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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