Journal of Solid State Chemistry 225 (2015) 256–260

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

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

Novel interpretation of the mean structure of feroxyhyte

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ARTICLE INFO

Article history:
Received 5 November 2014
Received in revised form
20 December 2014
Accepted 5 January 2015
Available online 12 January 2015

Keywords:
Feroxyhyte
Structure
XRD
Nanominerals

ABSTRACT

The structure of the iron oxyhydroxide called feroxyhyte (δ-FeOOH), which shows an elusive X-ray powder diffraction pattern, has been represented so far using models describing a mean structure based on the crystalline network of the iron(III) oxide hematite (α-Fe_2O_3). In this paper, a novel description of the mean structure of feroxyhyte is presented, which is based on the structure of the thermodynamically stable iron oxyhydroxide goethite. Starting from different local arrangements present in the goethite network, a mean structural model is determined which shows an X-ray powder diffraction pattern almost coincident with previous studies. This outcome enables to integrate the structure of feroxyhyte among those of other well characterized iron oxyhydroxides.

1. Introduction

The crystalline structure of some common materials is still controversial because of their elusive X-ray powder diffraction (XRPD) patterns. Examples are some iron oxyhydroxides, whose importance is related to their natural occurrence, to their properties and their role in controlling the formation and interconversion of iron oxides [1–5]. The elucidation of the structural features of these materials can have an impact on areas as diverse as environmental remediation through toxic ion adsorption on iron oxyhydroxides, optimization of oral therapy of iron deficiency, development of high surface area gas sensors, and design of nanostructured anode materials for alkaline batteries [6–10]. Specifically, various different interpretations of the XRPD pattern of feroxyhyte (also frequently indicated as feroxyhite), the mineral corresponding to δ-FeOOH synthetic iron compound, have been put forward, and debate remains about the exact nature of its crystalline structure [2,11–16]. A related compound δ′-FeOOH also exists in nature, and the XRPD patterns of this natural material and of synthetic δ-FeOOH show differences depending on the materials origin or preparation route, respectively [13].

The determination of the feroxyhyte structure appears rather complex (see details in Ref. [16]). Observations from electron microscopy have suggested that this oxyhydroxide is made of poorly crystallized nanometric material with coherent scattering domains (CSDs) of a few tens of nanometers [13]. Also its chemical composition is somewhat uncertain, most probably as a result of hydrolysis phenomena at the nanometric granule surfaces and of the possible presence of multiple phases [16]. The feroxyhyte XRPD patterns reported in the literature [2,13,16] show a diffuse background with a broad band at low angles and four discrete peaks, corresponding to $d(h\,k\,l)$ values around 2.55, 2.23, 1.70 and 1.47 Å. These well-defined Bragg peaks are peculiar to this material when compared to other nanocrystalline iron oxyhydroxide allotropic phases (the so called 2 line and 6 line ferrihydrites), which present different numbers of peaks (Ref. [1] p. 176).

Because of the poor crystallinity, a reasonable model for feroxyhyte can only be determined putting together different information. Not only the proposed unit cell and atom coordinates should be able to fit the experimental XRPD pattern, but the model should be also consistent with observations and experimental data from other techniques, e.g. Extended X-ray Absorption Spectroscopy (EXAFS). Moreover, the experimental peak broadening and the low angle features should be reproduced by introducing additional effects such as average size and shape distribution of the CSDs, occurrence of stacking faults, strain and stress within the CSDs, uncertainty in the composition, and presence of additional phases. These issues have been addressed by Drits et al. who proposed a crystalline model for δ-FeOOH with definite atom coordinates and site occupancy factors (SOFs). In this crystalline structure, which is an elaboration of the original model by Francombe et al. [11] and Patrat et al. [14], the smallest structural unit is described as trigonal, with a network consisting of anionic ABAB hexagonal layers and iron atoms set in the octahedral sites. Their final result, which includes some modifying effects to

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http://dx.doi.org/10.1016/j.jssc.2015.01.003
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improve the agreement with the experimental XRPD pattern, is an excellent reproduction of the experimental XRPD pattern (see Fig. 7 of Ref. [16]).

From this point of view, it does not seem necessary to revise the above mentioned model, which however as a major drawback does not share the common features of other Fe iron oxyhydroxides.

It should be pointed out that the smallest structural unit of the Drits model depicts a mean structure, as the presence of Fe atoms with occupancies of 1/4 would implies the definition of a larger cell; besides, O atoms from O^{2-} and OH^{-} are set in equivalent positions, so that they come out crystallographically undistinguishable. Basically, the entire structure appears quite similar to that of hematite, α-Fe_2O_3 [17], in which the coordination octahedra of iron atoms are connected by corners, edges and faces, with a ternary axis along the *c*-direction.

On the other hand, the networks of goethite [18], lepidocrocite [19] and akaganéite [20] do not present the ternary axis and any face sharing of octahedra. Besides, the face sharing occurrence predicted by the Drits model is in contrast with magnetic measurement results [12].

The aim of this paper is to find a way to integrate the structure of feroxyhyte among those of other well characterized iron oxyhydroxides showing that a mean structure for feroxyhyte, which comes out very similar to that proposed by Drits et al., can be derived using some network features typical of the goethite structure. It is demonstrated that a mean model can be built up by using a number of local structures sharing characteristics common to the other iron oxyhydroxides, that is to say that a mean structure very similar to that proposed by Drits can be obtained by taking into account local structures different from the one proposed by Drits.

2. Experimental

Feroxyhyte was prepared according to Carlson and Schwertmann [13] by adding dropwise a 5 M KOH solution to 100 mL of a 0.1 M solution of $FeCl_2 \cdot 4H_2O$, under constant stirring, until pH=8 was reached; then 15 mL of H_2O_2 (30%) were rapidly added. To improve flocculation, 5 M KOH solution was added again dropwise until pH=8. The product was centrifuged, washed and dried in an oven at 45 °C for 18 h, and characterized by XRPD.

XRPD data were collected on a Panalytical Empyrean diffractometer using a Cu*K*α tube operating at 40 kV and 40 mA, coupled with a graphite monochromator on the diffracted beam and a X-Celerator linear detector, scanning over an angular range from $10^\circ(2\theta)$ to $80^\circ(2\theta)$ with a step size of $0.05^\circ(2\theta)$ and a total acquisition time of 38 h. The sample holder was submitted to a spinning speed of 1 Hz in order to reduce any preferred orientation.

3. Relevant structural details

3.1. Mean structural model of feroxyhyte

The XRPD pattern of the synthetized feroxyhyte which is shown in Fig. 1 is in agreement with the experimental patterns available in the literature [2,13,16].

Detailed descriptions of the mean structure of feroxyhyte are given by Ref. [14] and by Ref. [16]. The basic idea is that feroxyhyte has a hematite-type structure defective with regard to Fe, that is, each unit cell contains $Fe_9O_9(OH)_9$ instead of $Fe_{12}O_{18}$. Therefore, a distribution of Fe atoms along the ternary axis of the feroxyhyte unit cell is defined so that the Fe–Fe distance set along the *c* axis comes out equal to 2.88 Å, typical value for face sharing octahedra; however, the *c* repetition period of feroxyhyte is 4.56 Å (about 1/3 of that of hematite), which implies a distance of 2.3 Å between the centers of the coordination octahedra at 0,0,0 and 0,0,1/2. The anionic network is described as that of hematite and the three Fe chains which in hematite run along the ternary axis are shifted so that the longer Fe–Fe distances (among chains) turn out in agreement with EXAFS results. Details of the proposed unit cell are reported in Table 1.

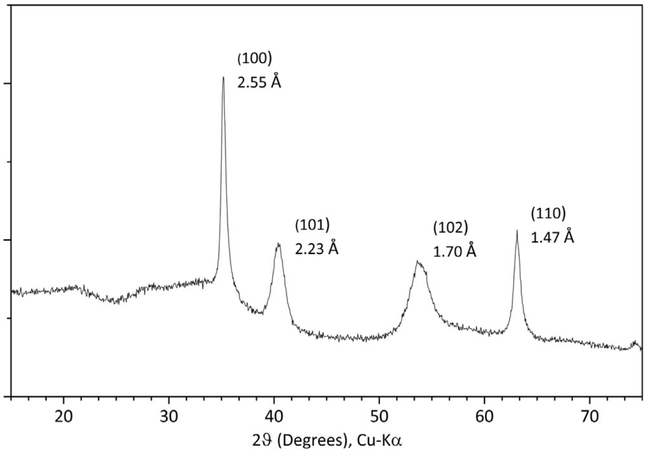

Fig. 1. Experimental XRPD pattern of feroxyhyte.

Table 1
Atomic coordinates and site occupancy factors (SOF) for feroxyhyte unit cell given by Drits et al. [16]; $a=2.947$ Å, $c=4.56$ Å, S.G. *P*-3*m*1 (N. 164).

Atom	Site	*x*	*y*	*z*	SOF
Fe1	2c	0	0	0.065	0.25
Fe2	2c	0	0	0.435	0.25
O	2d	1/3	2/3	0.25	1

Some observations on Drits model seem here appropriate: (i) the structural equivalence of O^{2-} and OH^{-} can be accepted only in a mean structure, certainly not in a short or medium range structural model; and (ii) the shortest Fe–Fe distance of 2.88 Å is typical of Fe atoms located inside face sharing coordination octahedra. In particular, concerning point (i) the analysis of the literature on the structure of oxy-hydroxides shows overwhelming examples of the orienting effects of the OH^{-} group, which significantly affects packing [21]: Fe–O^{2-} and Fe–OH^{-} distances differ up to 0.1–0.2 Å values, giving rise to covalent interactions Fe–O^{2-} along the octahedral chains (directional bonds) and to electrostatic interactions in O^{2-}–HO^{-} hydrogen bonds between chains. Concerning ii, it should be taken into account that the repetition of the feroxyhyte unit cell ($c=4.56$ Å) along the *z* direction up to the hematite cell dimension ($c=13.772$ Å) implies the presence of only three Fe atoms (compared to the four Fe atoms along the ternary axis of hematite), which does not allow pairs of octahedra to be formed using up all the Fe atoms. Overall, all the above considerations point out that the model by Drits et al. is representing a mean structural model, as also implied in the same paper.

3.2. Novel feroxyhyte structural model interpretation

In our attempt to find a possible structural reference for a novel description of the structure of feroxyhyte we left out poorly crystalline materials such as ferrihydrites, and instead we considered the known structures of common iron oxy-hydroxides such as goethite, lepidocrocite and akaganéite. Each of these