

Nonstoichiometric structures during dehydroxylation of goethite

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Abstract. Thermal dehydration of goethite (α -FeOOH) at low temperature leads to complete transformation into a hematite-like phase before less than one half of the stoichiometric water content in goethite is expelled. The character of the remaining water has not been explained as yet.

The variations of band positions in the infrared spectra and the specific changes in relative integrated intensities of X-ray lines with the increase of dehydration temperature suggested that OH-groups replace oxygen anions in the hematite crystal lattice, while the electroneutrality is preserved by the cation vacancies.

Comparison of integrated intensities observed with intensities calculated on this assumption fully confirms that the hematite-like phase is an iron deficient species with a general chemical formula α -Fe_{2-x/3}(OH)_xO_{3-x}.

The accurate measurements of lattice constants reveal that while the crystallographic c_0 -axis decreases steadily with progressing thermal dehydroxylation, the a_0 -axis reaches a minimum at the temperature at which the nonuniform X-ray line broadening disappears. The largest unit cell of hematite phase after the goethite/hematite transition and the smallest one after the disappearance of selected broadening of X-ray diffraction peaks represent two transitional phases with hematite structure, protohematite and hydrohematite, displaying their own structural and compositional characteristics. The smallest unit cell appearing when the crystalline phase still holds about three percent of structurally bound water

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suggests that the stoichiometric hematite is thermodynamically less stable than this intermediate state.

Introduction

As we now know due to numerous studies with sensitive sophisticated instrumental methods, stoichiometric goethite is practically non-existent (Murad, 1982; Johnston and Norrish, 1981; Murad and Johnston, 1987). Beside the substituents of iron, naturally occurring goethites and all α -FeOOH synthetics contain varying quantities of excess water and when that excess is to be removed, decomposition of the system begins. Again, when the stoichiometric goethite hydroxylation degree $(\text{OH})^-/\text{O}^{2-} = 1$ decreases just to about one half, the orthorhombic structure fully collapses, giving access to the pure monophasic hexagonal hematite-like system holding somewhat more than one half of the goethite-stoichiometric water content (Yapp, 1983; Hirokawa et al., 1986; Wolska, 1988).

The quantity and the character of H_2O in the hematite phase are not accountable in terms of adsorbed, absorbed, trapped or capillary water, surface or chemisorbed hydroxyl groups, or the relic of substratum. Yapp (1983), who during 2.5 days unsuccessfully tried to remove the 6% of "residual" water at 230°C from the goethite-derived product, found, calculated on the assumption of Gast et al. (1974), that even if the whole surface was covered with a layer of water it would account only for about 0.5% of it.

The numerous reports on the infrared absorption of chemisorbed hydroxyl groups on hematite are not of help here. As thorough as they are, they present very discordant views on the thermal resistance of such groups (cf. Blyholder and Richardson, 1962; Rochester and Topham, 1979) and relevantly to the matter of study, they do not deal with OH-deformation and lattice vibration regions of the infrared spectrum. Meanwhile, taking into account the easiness of intracrystalline exchange of the mineral-hydrogen during dehydration (Yapp, 1983; Yapp and Pedley, 1985) it is hardly to discuss the surface- or "in bulk"-OH groups without consideration of just these frequency regions. In highly sophisticated heat-flux differential scanning-calorimetry effects at 180° , 210° and 235° , corresponding to singly-, doubly- and triply-coordinated OH surface groups, was recorded before the principal peak of goethite dehydration at 260°C , but never after it (Paterson and Swaffield, 1980).

In the report of Watari et al. (1983), with no reference to the presence of water in the hematite phase, there is a tempting postulation of a blocking mechanism by which the escape of water or further decomposition of goethite would be prevented by the surrounding freshly built iron oxide. However, such stages of dehydroxylation would be easily checked with instrumental analysis. Furthermore, the lack of a slightest hint about the

temperature range at which they might occur makes this approach unserviceable for the explanation of the "illegitimate" water, not to mention the common unconformability between the interpretation of results from the observation "in situ" in high-resolution electron microscope and those from "in bulk".

The goethite-derived hematite phase displays the so called nonuniform broadening of lines on the X-ray diffraction pattern. However, that salient effect outshone another, much less conspicuous but not less important, anomaly. With rising temperature besides changes in the peak intensities related to the disappearance of the selective line broadening, we do observe on the X-ray pattern, if carefully checked, variations in relative integrated intensities of reflections. The purpose of this paper is to examine the changes in relative integrated intensities which occur during the progressive dehydroxylation of the hematite-like phase, to confront them with the variations of intensities calculated on the assumption that the newly formed hexagonal structure represents a cation-deficient system with hydroxyl groups in the anionic sublattice, as it was mentioned recently (Wolska, 1988) and to demonstrate that the intermediate phases built during the dehydration process have their own structural characteristics.

Experimental

In order to dispose with a starting material of different crystallinity and water content, goethite samples were prepared by three, variously modified main methods, namely by: 1) oxidation of Fe(II)-solution in the presence of a buffer, 2) storing of amorphous iron hydroxide in alkaline media and 3) partial oxidation of Fe(II)-solution and further bubbling of air in the presence of scrap iron.

Thermal treatment of specimens was carried out in air (up to 250°C in 10°-, above in 50°-intervals) for six hours.

X-ray powder diffraction studies were performed using a PW 1050-Philips diffractometer and a TUR-61 (GDR) equipped with HZG-3 proportional counter spectrometer, employing $\text{CoK}\alpha$ -radiation. For profile analysis the lines were recorded by step scanning using increments of 0.01° in θ and a fixed counting time of 30s/step. Intensity data were collected at a scan rate of 0.25° θ /min. To avoid texture effects a special brass sample-holder was used.

Infrared spectra were obtained on a Perkin-Elmer 180 spectrophotometer using CsI pellets.

Results and discussion

The loss of water as a result of thermal treatment begins in the goethite samples already above the ambient temperature and causes detectable and

Table 1. Structural, morphological and compositional features of synthetic goethite samples.

No	Unit cell parameters [Å]			WHH* (110)	Water content (wt. %) after			elimination of selective line broadening	
	a	b	c		heating orig. sample at 1050°C	hematite-like phase formation			T (°C)
						T (°C)	wt. % H ₂ O		
1	4.5973	10.0097	3.0180	1.296	21.9	180	6.6	400	3.2
2	4.6123	9.9578	3.0259	1.639	19.6	200	6.4	450	2.8
3	4.6082	9.9556	3.0242	0.943	18.6	200	6.0	500	2.9
4	4.6191	9.9614	3.0264	0.950	18.9	200	7.0	500	3.2
5	4.6247	9.9736	3.0298	1.005	17.7	200	6.5	500	2.7
6	4.6187	9.9612	3.0246	1.247	17.4	200	6.3	500	3.1
7	4.6139	9.9648	3.0236	0.306	14.9	250	5.5	600	2.8
8	4.6151	9.9656	3.0241	0.349	14.6	250	5.9	600	3.0
9	4.6125	9.9637	3.0232	0.313	14.7	250	5.2	600	2.6
10	4.6130	9.9654	3.0252	0.374	13.8	250	5.6	600	3.1

* Width at half height of (110) X-ray diffraction line ($^{\circ}2\theta$) corrected for instrumental broadening.

partly irreversible changes in their original properties. Within 60–105° the increasing desorption of water leads to an increase in microstrain and to an enhanced magnetic coupling between neighbouring microcrystals giving rise to the so called superferromagnetic behaviour (Koch et al., 1986), while heating at 110° C allows to record changes in crystallite size (Fey and Dixon, 1981). At 114° C, commonly regarded as still belonging to the temperature range of the removal of physically bound water only, changes in the lattice parameters have been recorded (Goss, 1987). Depending on crystallite dimensions, disintegration of goethite may take place at 150° C, while for a certain crystallite size-distribution the specimen may dehydrate continuously beginning from ambient temperatures (Ferrier, 1966).

As an illustration of the goethite hydration after formation and after its phase-transition ten preparations of goethite, selected from twenty four samples preliminary examined on composition and phase purity, are listed in Table 1. Samples 1, 2, 3–6 and 7–9 originate from the three quoted preparative procedures respectively, while sample 10 is a Bayer 7110-Standard goethite specimen. Except for samples 3–6 in which about 2–2.5% of the total water content could be attributed to the untransformed ferrihydrite, as determined by Schwertmann's method (1964), the whole excess water in the preparations is always related with the goethite phase. It is apparent from Table 1 that differences in the hydration grade are not reflected in the unit-cell parameters. Alterations in crystallite dimensions, however, characterized here by the change in half-height width of the main goethite X-ray line (110), correlate fairly well with the excess water, indicating that part of it may be classified as physically adsorbed or chemisorbed water which in some goethite preparations is estimated to reach about 5% (Schwertmann et al., 1985). A correlation between the temperature of transition into the hematite phase, the crystallite size and the amount of excess water is also to be noted, although the values obtained in isothermal conditions presented here, do not correspond to those recorded by dynamic methods (Schulze and Schwertmann, 1984).

What attracts notice, is the similar, high water content after the phase-transition and after disappearance of the preferential X-ray line broadening, independent of crystallite size and of the initial hydration of goethite, a correlation of a rather structural nature. To be sure that the transition goethite-hematite was completed we needed a reliable tool of identification. A huge number of experiments with mixtures of goethite and hematite of various crystallinity convinced us that in X-ray diffraction free background at the vicinity of the strongest goethite (110)-reflection may be withheld up to 3–6% of goethite, but the OH-deformation bands in the infrared spectrum allow for a comfortable identification of about 0.5% of it. With this accuracy we consider the results regarding the completion of the goethite transformation in this work. And here our data find some support in the recent results of Hirokawa et al. (1986) who found,

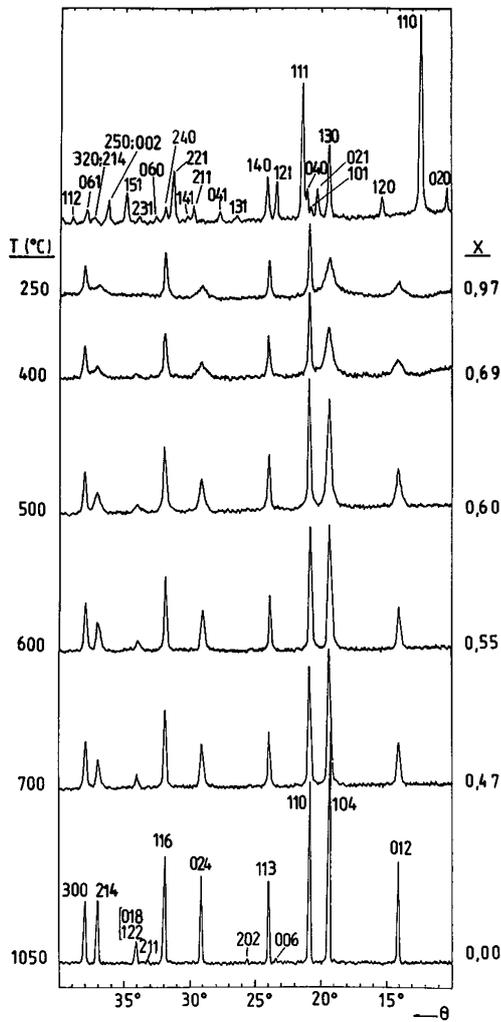


Fig. 1. X-ray powder diffraction patterns of the goethite sample 7 and of its thermal treatment products, $\alpha\text{-Fe}_{2-x/3}(\text{OH})_x\text{O}_{3-x}$.

monitored as well by ir-spectroscopy, that in the TGA-method no goethite was detected at 50% decomposition.

To exemplify the striking behaviour of goethite preparation when thermally treated, we present the X-ray powder patterns (Fig. 1) and the position of ir-absorption bands (Fig. 2) for the goethite sample no. 7. Visual inspection of X-ray patterns allows to note the appearance from the very beginning of sharp lines (110), (113), (116) and (300), and the successive

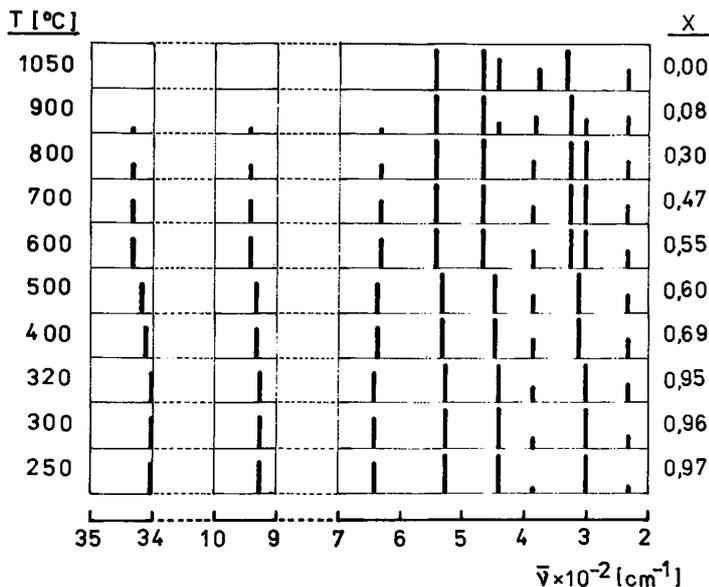


Fig. 2. Positions of the absorption bands of infrared spectra of hematite phases, $\alpha\text{-Fe}_{2-x/3}(\text{OH})_x\text{O}_{3-x}$, derived from goethite sample 7 at different temperatures.

disappearance of broadness of (012), (104), (024) and (214) reflections with rising temperature. Infrared spectra besides evolution and displacement of the hematite lattice vibration bands exhibit the absorption bands of the OH-group (~ 3400 , ~ 950 and $\sim 640\text{ cm}^{-1}$) which jointly occurring suggest their intracrystalline origin (Wolska, 1977; Wolska and Szajda, 1985; Wolska, 1988).

Another confirmation that the pure hematite phase contains the OH-groups in its structure, randomly distributed with oxygen ions in the anionic sublattice framework, are the results of thorough determinations of integrated intensity changes accompanying the further dehydroxylation with rising temperature. The measurements presented in Fig. 3 show a striking agreement with the theoretical values calculated on the assumption that the species after transition represent a monophasic system $\alpha\text{-Fe}_{2-x/3}(\text{OH})_x\text{O}_{3-x}$. Theoretical intensities were calculated using hematite structure coordinates and isotropic temperature factors after Blake et al. (1966), whereas the atomic scattering factors were taken from International Tables for X-ray Crystallography (1962). The strongest cation-independent reflection, (113), was chosen as a reference line to follow the increase in intensities with decreasing x in the above formula. Fig. 3 (a, b) shows that the intensity variations have nothing to do with the precursory properties. The values of integrated intensities observed (experimental points) for hematite phases

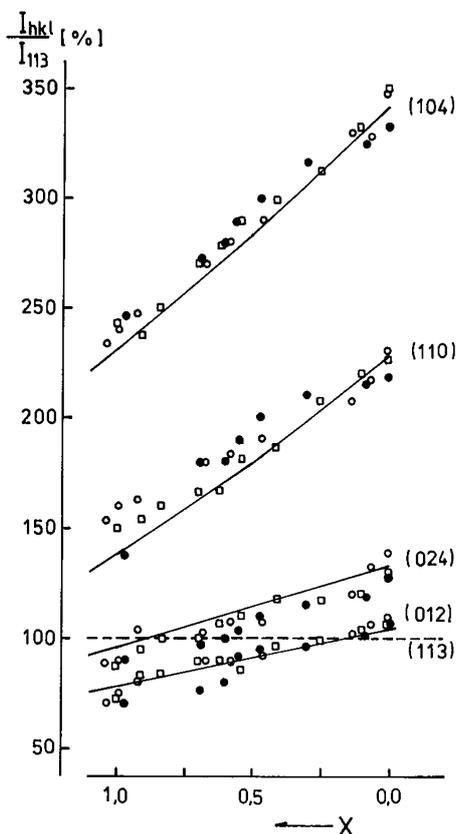


Fig. 3a

stemming from very small and very large goethite crystallites, from synthetics scanty and very rich in excess water, all cluster together around the values of calculated intensities (full lines). The intensities of X-ray reflections seem to depend exclusively on the iron deficiency stadium and they increase as the cation occupancy of octahedral sites in the hexagonal close-packed anionic sublattice rises from about 56% to 67%. The discrepancy factors, $R = \frac{\sum |F_{hkl}^{obs} - F_{hkl}^{calc}|}{\sum |F_{hk}^{obs}|}$, for the samples of Fig. 3 representing the three principal methods of goethite preparation, confirming this view, are given in Table 2. The remaining samples obtained from goethite listed in Table 1 show a similar agreement between observed intensity changes and those of assumed models.

Further experiments give evidence that the goethite-hematite transformation goes via intermediate stages with their own structural characteristics. The idea of transitional states involved in the formation of goethite-derived hematites came into existence in 1959 (Francombe and Rooksby)

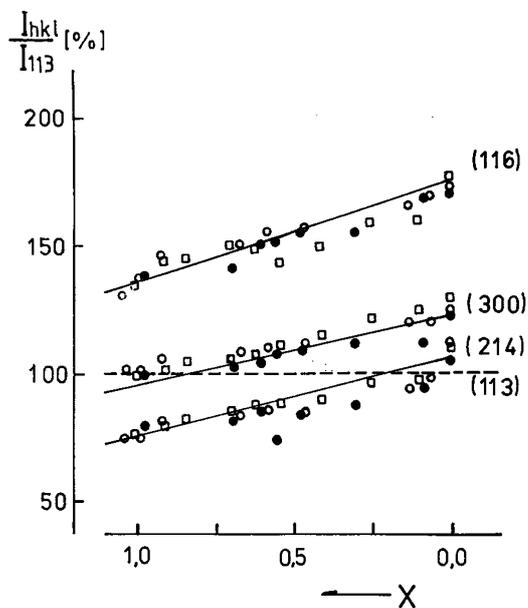


Fig. 3a and b. Variations of the integrated intensities of X-ray lines (I_{hkl}/I_{113}) with x in $\alpha\text{-Fe}_{2-x/3}(\text{OH})_x\text{O}_{3-x}$ derived from goethites: \circ sample 1, \square sample 3 and \bullet sample 7.

and was since then adopted by other authors with the purpose of explaining the preferential X-ray line broadening in terms of structure imperfections (Lima-de-Faria, 1963; Yamaguchi and Takahashi, 1982). Sometimes special names were introduced in order to distinguish these states, e.g. “protohematite” (Yariv and Mendelovici, 1979) or “embryo disordered hematite” (Brown, 1984). However, only in the paper of Mendelovici et al. (1982) there is a reference to the presence of structural water as one of the transitional-state features.

According to Brown (1984) the unit cell of the first produced hematite-like phase appears to be about 0.3% longer than that of the well-crystallized final product of fully developed hematite. The accurate determination of lattice constants of hematites derived from three representative goethite samples (Fig. 4) confirms the largest hexagonal unit cell for the first formed hematite phase and reveals the variations in a_0 and c_0 parameters during thermal treatment. But Fig. 4 shows another, not yet observed, structural peculiarity of transitional stages, namely, that the a_0 parameter reaches its lowest value not as expected when the system acquires the final perfection of its network, but just when the nonuniform X-ray line broadening disappears, although the water held in the hematite phase is still far from being driven off.

Table 2. Discrepancy factors, $R = \frac{\sum |F_{hkl}^{obs}| - |F_{hkl}^{calc}|}{\sum |F_{hkl}^{obs}|}$, calculated from the experimental results presented in Fig. 3 for the assumed model $\alpha\text{-Fe}_{2-x/3}(\text{OH})_x\text{O}_{3-x}$.

Temp. (°C)	Sample 1		Sample 3		Sample 7	
	x	R	x	R	x	R
180	1.04	0.025	—	—	—	—
200	0.99	0.028	1.00	0.024	—	—
250	0.92	0.019	0.91	0.018	0.97	0.029
300	0.67	0.020	0.84	0.017	0.96	0.038
320	0.58	0.020	0.70	0.023	0.95	0.034
400	0.46	0.025	0.62	0.018	0.69	0.033
500	0.13	0.023	0.54	0.022	0.60	0.027
600	0.06	0.020	0.41	0.022	0.55	0.040
700	—	—	0.25	0.022	0.47	0.034
800	0.00	0.022	0.10	0.025	0.30	0.034
900	—	—	0.00	0.014	0.08	0.030
1050	—	—	—	—	0.00	0.013

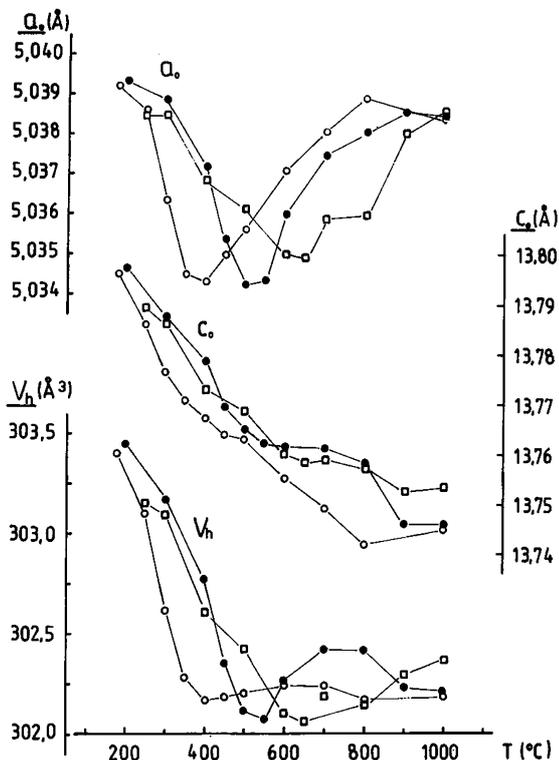


Fig. 4. Lattice constants, a_o and c_o , and the volume of the hexagonal unit cell, V_h , of hematite phases obtained from goethite samples at different temperatures. \circ sample 1, \bullet sample 3 and \square sample 7.

That paradoxical behaviour might be explained if we consider the structural relationship between the parent and product phases. Parallel to the goethite *c*-axis (forming with its *b*-axis a plane at which lie the a_0 -axes of hematite) the double strings of occupied and empty octahedra with hydrogen bonds run alternately. During a “catastrophic” transition, using Yapp’s (1983) relevant expression, a vast amount of them remains unbroken while the iron occurring in deficiency yet, reorganize themselves in a disordered manner, as the characteristic line broadening indicates, from a rod-like arrangement in goethite into a honey-comb pattern of hematite structure. The minimum of the a_0 parameter seems to appear at a point at which the shrinkage in the former goethite *bc*-plane caused by the successive intense breaking of hydrogen bonds progressing with rising temperature, ceases to outweigh the expanding effect of the increasing number of iron ions per oxygen layer, tending to the right stoichiometry. The disappearance of selective line broadening signals the attainment of correct positions in the honey-comb arrangement of existing iron ions, able now to coherent X-ray diffraction, but the filling of vacancies goes further and the a_0 -parameter continues to expand.

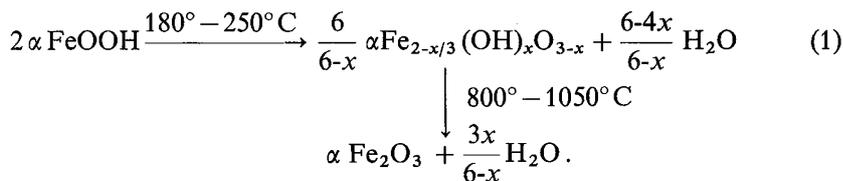
Changes in the direction perpendicular to (001)-planes are less spectacular. As the topotactic transition takes place within the framework of the same close-packed hexagonal anionic sublattice, only minor corrections in the stacking of oxygen sheets are necessary to attain the small c_0 diminution resulting from the axial relation $3a$ (goethite) = c_0 (hematite).

This has an impact on the variation of the unit cell volume with x in $\text{Fe}_{2-x/3}(\text{OH})_x\text{O}_{3-x}$. Except for Bayer-specimen (sample 10) serving in fact as a starting material for recording tapes and containing therefore some amount of admixtures or perhaps for another reason, all remaining hematites derived from goethites listed in Table 1 follow the type of curves exemplified in Fig. 4. They suggest that further diminution in OH-content, after the point of preferential line-broadening disappearance is reached, tends to expand the unit cell, in other words, the stoichiometric hematite appears to be thermodynamically less stable than the transition phase with a a_0 -minimum.

Postulations that the peculiarities of the goethite-hematite transition are manifestations of morphological features, as for example of particular shape of goethite crystallites (Rooksby, 1951), degree of hematite crystallinity (Yariv and Mendelovici, 1979), “texture” of hematite (Watari et al., 1979), shape anisotropy of formed crystallites (Devigneaud and Derie, 1980), formation of slit-shaped micropores (Naono and Fujiwara, 1980), twin building (Watari et al., 1982), lath-like morphology of hematite (Serna and Iglesias, 1986) or evolution of coarsening of the twin hematite crystallite (Goss, 1987), to some extent at variance with each other by the way, do not foresee transitional stages with structural features at all. Describing the reaction $2\alpha\text{FeOOH} \rightarrow \alpha\text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$ as a direct one, they

assume an immediate transition of iron ions from the one-half octahedral sites occupancy system into two-thirds one, without intermediate states. During further thermal treatment the hematite, stoichiometric from the beginning, undergoes only intercrystalline evolutions till the postulated morphological reason responsible for the anomalies is stamped out.

Our experimental results presented above allow to express the transition with the following chemical equation, if started from a point when the stoichiometric hydroxylation degree $\text{OH}^-/\text{O}^{2-} = 1$ of goethite has been reached:



The first stage of transformation, the pure hematite-like phase, is distinguished by the largest unit cell, the most acute X-ray preferential line broadening and chemically by the highest x -value (~ 1). For this structurally and chemically distinctive species the most correct name seems to be "protohematite", already widely in use since its introduction in 1979 (Yariv and Mendelovici).

Before the final product, $\alpha\text{-Fe}_2\text{O}_3$, is achieved, a second characteristic intermediate phase is formed at a temperature of $400^\circ - 600^\circ \text{C}$, distinguishable compositionally by $x = 0.5$ in formula (1) and structurally by the disappearance of preferential line-broadening, by a minimum in a_0 -parameter and the smallest unit cells. Thus it exhibits features similar to the product of mild dehydration of ferrihydrite (Wolska, 1981), for which after Hüttig and Strotzer (1936) the name "hydrohematite" was adopted, and to the distinct $\alpha\text{-Fe}_2\text{O}_3$ variety formed when synthetic αFeOOH is dry-ground at ambient temperature (Mendelovici et al., 1982; Mendelovici, 1988).

Conclusions

Experimental data gathered during our investigations on the goethite-hematite transition assign a rather secondary role to the morphology of hematite in its anomalous behaviour. It is limited mainly to the crystallinity of the initial goethite specimens, which then governs the conditions of thermal treatment necessary to obtain the particular stage of transformation.

The thermal dehydration of goethites yields products with hematite structure which contain similar amounts of water of an intracrystalline character. The variation in positions and number of absorption bands of

the infrared spectrum with decreasing water content points to the presence of water in the form of lattice OH-groups in the anionic sublattice of hematite.

Measurements of integrated intensities of the X-ray lines fully confirm that the hematite-like phase is an iron-deficient species of a general chemical composition $\alpha\text{Fe}_{2-x/3}(\text{OH})_x\text{O}_{3-x}$.

Two transitional phases may be identified during dehydroxylation. Directly after the goethite-hematite transformation a hematite phase is formed, distinguishable by the selective X-ray line-broadening, the largest unit cell, the characteristic infrared spectrum and the value of $x \simeq 1$ in the given formula.

The vanishing of the line-broadening effect takes place when x attains the value of ~ 0.5 . At that point the a_0 -parameter and the volume of unit cell reach their lowest values. The smallest unit cell suggests that this intermediate phase is thermodynamically more stable than the hematite structure with the correct iron to oxygen stoichiometry. It further explains why hydrated hematites obtained at low temperature from ferrihydrites have such as ideal crystallinity and why water is so often found in hematite minerals.

We suppose that the idea of transitional stages employed by advocates of structural origin of preferential X-ray line-broadening in the goethite-derived hematites, connecting them, however, only with imperfections in rearrangement of atoms in the newly built hematite lattice, finds in our results full support and their larger specification. We do hope as well that the room for speculations on the status of water present in the hematite phase has been considerably reduced by these results.

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