Journal of Solid State Chemistry 181 (2008) 2697–2704

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Impact of structural features on pigment properties of α-Fe_2O_3 haematite

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ARTICLE INFO

Article history:
Received 4 March 2008
Received in revised form
17 June 2008
Accepted 19 June 2008
Available online 1 July 2008

Keywords:
Red pigments
Haematite
X-ray diffraction
Mössbauer spectroscopy
Vis–NIR spectroscopy

ABSTRACT

Various α-Fe_2O_3 haematite samples were synthesized by precipitation routes (under standard or hydrothermal conditions) followed by thermal treatments under air. The trigonal distortion (C_{3v} point group) of the Fe^{3+} octahedral sites, which depends on the synthesis route and thermal treatment, was investigated by X-ray diffraction, Mössbauer spectroscopy and visible–near infrared (Vis–NIR) spectroscopy. The correlation between diffuse reflectance spectra and structural features of the haematite samples is reported and discussed herein. The slight increase of the average distortion of the Fe^{3+} octahedral sites, which depends on the annealing temperature of the precipitated sample, directly linked to the crystallite size, contrasts with the larger reduction of the sites distortion for the compound prepared by hydrothermal route due to the occurrence of hydroxyl groups substituted for O^{2-} anions as well as Fe^{3+} cationic vacancies. On a local point of view, as shown by Mössbauer spectroscopy, the Fe^{3+} octahedral sites distortion decreases from the centre towards the surface of the grains. Then the smaller the grain size, the lower the average site distortion. Finally, the reduction of the octahedral distortion was directly correlated to the two Fe–O charge transfer bands in the visible range and the colour of as-prepared haematites.

1. Introduction

α-Fe_2O_3 is an inorganic red pigment largely used for several industrial applications, for instance colouring paints, plastics and enamels, thanks to its low price, low toxicity, and high thermal and chemical stability [1,2]. Nevertheless, the dark-red colour of this mineral can strongly depend on precursors or synthesis routes [3]. In iron (III)-rich oxides such as haematite or spinels, the intense reddish-brown colour is due to an almost total absorption of the high-energy region of the visible spectrum [400–550 nm] and due to an important reflectivity in the low-energy part of the visible spectrum [550–800 nm] [4–6]. In a previous paper [7], visible–near infrared (Vis-NIR) absorption properties of haematite and spinel ferrites (AFe_2O_4) were correlated to their structural parameters. Even though numerous authors consider that all absorption bands in ferrites spinel or haematite result from Fe^{3+} 3*d* crystal field (CF) transitions [5,6,8,9], in our recent study the two main absorption edges (band-gaps) occurring in the visible range [400–800 nm] were attributed to ligand to metal $2p(O^{2-})\rightarrow 3d(Fe^{3+})$ charge transfers. C_{3v} trigonal distortion of $[FeO_6]$ octahedra in haematite leading to an additional *d* orbitals splitting is at the origin of this double charge transfer. Then, it seemed obvious that the octahedral sites distortion is directly linked to the energy positions of the two band-gaps as well as the two *d*–*d* intra-atomic transitions in Vis–NIR range. The aim of this work is to prepare various α-Fe_2O_3 compounds synthesized via different routes and/or with different thermal treatments and to characterize the octahedral site distortion of the various haematite compounds.

The crystal structures of these haematite samples have been studied by powder X-ay diffraction (Rietveld refinement). The local environments of the Fe^{3+} cations and the magnetic behaviour have been investigated by Mössbauer spectroscopy. Finally, the correlation of their Vis–NIR absorption spectra with their structural features will be presented.

2. Experimental details

2.1. Preparation

α-Fe_2O_3 compounds were prepared by a precipitation process in basic medium (i) or by hydrothermal route assisted by microwave (ii).

(i) A 7.2 M NH_4OH solution was added to a 0.5 M aqueous solution of iron nitrate ($Fe(NO_3)_3\cdot 9H_2O$; Aldrich) in order to precipitate metal ions with hydroxide form $Fe(OH)_3$. According to the iron Pourbaix diagram, iron hydroxide is stable in a large pH range, from 4.5 to 10. The working pH is 9.5. The

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doi:10.1016/j.jssc.2008.06.049

brown precipitate was dried overnight at 100 °C. Then, in order to obtain the final α-Fe_2O_3 oxide, a thermal treatment at various temperatures (400, 600, 800 °C) for 6 h under air was performed.

(ii) The microwave-assisted synthesis was performed with a microwave digestion system (Model MARS 5, CEM Corp.) operating at a frequency of 2.45 GHz. The α-Fe_2O_3 compound was prepared from a 0.05 M $Fe(NO_3)_3 \cdot 9H_2O$ solution prepared as in the standard precipitation process (50 mL), placed in an autoclave and then treated for 2 h at 160 °C. During the process, the maximum pressure reached was about 8 bars. The precipitate powder is directly obtained with a crystallized haematite structure. The powder is just dried a few hours under primary vacuum at 100 °C.

2.2. X-ray powder diffraction

X-ray diffraction (XRD) measurements were carried out on a PANalytical X'PERT PRO diffractometer, equipped with an X-celarator detector, using Co*K*α radiation because of the fluorescence of Fe created by Cu*K*α irradiation. XRD data were recorded with 2θ steps equal to 0.017°. Diffractograms have been refined with Rietveld refinement method [10,11] using FULLPROF® software [12].

2.3. Vis– NIR diffuse reflectance measurements

The UV–Vis–NIR diffuse reflectance spectra have been obtained using a VARIAN CARY 5000 spectrophotometer equipped with an integrating sphere coated with polytetrafluoroethylene (PTFE). Measurements were performed at room temperature for wavelengths varying from 200 up to 800 nm. HALON was used as white reference. $L^*a^*b^*$ colouring space parameters of the different samples have been calculated from diffuse reflectance curves $R(\lambda)$ and from the three relative sensibility curves: $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$ defined by the CIE-1964. In this system, L^* is the lightness axis [black (0) to white (100)], a^* is the green (<0) to red (>0) axis, and b^* is the blue (<0) to yellow (>0) axis. Hence, stronger the a^* value, better the red pigment for industrial applications.

2.4. Mössbauer spectroscopy

^{57}Fe Mössbauer measurements were performed at 293 K on a conventional constant acceleration spectrometer (HALDER) using rhodium matrix source. As the samples contain 8 mg natural iron per cm^3, the line broadening due to thickness of samples can be neglected.

The spectrum refinement was performed in two steps. Initially, the fitting of Mössbauer patterns as a series of Lorentzian profile peaks allowed the calculation of chemical shift (δ), amplitude and width (Γ) of each peak: thus, experimental hyperfine parameters were determined for the iron octahedral site. Then, spectra analysis was made in terms of hyperfine field distribution $P(H)$ using the Hesse and Rubartsch method [13]; Γ and δ were fixed at values determined in the first refinement. This method is often used for disordered compounds with a distribution of various environments characterized by line broadening and peak shapes. This method was notably used here because of the line broadening observed for the 400 °C annealed and the hydrothermal-route compounds, leading to a peak shape differing from a Lorentzian profile and so characteristic of disordered compounds.

3. Results and discussion

3.1. Structural description

The haematite phase α-Fe_2O_3 crystallizes in hexagonal symmetry with *R*-3*c* space group related to the corundum-type structure. The Fe^{3+} iron cations are distributed with an ordering of 2/3 of the octahedral sites (12*c* wickoff positions) within the framework of a hexagonal close-packed array of O^{2-} ions. The crystallographic network can be described as "chains" of octahedral sites directed along the *c*-axis and constituted by $[Fe_2O_9]$ dimers—two face-sharing Fe^{3+} octahedral sites—separated from each other by an empty octahedral site (Fig. 1A). Actually, the iron octahedral environment exhibits a non-centro-symmetric configuration with C_{3v} point symmetry. This trigonal distortion is induced by the strong Fe–Fe electrostatic repulsion into the face-sharing octahedral sites forming dimers. Without considering the metallic centre, the octahedral anionic cages already exhibit a C_{3v}-type distortion linked, on one hand, to the rhombohedral deformation of the unit cell (octahedral sites are flattened along the *c*-axis) but also because of the face-sharing octahedral site. Indeed, consequently to this configuration, only the two octahedral triangular faces perpendicular to the *c*-axis remain equilateral, but not equivalent: the area of the common face of two octahedra forming a dimer is smaller than that of the faces sharing an empty cationic site. At last, the cation is displaced from the geometric centre of the octahedral site along the *c*-axis towards the large equilateral face of the $[FeO_6]$ octahedra forming two sets of O–Fe bond distances: three short bonds between the ligands of the large equilateral face and the metallic centre and three long bonds between the ligands of the small equilateral face and the metallic centre (Fig. 1B). Hence, the longer O–Fe bonds are associated with the strongest Fe–Fe interaction in order to relax the constraints of the network and allow optimizing the Madelung energy.

3.2. Structural study

The structural parameters of each studied compound were evaluated by powder XRD. Whatever the synthesis route, a pure phase has been obtained with the corundum-type structure. The Rietveld refinement plots (experimental, theory and difference) of the "precipitated route haematites" obtained after heat treatment at 400 and 800 °C as well as the "hydrothermal route haematite" are presented in Figs. 2a–c, respectively, as illustration. Refined parameters, i.e. cell parameters, atomic positions, occupancies as

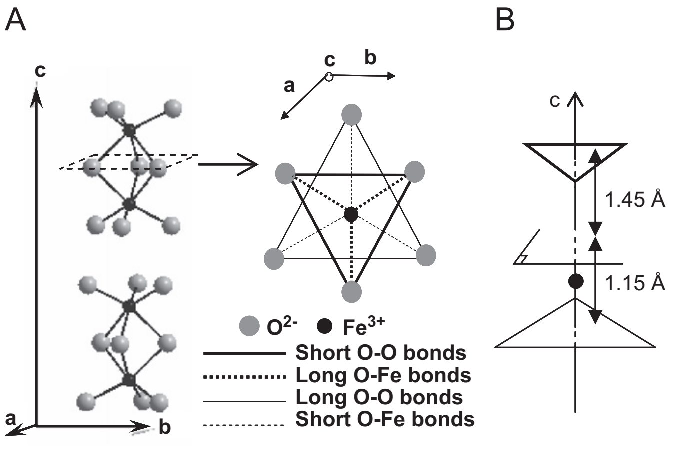

Fig. 1. Structural representations of haematite: chains of $[FeO_6]$ dimers along the *c*-axis (A) in corundum structure. Illustration of the "small" and the "large" equilateral triangles and the Fe^{3+} displacement from the octahedral site centre (B).