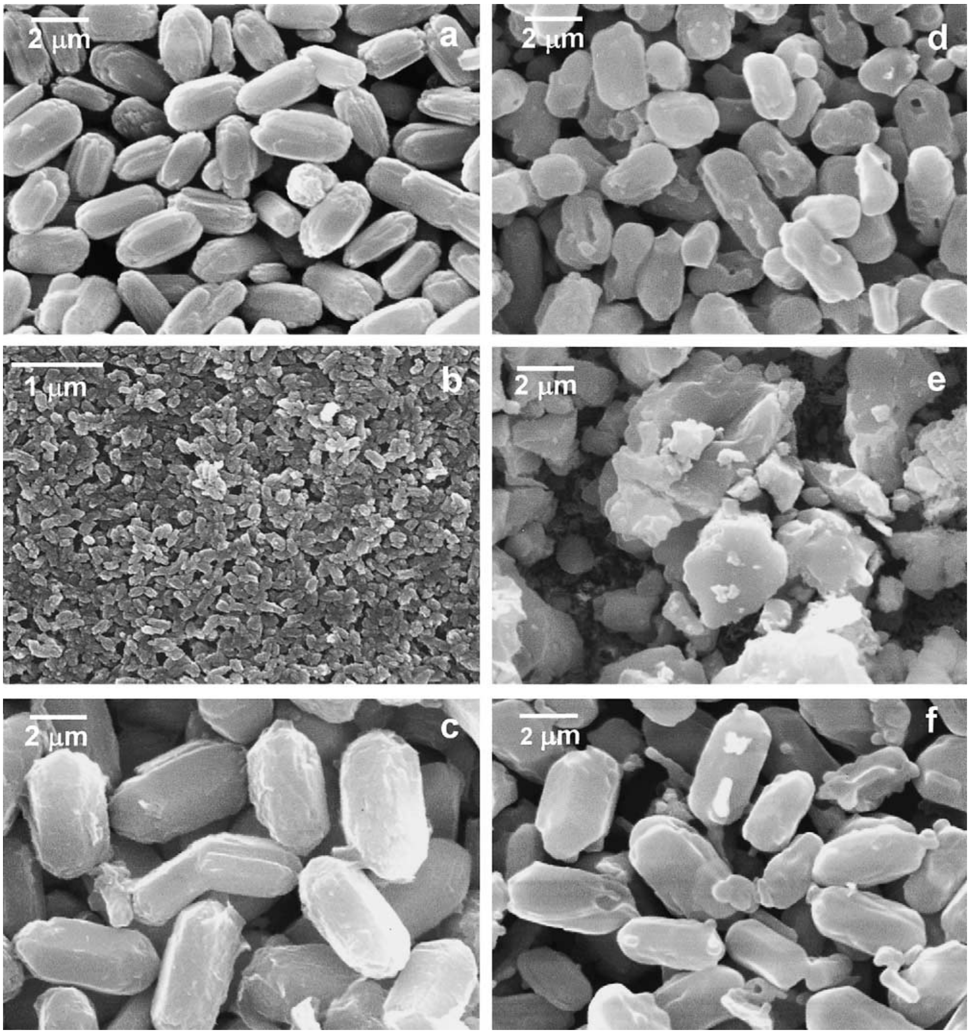

Fig. 1. SEM micrographs obtained for samples A, B and C (Tables 1 and 4), as prepared (a, b and c, respectively) and after heating for 2 h at 1200 °C (d, e and f, respectively).

the Co/Si atomic ratio in the willemite particles increased as increasing pH almost reaching (0.09) the nominal value (0.1) for a pH 9.4 (Table 1). This Co content increase was accompanied by the development of a bluer (lower b^*) and darker (lower L^*) colour, which was characterised by $L^* = 64.4$, $a^* = -4.0$ and $b^* = -23.7$, for the most Co concentrated sample (sample B) (Table 1). No changes in the Co content were observed when the pH was further increased from 9.4 to 10.2 (Table 1). However, the so obtained sample showed a bluish colour ($L^* = 60.1$, $a^* = -4.1$ and $b^* = -17.1$) with a grey hue (Table 1), due to the presence of a small amount of Co_3O_4 (black) in this sample as detected by X-ray diffraction (Fig. 2).

To investigate the formation of a solid solution between the Co cations and the willemite lattice in the hydrothermally prepared samples, we studied the stability of the blue colour on calcination, since other more appropriate methods such as the refinement of the willemite unit cell parameters are not useful in this case due to the similarity between the ionic radius of tetrahedral Co(II) (0.58 Å) and tetrahedral Zn(II) (0.60 Å) cations[12] and the low Co content. The evolution of the $L^*a^*b^*$ parameters for the bluer sample (sample B) on thermal treatment at increasing temperatures up to 1200 °C are shown in Table 2. As observed, the value of the blue parameter (b^*) shifted from −23.7 to 4.5 after heating at 500 °C, in agreement with the disappearance of the blue hue in the sample, which was slightly more achromatic (b^* approached to zero) when calcined at 800 °C. A blue colour characterised by $L^*a^*b^*$ parameters similar to those of the original sample appeared again after heating at 1000 °C, and

Table 2
Colour and $L^*a^*b^*$ parameters obtained for sample B (Table 1), as prepared and after heating for 2 h at different temperatures

Heat treatment (°C)	Colour	L^*	a^*	b^*
As prepared	Blue	64.4	−4.0	−23.7
500	Green	56.6	−6.6	4.5
800	Greenish grey	53.5	−4.2	−1.1
1000	Blue	64.7	−4.4	−23.6
1200	Blue	51.1	−1.5	−30.8

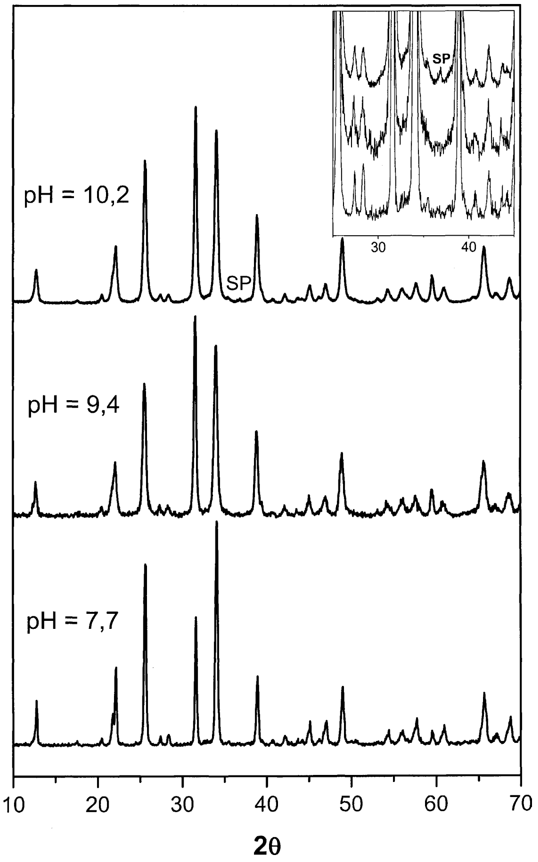

Fig. 2. X-ray diffraction patterns for the samples obtained at different pH values from the same raw cobalt (Co/Si = 0.1) and Zn (Zn/Si = 2) contents as described in Table 1. The main peak of the Co_3O_4 spinel, which can be better observed in the magnified patterns (inset) has been labelled with SP.

became bluer (b^* decreased) and stronger (L^* decreased) on a further calcination at 1200 °C. These colour changes, which were also observed for the other prepared samples, suggested variations in the oxidation state and/or atomic environment of the Co cations on heating, which were first investigated by optical absorption spectroscopy. We only give here a qualitative discussion of the effect of the thermal treatments on the distribution of the Co species in the samples based on the changes of the spectral features. It should be noted for an accurate quantitative determination of the concentration of the absorbing species, some sample factors such as the particle size or surface preparation must be thoroughly controlled, since they affect the intensity and width of the reflectance bands.

The optical absorption spectra in the NIR and VIS regions for sample B as prepared and after heating at different temperatures are given in Fig. 3. The two main absorption band triplets detected in the 1000–1850 nm and 500–700 nm spectral ranges for the as prepared sample coincide with those previously reported for Co^{2+} doped Zn_2SiO_4 single crystals[13] which were assigned to the $^4A_2 \rightarrow {}^4T_1$ (^4F) and $^4A_2 \rightarrow {}^4T_1$ (^4P) optical transitions of Co^{2+} ions in the distorted tetrahedral environment of the Zn^{2+} cation site of the willemite lattice. This finding suggests the formation of a Co(II)-willemite solid solution in our sample, which is responsible for the blue colour. In agreement with the colour change from blue to green, the spectrum recorded after heating at 500 °C displayed, in addition to the bands due to dissolved Co(II), a new band around 900–1000 nm, a shoulder around 600–700 nm and a very large absorption band edge in the blue region (<500 nm). These features can be attributed to the presence of CoO,[14] which would confer the green colour to the sample.[15] It should be noted that this phase could not be detected by X-ray diffraction probably due to its low concentration or its low crystallinity. After heating at 1200 °C, only the VIS and NIR triplets characteristic of dispersed Co^{2+} ions in tetrahedral coordination were detected (Fig. 3), which were much more intense than those in the original sample, in agreement with the deeper and bluer colour observed. Such behaviour seems to indicate that at least two kinds of Co species are present in the original blue Co-doped willemite particles. The appearance of the bands triplets due to tetrahedral Co(II) in all spectra irrespective of the heating temperature is a clear indication of the presence of Co(II) ions dissolved in the willemite lattice in the original sample. The identification of the other possible Co compounds is more difficult. They should be blue or show a low optical activity so that the blue colour due to the Co(II)-willemite solid solution is not appreciably modified. Therefore, the presence of CoO (green) and Co_3O_4 (black) must be disregarded. Such an unreacted Co compound might consist of α-$Co(OH)_2$ considering that the precipitates obtained just after the addition of ammonia to the starting solutions showed a pale pink colour as that corresponding to this Co hydroxide phase.[16] This pale pink shade should not affect the stronger blue hue due to dissolved Co(II) in a significant manner. This hydroxide phase dehydrates on heating from 25 to 200 °C,[17] in agreement with the TG analysis of this sample which showed a weight loss in this temperature range higher (1%) than an undoped willemite blank (0.5%) prepared by the same procedure (Fig. 4). As a consequence, CoO was formed in our case, which was detected after heating at 500 °C, as above stated. This finding is in contrast with other previous studies in which Co_3O_4 was reported as the main decomposition product,[17] suggesting a certain influence of the presence of willemite on this process. A CoO–Co_3O_4 transformation might occur on a further calcination at 800 °C, which would justify the grey hue observed after this treatment (Table 2) due to the presence of the black Co_3O_4 spinel. It is well known that this compound reduces to the Co monoxide in air atmosphere at ∼950 °C,[17] which would account for the weight loss (0.8%) detected between 800 and 1000 °C by TGA for this sample (Fig. 4). The Co(II) cations finally diffuse toward the willemite structure at ≥1000 °C, thus increasing the amount of Co(II) in solid solution and therefore yielding a bluer and more intense colour.

A further support to this interpretation is afforded by the variation of the Co/Si atomic ratio obtained from the intensity of the Co2p and Si2p peaks of the XPS spectra obtained for this pigment as a function of the heating temperature. As observed in Fig. 5, the value of this magnitude for the as

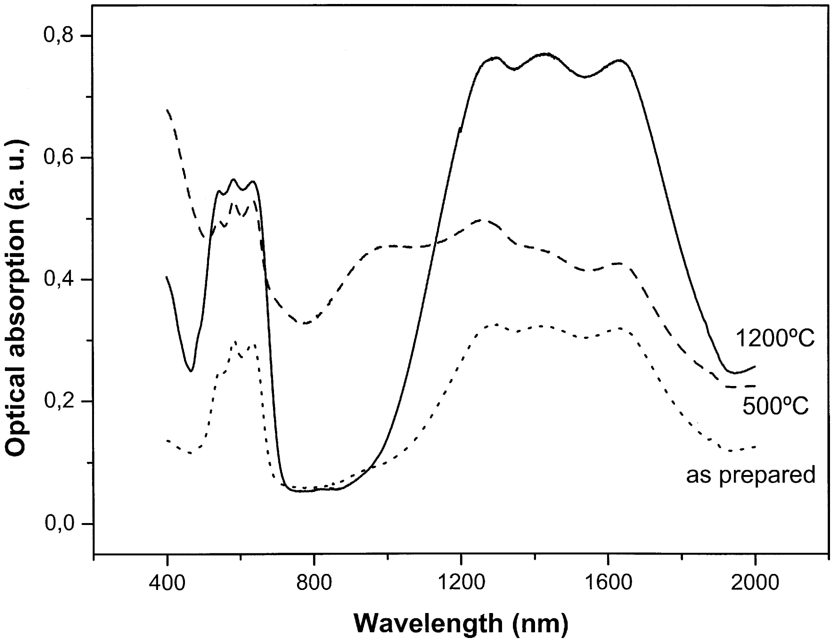

Fig. 3. Optical absorption spectra for sample B (Table 1), as prepared and after heating for 2 h at different temperatures.

prepared sample was much higher (0.23) than the value corresponding to the overall solid (0.09) (Table 1) indicating an enrichment of Co in the willemite particle outer layers, which should be mainly associated to the Co species undissolved in the willemite lattice. This Co/Si ratio progressively decreased on heating at increasing temperatures reaching a value of 0.1 at 1200 °C, confirming the progressive diffusion of the Co cations to the inner part of the willemite particles and therefore the progress in the solid solution formation. In addition, the intensity of the two satellites observed at lower binding energy than that of the Co2p bands in the Co2p XPS spectra of the sample as prepared and after heating and 1200 °C (Fig. 6), indicated that only Co(II) species are present in these samples,[18] as above suggested. It should be also noted that the Co2p spectrum of the sample heated at 500 °C was similar (Fig. 6), which would be in agreement with the formation of CoO on calcination at 500 °C.

In view of these results, the raw Co/Si atomic ratio was varied from 0.05 to 0.2 in order to evaluate the effects of this parameter on the amount of Co(II) incorporated to the

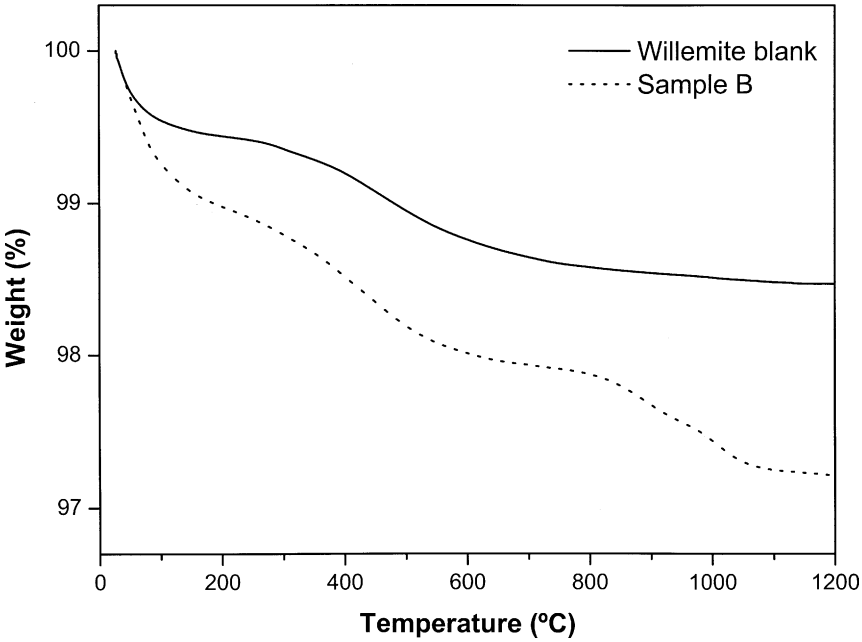

Fig. 4. TGA curve obtained for sample B (Table 1) and for an undoped willemite blank.

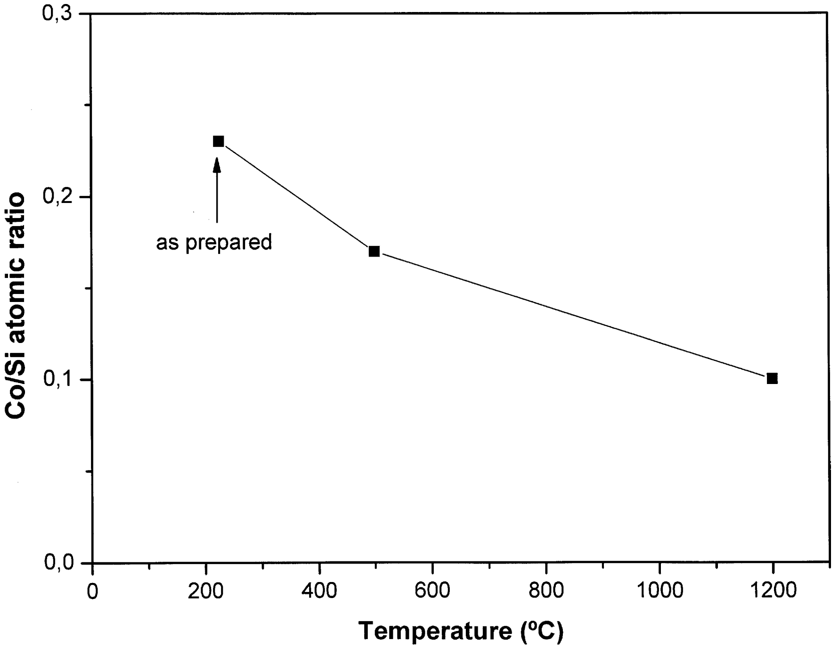

Fig. 5. Co/Si atomic ratio obtained from the XPS spectra for sample B (Table 1) as prepared and after heating for 2 h at different temperatures.

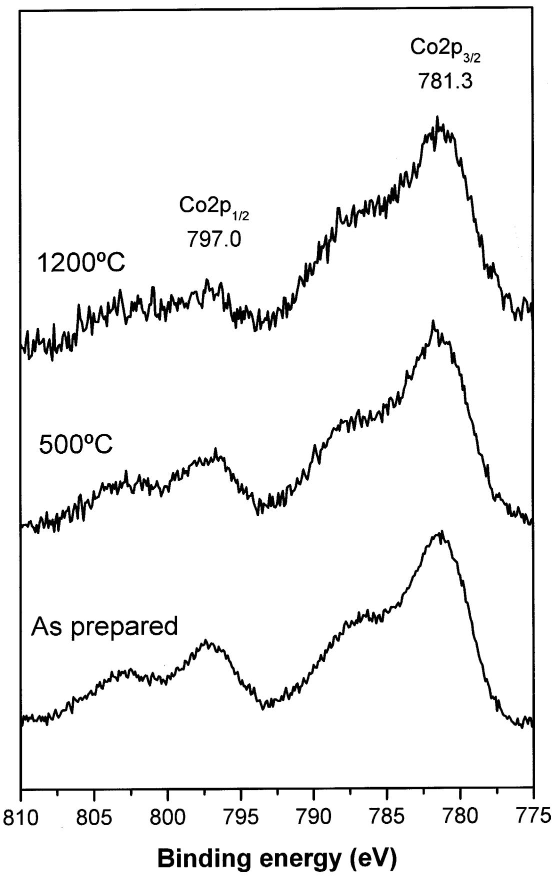

Fig. 6. Co2p XPS spectra for sample B (Table 1), as prepared and after heating for 2 h at different temperatures.

as prepared willemite particles and on the colour developed after calcination. These experiments were carried out for the optimum pH value (9.4) above determined (Table 1), i.e. the minimum pH at which the amount of Co precipitated was maximum. It was found that in all cases most of the initially added Co (≥80%) was incorporated to the precipitates and that the colour shifted from blue to grey as increasing the Co content (Table 3). Thus, the sample most diluted in Co (Co/Si atomic ratio = 0.04) showed a blue colour with similar hue (a^* and b^* parameters) (Table 3) than that having a Co/Si atomic ratio = 0.09 (Table 1), although it was lighter (higher L^*) due to its lower Co content. However, the increase of the Co amount from 0.09 to 0.12 gave a grey hue to the sample characterised by a b^* increase from −23.7 (Table 1) to −14.4 (Table 3). A further increase in the Co content (Co/Si = 0.16) yielded a dark grey sample with almost no blue shade (b^* = −3.7) (Table 3). As above mentioned, the appearance of the grey hue can be attributed to the presence of the Co_3O_4 spinel, detected by X-ray diffraction for this sample (Fig. 7). Finally, all these samples showed a blue colour after calcination at 1200 °C, irrespective of their Co content (Table 3). However, the sample containing a Co/Si atomic ratio of 0.09 was even bluer (lower $b^*$and L^*) (Table 2) than those having a higher Co content (Table 3) probably due to an incomplete solid solution formation in the later samples, which seems to indicate that the presence of the Co spinel in the as prepared samples unfavours Co diffusion.

It should be noted that all samples prepared at pH ~9.5 showed irregular particle size and shape after calcination at 1200 °C as a consequence of sintering as observed in Fig. 1e for the case of sample B. As expected, such a sintering process was much less important in samples with higher particles size

Table 3
Experimental Co/Si atomic ratio obtained for the Co-doped willemite samples prepared at pH 9.5 by hydrothermal treatment at 225 °C from different nominal Co contents and a nominal Zn/Si atomic ratio = 2

As prepared						1200 °C			
$(Co/Si)_{nom}$	$(Co/Si)_{exp}$	Colour	L^*	a^*	b^*	Colour	L^*	a^*	b^*
0.05	0.04	Blue	69.9	−2.2	−22.7	Blue	57.4	−5.6	−21.4
0.15	0.12	Bluish grey	55.5	−5.7	−14.4	Blue	48.6	−5.4	−19.2
0.20	0.16	Grey	46.5	−3.1	−3.7	Blue	46.7	−3.0	−21.9

The colour and $L^*a^*b^*$ parameters observed for these samples, as prepared and after heating for 2 h at 1200 °C are also included.

obtained at lower pH as is illustrated for sample A (Fig. 1d). Unfortunately, we have shown that under these conditions the amount of Co incorporated to the willemite samples is much lower than that added to the starting solutions, which therefore results in a much lighter blue colour (Table 1). Several experiments were finally conducted in order to achieve a Co content (Co/Si = 0.09) similar to that of the best pigment obtained at pH 9.5 (sample B, Table 2) in samples with larger particle sizes. For this purpose, the synthesis was carried out at lower pH (8.5) and the raw Co content was progressively increased. We found that a similar Co content (Co/Si atomic ratio = 0.08) to that of sample B could be obtained from a raw value of 0.2 (Table 4). However, the pigment obtained after calcination at 1200 °C showed a lighter colour (L^* = 60.5 and b^* = −19.5) (Table 4) than that observed for sample B (L^* = 51.1 and b^* = −30.8) (Table 1). A further increase of the raw Co/Si ratio to 0.3 resulted in uniform elongated particles with length ~4.5 μm and axial ratio ~2 (Fig. 1c), having a Co/Si mol ratio of 0.13 (sample C, Table 4). After heating this sample at 1200 °C, no important sintering was detected (Fig. 1f) and the $L^*a^*b^*$ parameters of this pigment (L^* = 55.4, a^* = −4.8 and b^* = −25.8) were more similar to those of the sample B.

Table 4
Experimental Co/Si atomic ratio obtained for the Co-doped willemite samples prepared at pH 8.5 by hydrothermal treatment at 225 °C from different nominal Co contents and a nominal Zn/Si mol ratio = 2

	$(Co/Si)_{nom}$	$(Co/Si)_{exp}$	Colour	L^*	a^*	b^*
Sample C	0.2	0.08	Blue	60.5	−7.9	−19.5
	0.3	0.13	Blue	55.4	−4.8	−25.8

The colour and $L^*a^*b^*$ parameters observed for these samples after heating for 2 h at 1200 °C are also included.

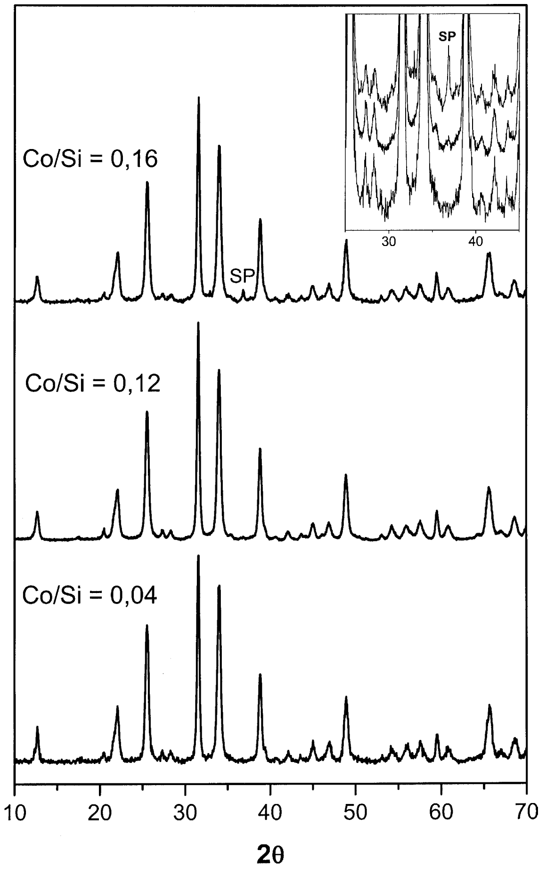

Fig. 7. X-ray diffraction patterns for the Co-doped willemite samples prepared at pH 9.5 with different Co contents as described in Table 3. The main peak of the Co_3O_4 spinel has been labelled with SP.

4. Conclusions

We have shown that uniform elongated (axial ratio ~2) particles with different mean size (length from 0.2 to 4.5 μm) and Co content (Co/Si atomic ratio ≤ 13) of Co-doped willemite (Zn_2SiO_4) blue pigments can be synthesised by hydrothermal treatment at 225 °C for 5 h of the dispersions obtained after the precipitation by the addition of ammonia of Zn(II) and Co(II) sulphate aqueous solutions containing Ludox silica, by an adequate control of pH and Co content. The amount of precipitated Co in relation to that initially added increased as increasing the pH of the dispersions, which also caused a decrease of particle size. The hydrothermally prepared blue samples consisted of a Co-willemite solid solution along with a small amount of an amorphous Co(II) compound, probably α-$Co(OH)_2$. On calcination up to 1200 °C, the later compound experimented several transformations (α-$Co(OH)_2$–CoO–Co_3O_4–CoO) after which, most Co(II) cations diffused toward the willemite lattice, thus resulting a deeper a more intense blue colour. After this treatment, only the pigments composed by the bigger particles (length ~4.5 μm) retained their original elongated shape and size.

Acknowledgements

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