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Anisotropic X-ray peak broadening and twin formation in hematite derived from natural and synthetic goethite

L. Löffler, W. Mader *

Universitat Bonn, Institut für Anorganische Chemie der Universität Bonn, Römerstrasse 164, D 53117 Bonn, Germany

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Abstract

Hematite obtained by dehydration of goethite at temperatures between 250 °C and 1000 °C was studied by X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and differential scanning calorimetry (DSC). Starting materials were goethite mineral and synthetic goethite, respectively. Hematite derived from natural goethite shows narrow X-ray diffraction peak widths with little variation between the reflections and marginal dependence on dehydration temperature. TEM imaging reveals the existence of large (>200 nm) hematite twin domains, which is attributed to slow dehydration kinetics associated with the formation of few hematite nuclei.

In contrast, strong anisotropic X-ray diffraction peak broadening is observed for hematite obtained from synthetic needle-shaped goethite at low dehydration temperatures ($T < 500\,^{\circ}$C); the peak widths significantly decrease with increasing dehydration temperature. Anisotropic peak broadening is observed only for reflections, which structure factors are dominated by the iron sub-lattice and which are not common to both twin variants of hematite. In hematite producing the strong anisotropic X-ray peak broadening extremely small twin domains with sizes ranging from 5 nm to 10 nm could be imaged by high-resolution TEM. Further, DSC and TEM observations indicate that dehydration kinetics in coarse-grained natural goethite and fine-grained synthetic goethite differ considerably. It is concluded that during the dehydration reaction taking place at the large surface area of synthetic goethite crystals hematite nuclei with ambient orientation are rapidly formed, thereby creating a finely twinned dehydration product. The experimental results prove that XRD peak broadening is mainly caused by fine twinning.

Keywords: Goethite; Fe_2O_3; Electron microscopy

1. Introduction

Iron oxides and hydroxides, particularly goethite, hematite and magnetite, are ceramic materials of utmost industrial importance, e.g. as colour pigments for inorganic dyes and as magnetic pigments in recording media. For ferric pigments, the dehydration of goethite (G), α-FeOOH, into water-free hematite (H), α-Fe_2O_3, is one of the key steps in the production. With respect to the reaction process, much attention has been paid to two problems since the 1950s: (i) the mechanism of transformation and (ii) the non-uniform broadening of X-ray diffraction peaks of the resulting hematite. In connection with the latter phenomenon, the microstructure of hematite as a function of dehydration temperature was extensively studied.

Porosity is one of the characteristics observed as a result of the loss of water according to the dehydration reaction:

$$2FeO(OH) \rightarrow Fe_2O_3 + H_2O \uparrow .$$

In low temperature dehydration products, Lima-de-Faria[1] and other authors observed a very regular pore system parallel to the basal plane of hematite consisting of lamellae with a periodicity length of 3–4 nm.[2–5] The pores serve as diffusion paths for the water during the reaction. Dehydration at higher temperatures leads to a decrease in the regularity of the pore system.[4,6,7] There is great technological interest in generating nanometer-sized domains of magnetite for magnetic recording media.

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* Corresponding author.
E-mail address: mader@uni-bonn.de (W. Mader).

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The goethite to hematite transformation was first studied by Goldsztaub[8] in the 1930s showing that the transformation is topotactic with the lattice planes being parallel:

$$(100)_G||(00.1)_H \quad \text{and} \quad (010)_G||(11.0)_H.$$

The hexagonal closed-packed oxygen stacking sequence, ABABAB, is preserved during the reaction. Hence, apart from the loss of water, the dehydration reaction requires little rearrangement of iron ions. Thereby, two twin orientations of the hematite crystal may result, which differ only in the iron sub-lattice, i.e. in the stacking sequence of the iron honeycomb layers on positions γ, γ', γ'' within the oxygen layers A and B. The two possible stacking sequences are:

(1) $A\gamma B\gamma' A\gamma'' B\gamma A\gamma' B\gamma''$,
(2) $A\gamma B\gamma'' A\gamma' B\gamma A\gamma'' B\gamma'$.

Since none of the two stacking sequences is preferred, the resulting hematite will consist of a twinned microstructure with two twin variants (1) and (2). The variants can be transformed to each other by a mirror operation at the basal plane of hematite (“basal” twins).[1,9]

Upon characterization of the dehydration product by X-ray diffraction (XRD), it was observed already in the 1950s that certain peaks in XRD powder spectra are unusually broadened.[10] The reflections of type (01.2), (10.4), (11.6), (02.4), (01.8) and (21.4) are much broader than the reflections of type (11.0), (11.3) and (30.0). This non-uniform peak broadening is observed exclusively in low-temperature dehydration products, i.e. $T < 600\,^\circ\mathrm{C}$. In principle, three different approaches have been made since then to explain the diffraction peak broadening: (i) the system of regularly aligned pore lamellae has been identified to produce satellite reflections in electron diffraction,[1,11] and it was suggested to cause the peak broadening also in recent studies.[12] (ii) The fine twinning of the dehydration product may be a further origin of the peak broadening,[13] and this has been shown recently on corundum derived from dehydrated diaspore—the closely related oxide–hydroxide system of aluminium with identical structures of the oxyhydroxide and the oxide.[14] (iii) The majority of the studies was performed on hematite derived from synthetic goethite which consists of fine needles with few nanometres in thickness, and therefore, the shape anisotropy of the crystals may be the origin of the peak broadening.[12]

In the present study, powder XRD and transmission electron microscopy (TEM) are applied to relate the peak broadening of goethite-derived hematite to the microstructure of the material. In order to examine crystal size effects, the dehydration product derived from synthetic goethite powders and large-grained goethite mineral specimens are compared in detail, including differential scanning calorimetry (DSC). Our experimental results shed some fresh light on the processes involved in the dehydration of goethite, and we shall be able to discuss and explain the non-uniform peak broadening in connection with the observed microstructure. Furthermore, the dehydration and the product’s microstructure can be shown to critically depend on the crystallinity of the parent phase.

2. Experimental

The dehydration experiments were conducted on two different samples: (i) natural goethite from Lost Withiel, Cornwall, England, and (ii) fine synthetic goethite powder produced by Bayer (“Bayferrox AC 5104”). Prior to thermal treatment the mineral samples were crushed to a powder (crystal size $\sim 1\,\mu\mathrm{m}$). For each sample, different reaction temperatures and times were chosen, as listed in Table 1. The samples were directly placed into the hot tube furnace, and were quickly removed after the reaction time. This was done to avoid modification of the product by the heating or cooling procedure.

2.1. X-ray diffraction

In order to minimize intensity modification due the $(010)_G$ crystal texture, which is common for natural goethite samples, the XRD powder scans of the crushed mineral samples were recorded in Debye–Scherrer geometry. The data were collected on a STOE powder diffractometer Stadi P, which was equipped with a position sensitive detector (PSD, angle resolution: 0.03°) and operated with monochromatic Co $K\alpha 1$ radiation. For the hematite samples obtained from synthetic goethite material, a Philips PDM 3000 (Co $K\alpha 1,2$ radiation) with Bragg-Brentano geometry was used. All powder XRD scans were evaluated using DIFFRAKT 97, which allowed profile fitting with high accuracy for each of the reflections.

2.2. TEM studies

For TEM studies, the natural goethite crystals were cut into blocks of 6 mm × 1.8 mm × 0.3 mm. Since the starting material consisted of several smaller crystals of various ori-

Table 1
Heat treatment (temperature and time) of powder samples prepared for the XRD studies

Temperature (°C)	G_{nat} (h)	G_{syn} (h)	G_{nat}, TEM
240	–	–	100 d[a]
250	–	100	–
270	24	20	1 d[a]
300	18	16	90 min[a]
350	1	1	7 min[a]
400	1	1	1 min[a]
500	1	1	–
600	1	1	1 h
700	1	1	1 h
800	1	1	1 h
1000	1	1	1 h

G_{nat}: natural goethite sample, crushed to powder; G_{syn}: synthetic finely grained goethite; G_{nat}, TEM: samples prepared for TEM investigations.

[a] Indicates only partial transformation to hematite.

entations, which penetrated each other, only few cuts along defined crystallographic planes were possible.

The specimens were annealed at constant temperatures ranging from 250 °C up to 1000 °C for different times, which led to partial or complete transformation into hematite, respectively. Heating parameters are given in Table 1. After heating rapid cooling to room temperature was realized by dropping the blocks on a cold metal plate. The cut specimen pieces were glued together with their large faces and were embedded in a corundum tube. TEM specimens were prepared following standard techniques including cutting, grinding, dimple grinding and ion beam thinning. The TEM studies were performed on electron microscopes type Philips CM30ST and type Philips CM300UT, both operated at 300 kV.

2.3. Differential scanning calorimetry

The DSC studies (DSC 404, Netzsch, Germany) were carried out with samples in platinum crucibles between room temperature and 1000 °C at a heating rate of 15 °C/min. Enthalpy effects were carefully calibrated with respect to polymorphous transformations of pure compounds such as $KClO_4$ and Ag_2SO_4.

3. Results

3.1. X-ray diffraction

3.1.1. Natural goethite

A set of four powder diffraction scans of hematite is given in Fig. 1, obtained from natural goethite after dehydration at 270 °C, 400 °C, 600 °C and 1000 °C, respectively. The full width at half maximum (FWHM) of the eight strongest peaks was measured for all spectra. From powder XRD theory, it is known that peak width depends on the Bragg angle by $1/\cos\theta$ for isotropic materials. Thus, for better comparison, the peak widths are plotted in terms of $\mathrm{FWHM}\cdot\cos\theta$ versus dehydration temperature as shown in Fig. 2. The FWHM values were determined by multiple fitting with an accuracy of 0.015°. Up to 800 °C, all reflections produce rather sharp peaks with similar FWHMs of approximately 0.25°. In materials dehydrated between 800 °C and 1000 °C, a slight decrease in peak width is detectable for all observed reflections which is due to coarsening of powder grains.

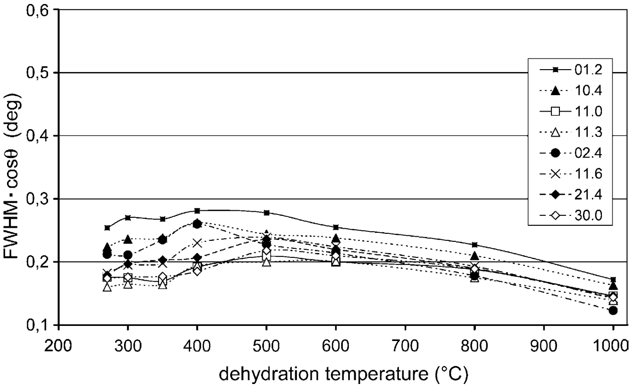

Fig. 2. Full width at half maximum height (FWHM, representation as $\mathrm{FWHM}\cdot\cos\theta$) of eight dominant hematite reflections obtained from natural goethite as a function of dehydration temperature.

3.1.2. Synthetic goethite

Fig. 3 shows a set of XRD scans of hematite obtained from synthetic goethite powder after dehydration. Although the dehydration parameters are the same as for the natural sample, the scans look very different. After low-temperature dehydration, e.g. at 270 °C, certain peaks are extremely broadened; for some of the diffraction lines FWHM values in excess of 1° are observed. This result is in contrast to the sharp peaks obtained from the natural goethite sample, however, it is in good agreement with earlier studies on synthetic goethite.[2,6] The values of $\mathrm{FWHM}\cdot\cos\theta$ versus dehydration temperature are shown in Fig. 4, estimated errors in the FWHM measurements are <0.04°.

Based on peak widths measured after dehydration at temperatures <400 °C (Fig. 4), the XRD reflections may be classified in three groups:

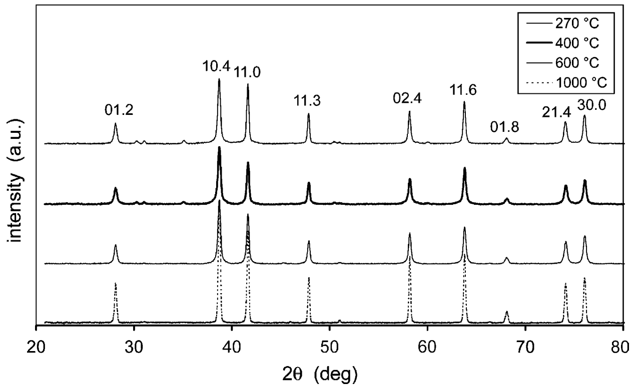

Fig. 1. XRD powder scans of hematite obtained from crushed natural goethite samples after dehydration at 270 °C, 400 °C, 600 °C and 1000 °C.

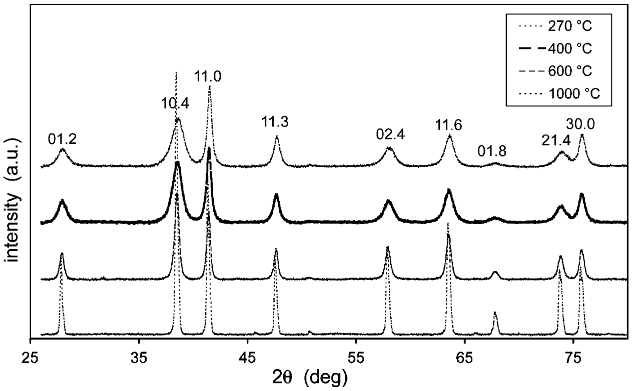

Fig. 3. XRD powder scans of hematite obtained after dehydration of synthetic goethite at 270 °C, 400 °C, 600 °C and 1000 °C.

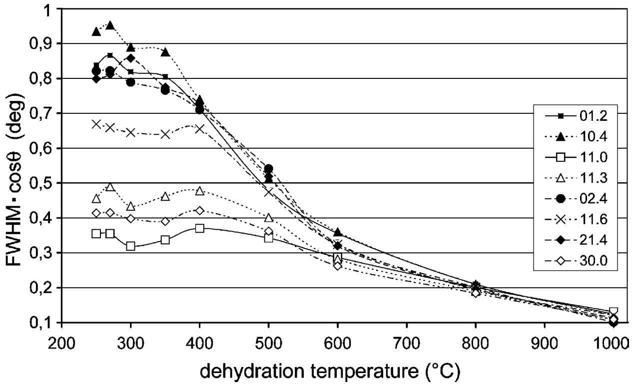

Fig. 4. Full width at half maximum height (FWHM, representation as FWHM·cos θ) of eight dominant hematite reflections obtained from synthetic goethite as a function of dehydration temperature.

- Group I includes the narrow peaks of the reflections (11.0), (11.3) and (30.0), for which the peak widths are 0.3–0.5°. These reflections are of type (*hk.l*) with $l = 0$ or $l = 3n$ (n = odd).
- Group II comprises the extremely broadened reflections (01.2), (10.4), (02.4), and (21.4), with peak widths (FWHM·cos θ) between 0.8° and 1°. The reflections are of type $l = 2n$ ($n \neq 0$ and $n \neq$ multiple of 3).
- The (11.6) reflection exhibits peak widths of approximately 0.65° which makes it belong to a separate group ($l = 6n$). The three groups of reflections will be discussed below.

The measured peak widths of all reflections remain nearly constant for dehydration temperatures up to 400 °C. In materials dehydrated at temperatures >400 °C, all observed reflections continuously sharpen with increasing temperature. At temperatures ≥800 °C, the reflections of all three groups converge to the same small width (≈0.2°), thus approaching the FWHM values as observed for hematite derived from natural goethite.

3.2. TEM observations

3.2.1. Natural goethite

Upon dehydration, the natural goethite sample developed a very regular pore system in the product (Fig. 5a), similar to the ones described in literature for much smaller goethite crystals. The regularity of the pore lamellae causes satellite spots in the electron diffraction pattern (Fig. 5b). From bright field images and from diffraction patterns, the spacing of the lamellae is measured to 3.7(2) nm.

Also, twin domains in hematite derived from natural goethite can be easily visualised in dark field TEM images. Regardless of the dehydration temperature, large twin domains develop in the product. Therefore, all the dark field images of the "natural" hematite appear similar. A typical example is shown in Fig. 6 where twin domains with sizes

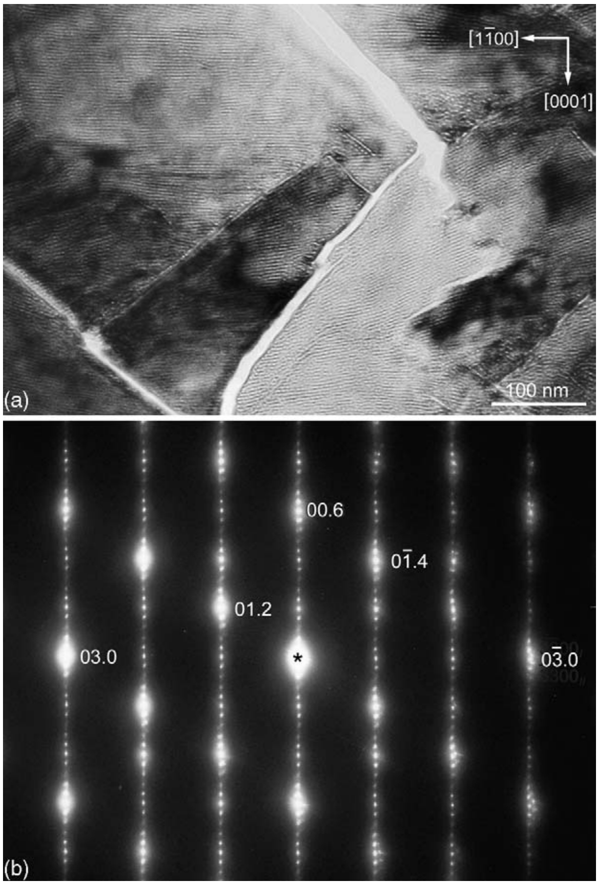

Fig. 5. Transmission electron microscopy of hematite derived from natural goethite by dehydration at 300 °C for 1.5 h: (a) bright field image in $[\bar{2}110]_H$ showing typical porous lamellae parallel to the basal plane of hematite and (b) corresponding electron diffraction pattern in $[\bar{2}110]_H$ which is of virtually one twin domain. Periodically spaced pore lamellae cause satellite reflections, also near hematite reflections due to double diffraction.

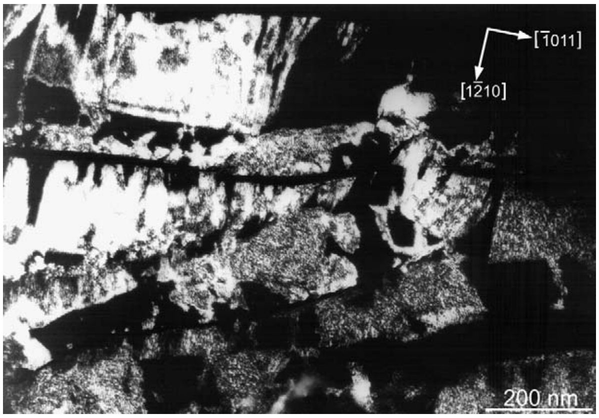

Fig. 6. TEM dark field image of hematite derived from natural goethite by dehydration at 350 °C for 7 min: image taken with reflection of type (10.4) and illuminating one of the twin variants. Dark regions are of the second twin variant.

>100 nm are obtained after (partial) dehydration at 350 °C. At lower temperatures, even somewhat larger domains are observed.

3.2.2. Synthetic goethite

A similar pore system is also observed in the low-temperature dehydration products of the synthetic goethite powders. Bright field images (Fig. 7a–d) support the findings of previous studies:[4] the pore lamellae are almost perfectly arranged in the 250 °C sample (Fig. 7a). In the 400 °C sample (Fig. 7b), the pore system has already merged, although the overall shape of the goethite needles is preserved during dehydration. After dehydration at 600 °C (Fig. 7c), the needles are rounded and only few residual and almost spherical pores are observed, whereas after the dehydration at 1000 °C (Fig. 7d), the needles have agglomerated and sintered to large hematite crystals of more than 500 nm in size. Electron diffraction patterns indicate that these grains are single crystalline, i.e. they exclusively show one singular twin orientation.

TEM dark field imaging or lattice imaging of hematite needles produced from synthetic goethite at low temperatures is extremely difficult and was never reported in the literature. The material is extremely sensitive to radiation damage and electron beam heating, which becomes apparent in the electron microscope by fluctuating contrasts and changes in the pore structure inside the hematite needles upon imaging with electron doses regularly used for imaging. To overcome the radiation problem, we used a low-dose technique where coarse focussing was performed on the carbon film at some distance from the region of interest. High resolution imaging of the hematite needles was achieved by subsequently acquiring focus series on the CCD camera with a low electron dose. Since the needles are usually stacked in different heights on the carbon support, chances to obtain optimally focussed images of the crystals are improved by taking focus series. One member of a focus series is shown in Fig. 8 where two hematite needles with lattice fringe contrast are imaged. Crystal 1 exhibits (01.2) lattice fringes only in the lower part indicated by black arrow, the fringe contrast abruptly terminates at the tip of the needle. Crystal 2 exhibits lattice fringes of type (10.4), however, they unpredictably disappear at some locations (white arrows). Another example is shown in Fig. 9 where a larger crystal is imaged and studied (marked by boxed area). The crystal is orientated close to $\langle 2\bar{2}01\rangle$, and one set of the $\{01.2\}$ planes is strongly excited (coarse fringes on the left is Moiré contrast). The strong $\{01.2\}$ fringe contrasts are visible in more detail in the magnified image (Fig. 9b). Similar to the contrast behaviour observed in Fig. 8, the fringes vanish in some regions of the crystal. The regions imaged with and without fringe contrast are shown schematically in Fig. 9c. Such contrast changes can be observed in many of the hematite crystals imaged under low-dose conditions. This phenomenon cannot be explained by crystal bending; it must be rather associated with an abrupt change in crystal orientation. The

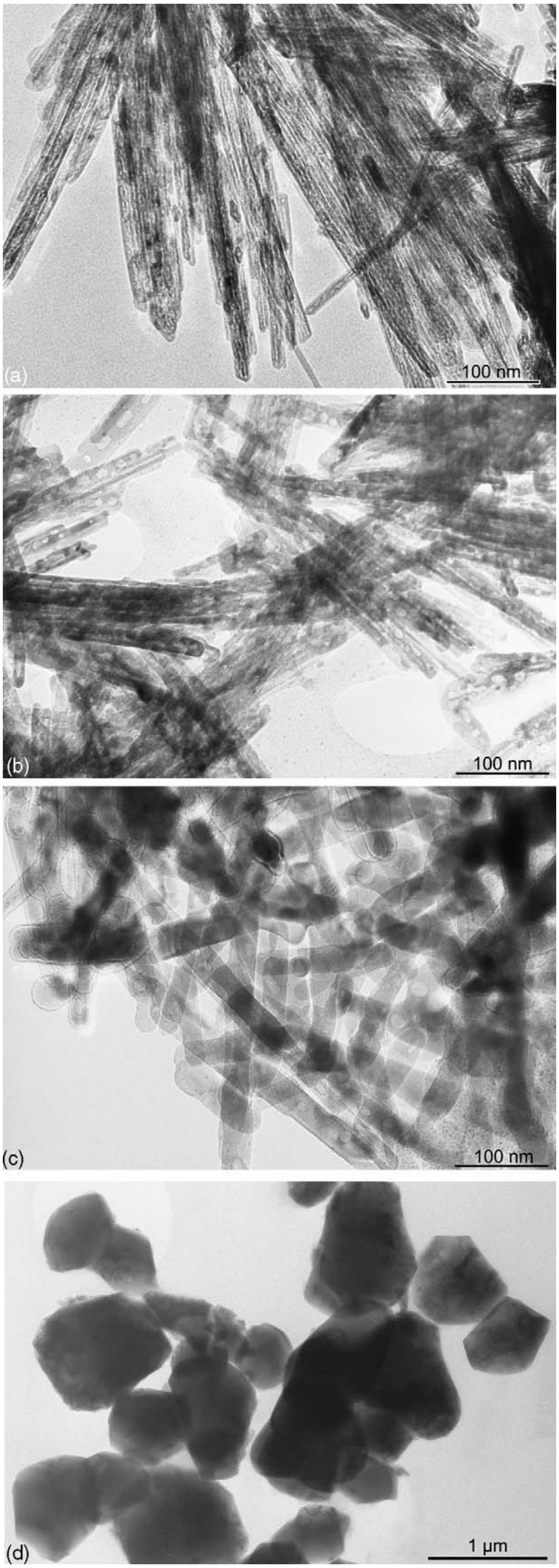

Fig. 7. Transmission electron micrographs of hematite produced from synthetic goethite needles by dehydration: (a) 250 °C for 100 h; (b) 400 °C for 1 h; (c) 600 °C for 1 h; and (d) 1000 °C for 1 h.

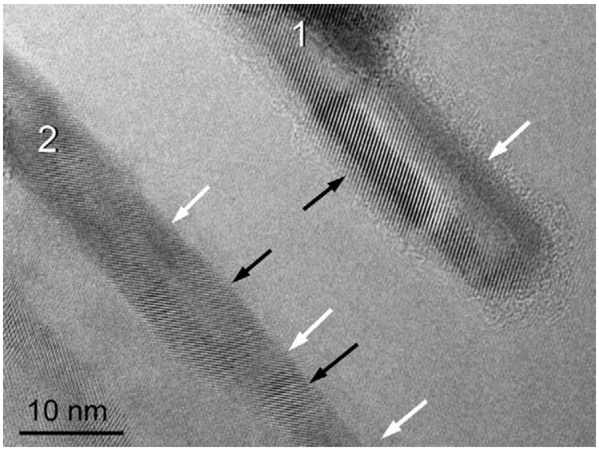

Fig. 8. High resolution TEM image of hematite derived form synthetic goethite by dehydration at 300 °C for 16 h. Crystal 1 shows (01.2) lattice fringes only on one side of the hematite needle (black arrow). Crystal 2 shows alternating appearance of (10.4) fringes (black arrows) separated by regions without fringe contrast (white arrows).

only reasonable explanation is twinning of the hematite crystals. As could be shown in Figs. 8 and 9, one twin variant may be (accidentally) oriented to fulfil the Bragg condition for a set of lattice planes. However, the second twin variant is usually out of contrast. In thick hematite crystals, as the one shown in Fig. 9 with thickness of approximately 20 nm, the domains without fringe contrast appear smaller because diffracting twin domains may overlap in the direction of projection and thus dominate the image, even if their dimensions are only a small fraction of the crystal thickness in projection. From the present analysis, the sizes of the twin domains can be estimated to be between 5 nm and 10 nm under the assumption that coarsening of twin domains did not occur during imaging in the electron microscope. Such domain sizes are close to the limit where nanometre-sized crystallites appear amorphous in X-ray diffraction.

3.3. DSC measurements

The DSC scans are displayed in Fig. 10 for the natural and the synthetic goethite samples, respectively. The synthetic goethite sample dehydrates at much lower temperature (240–320 °C, Fig. 10b) compared to the natural sample (340–400 °C, Fig. 10a). Additionally, the endothermic peak for the synthetic sample is split into (at least) three different maxima, whereas the DSC curve for the natural sample indicates a single step dehydration process.

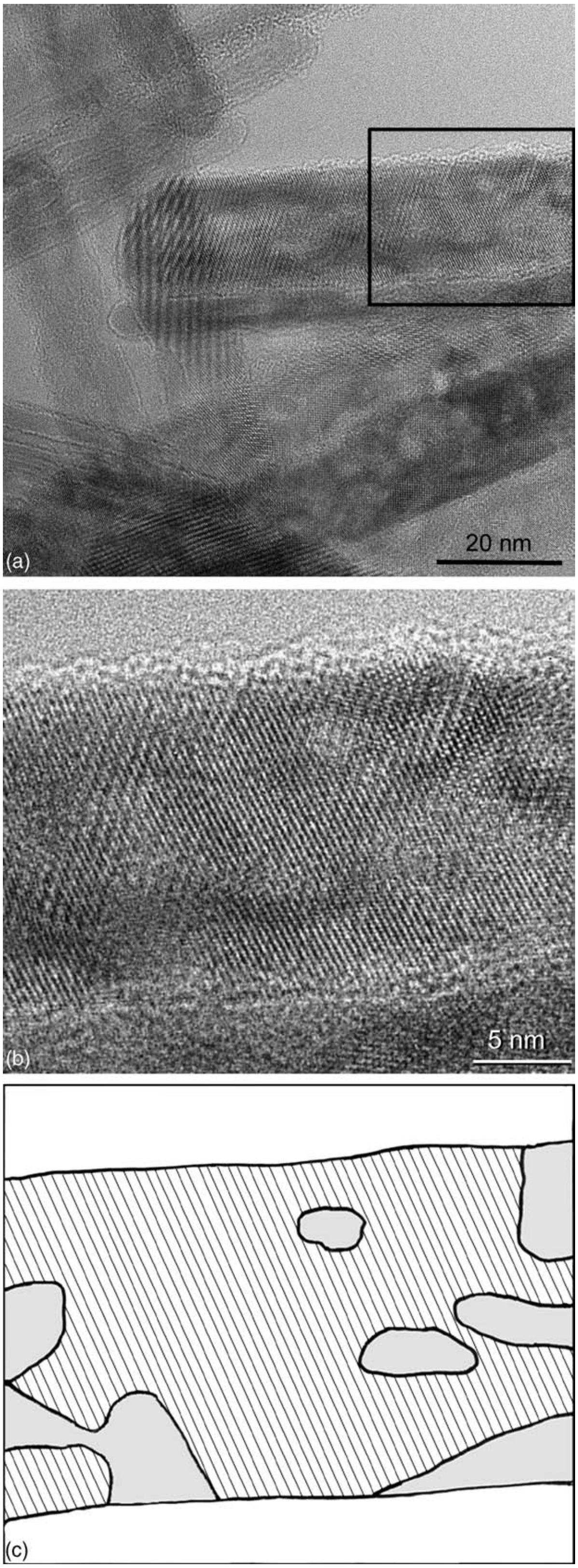

Fig. 9. High resolution TEM image of hematite derived form synthetic goethite by dehydration at 300 °C for 16 h: (a) Agglomerate of hematite needles. The crystal with the boxed area is oriented close to $\langle 2\bar{2}01\rangle$ and shows Moiré fringes on the left from overlapping needle; (b) blow up of the boxed area of (a) shows (01.2) lattice fringes (3.684 Å) at this focus setting. Note that the fringes appear only in some regions; second twin variant is not in contrast; (c) schematics of the distribution of twin variants in the hematite needle. Hatched: twin variant I including regions where both twin variants overlap. Grey: regions of twin variant II only.

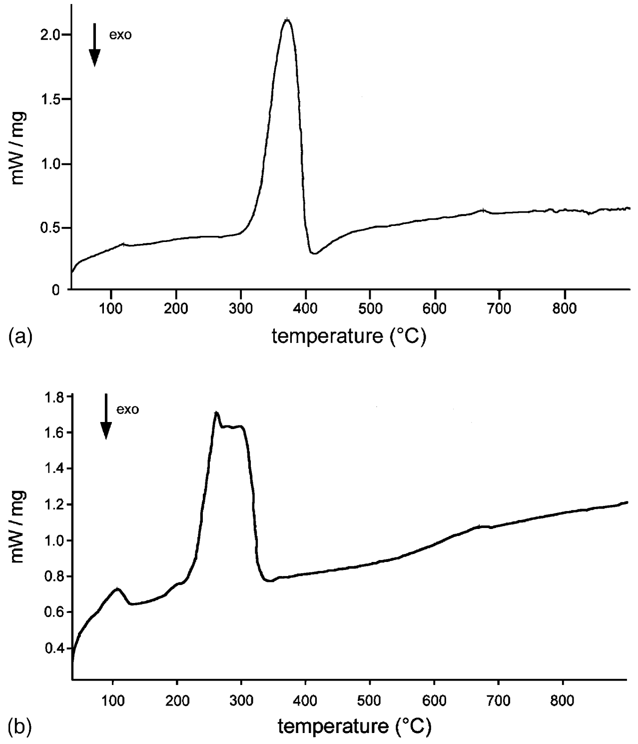

Fig. 10. Differential calorimetric scans. Scan from (a) crushed goethite mineral and (b) synthetic goethite needles. Endothermic peaks at approximately 100 °C stem from surface-adsorbed water.

4. Discussion

4.1. Non-uniform peak broadening and structure factors

The lamellar pore system in goethite-derived hematite, as it is displayed in Fig. 5a, was believed to be responsible for the XRD peak broadening even in recent literature.[12] However, the present study reveals that sharp XRD reflections are observed in hematite derived from natural goethite. This observation clearly proves that the pore lamellae are not causing any XRD peak broadening. The origin of the satellite spots in electron diffraction has been discussed in detail in recent studies on the dehydration process of diaspore.[15] Only the satellite spots around the primary beam are kinematic diffraction phenomena originating from single scattering processes, whereas satellites associated with reflections of the hematite crystal are caused by double diffraction. This phenomenon, hardly avoided in electron diffraction, is the result of the rather strong interaction of electrons with matter. However, double X-ray diffraction could also occur in large crystals. In fact, Lima-de-Faria has been able to observe these satellite spots in X-ray single crystal diffraction patterns of large corundum and hematite crystals.[1] Additional information on the pore system could also be obtained by means of small angle X-ray scattering experiments (SAXS).

Also the presence of residual hydrogen has been repeatedly discussed as a possible reason for the peak broadening, as it might introduce stacking faults into the cation stacking of hematite.[16,17] However, hydrogen analysis revealed that the highest residual concentrations of hydrogen were found in the low temperature dehydration products of natural goethite. In these samples, however, peak broadening is not observed, thus a hydrogen-related interpretation can be ruled out.

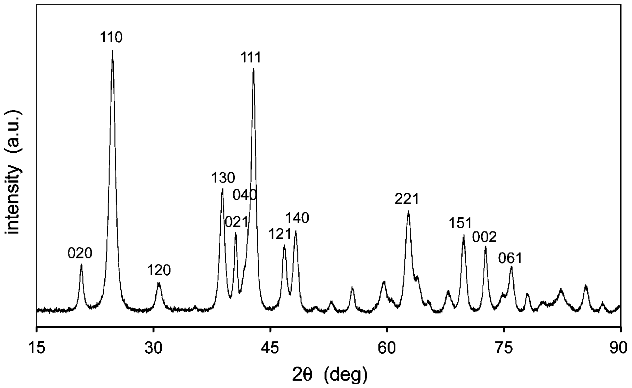

Fig. 11. XRD powder scan of synthetic goethite needles showing line widths (FWHM·cos θ) between 0.3° and 0.65°.

The fine crystalline synthetic material exhibits drastic broadening after low temperature dehydration. Such nano-sized material with crystals of approximately 200 nm in length and only 10–20 nm in thickness is expected to produce non-uniform broadening of diffraction peaks. In line with this conclusion, it would be essential to compare diffraction lines of the starting material with the dehydration product. Since the size of the needle-shaped crystals remain virtually unchanged during dehydration at low temperature, it would be interesting to study possible differences in the diffraction peaks—a study so far not reported in the literature. The XRD scan of the synthetic goethite sample is shown in Fig. 11. Despite of the anisotropic shape of the goethite needles the XRD data show little texture-related variation of diffracted intensity. Relative intensities of all reflections observed in XRD agree will with reported diffraction data of goethite.[18] Peak widths for the starting material range from 0.3° to 0.65°; these values correspond very well to the widths of the narrowest reflections after dehydration to hematite. Hence, the "residual" broadening of the narrow group I reflections of hematite should indeed be ascribed to crystal shape anisotropy, whereas the additional peak broadening of group II reflections is not explicable by crystal shape arguments alone.

Nanometre-scaled twinning of hematite appears to be the only plausible explanation for XRD peak broadening. As described above, the observed hematite twinning results from two different iron stacking sequences in the same oxygen framework. In a finely twinned product, only the iron stacking shows two variants and hence is discontinuous, while the oxygen sub-lattice remains apparently unaffected.[9,14] Thus, it is important to analyse which of the X-ray reflections are dominated by scattering at iron atoms and oxygen atoms, respectively. For this purpose simulated XRD spectra of the

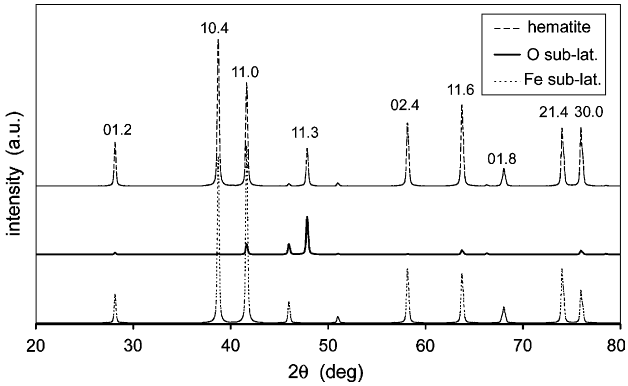

Fig. 12. Calculated XRD scans: hematite structure (top), oxygen sub-lattice of hematite (centre), and iron sub-lattice of hematite (bottom).

hematite crystal, as well as of the oxygen sub-lattice and the iron sub-lattice were calculated separately; the results are displayed in Fig. 12. It is evident that reflections such as (01.2), (10.4), (01.8), (02.4) and (21.4) are strongly dominated by scattering at the iron sub-lattice. In contrast, the (11.3) reflection originates from the oxygen sub-lattice only (reflections $l = \text{odd}$ are forbidden for atoms on Wyckhoff position 12*e*, i.e. for iron). Some of the reflections contain contributions from both sub-lattices, e.g. the reflections (11.0), (11.6) and (30.0).

By comparing these findings with the experimental results (Figs. 3 and 4), it is obvious that the strongly broadened reflections in group II are essentially originating from the iron sub-lattice, whereas the (11.3) reflection of the oxygen sub-lattice remains sharp. This is the first support for the twinning argument. Different broadening behaviour is found for the "mixed reflections": while the (11.6) reflection is significantly broadened, the (*hk*.0) prism plane reflections remain sharp due to the fact that the prism planes of hematite are not affected by the twinning operation. Reflections of type (*hk*.0) are common reflections of both twin variants which may be visualized in electron diffraction patterns (see Fig. 5b). A final and strong argument for twinning-related diffraction peak broadening is the direct proof of nanometre-scaled twin domains in high resolution TEM images. Such fine-scaled twinning could be observed only in hematite crystals dehydrated from synthetic goethite at low temperatures. And only that material shows extreme anisotropic peak broadening in X-ray powder scans. It is worth mentioning that there is a direct analogy between diffraction peak broadening in hematite from dehydrated synthetic goethite and diaspore-derived corundum.[14] One difference is that the (11.6) reflection is much more broadened in hematite as compared to corundum due to the higher atomic scattering amplitude of iron in comparison with aluminium.

It can be seen from the plots of peak widths as function of temperature that not only the iron-dominated, but also the oxygen-related reflections sharpen with increasing dehydration temperature. Increasing overall crystallite sizes at elevated temperatures were confirmed by TEM imaging. Hence, two different effects are influencing the angular width of the X-ray reflections with increasing dehydration temperature: annihilation of twin domains and coarsening of powder grains, respectively.

It is astonishing that most of the reports on XRD peak broadening on goethite-derived hematite did not compare their findings to the results of one of the most essential article on goethite dehydration by Lima-de-Faria[1] who did not observe broadening at all. The discrepancy between differing results is explicable by the fact that most of the articles in recent literature refer to fine-grained synthetic goethite samples, whereas Lima-de-Faria reported on the dehydration of large-grained natural mineral samples.

4.2. Generation of twins by nucleation and growth

Obviously there exists a correlation between the crystal size and the size of twin domains in the dehydration product. For this discussion, we refer to our results on corundum produced by dehydration of diaspore.[14,19] It has been proposed that the size of the twin domains depends on the rate of nucleation and the rate of phase growth: finely twinned crystals are developed when the nucleation rate is high, i.e. many new twin nuclei are formed during dehydration. Otherwise, if the nucleation rate is low, a once formed nucleus will gradually grow to one large twin variant. In other words, large twins refer to a low nucleation rate. As shown in the closely related diaspore/corundum system, the topotactic reaction always starts at the free crystal surface where nucleation is facilitated by little mechanical constraints and by the easy release of water.

At this point, we refer to our calorimetric studies of the two types of goethite samples. In accordance with the results of Ford and Bertsch[20], we observed (at least) three distinct endothermic events in the dehydration process of the synthetic goethite sample. These authors[20] distinguished between surface and bulk dehydration by relating three (of four) endothermic peaks to surface dehydration and the last and strongest one to bulk dehydration. Similar yet less specific conclusions were drawn by Goss[21] and Walter et al.[22] According to these authors, the activation energies for surface and bulk dehydration differ significantly.

The most significant difference between natural and synthetic goethite is the grain size and thus its surface-to-volume ratio of the material. The results of the present study strongly indicate that this difference can be referred to the nucleation energy of the new phase, i.e. hematite. Synthetic goethite with a large surface-to-volume ratio dehydrates at significantly lower temperatures in comparison with the natural goethite mineral. Surface dehydration is likely to be accompanied by spontaneous formation of a large number of hematite nuclei. As the nuclei randomly adopt one of the two twin orientations, a finely twinned material is obtained from the synthetic samples. In contrast, few nuclei are formed in the bulk material. The reaction will slow down as the reaction front proceeds into the interior of the goethite crystal due to increasing constraints for nucleation of hematite. Iron ions released from decomposing goethite are re-precipitating on existing hematite nuclei. Thus the prevailing twin variants will further grow to dominating twin domains. This conclusion is strongly supported by TEM dark field imaging of partially transformed material, where the prevailing twin domains are in contact with goethite. Therefore, transformation of large-grained natural goethite is dominated by bulk dehydration, i.e. at inner goethite–hematite phase boundaries, where constraints for the reaction are likely to be independent of the location. Hence, only one peak is observed in the differential calorimetric scan for dehydration of the goethite mineral.

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