Structural and spectroscopic characteristics of synthetic hydrohaematite

EMILIA WOLSKA, WOJCIECH SZAJDA
Department of Magnetochemistry, Adam Mickiewicz University, Poznań, Poland

In order to investigate the identity of water-containing haematite, a method of preparation has been elaborated which leads to samples of hydrohaematite which are "structurally pure" and free of amorphous iron hydroxide. Differential thermal analysis by a lack of endothermic effect at 423 to 473 K on the DTA-curves and by a steady fall of the TG curves up to ~1150 K revealed that water in the preparations must be tightly held in the lattice of haematite. Measurements of intensities of X-ray reflections of the (1 0 4) and (0 2 4) planes in relation to the (1 1 3) plane confirmed Fe^{3+}-deficiency in the haematite cationic sublattice brought about by the presence of OH^- ions in the anionic sublattice. The infrared spectrum of hydrohaematite, in addition to six bands from Fe–O variations, exhibits three bands from hydroxyl groups. The effect of silicates on the pattern of the infrared spectra of natural and synthetic hydrohaematites and the discrepancies in the infrared spectra of haematites published to date are discussed.

1. Introduction

Although the structure of iron oxides and hydroxides has been the subject of extensive studies, considerable uncertainty still exists about the structural identity of hydrohaematite. In mineralogical and solid state chemistry handbooks hydrohaematite is defined as a "solid solution of water in haematite lattice" or "haematite with adsorbed water" [1, 2]. In the earlier experimental papers, the term "hydrohaematite" was proposed for haematite preparations obtained hydrothermally from amorphous iron (III) hydroxide $Fe(OH)_3$, or by thermal decomposition of goethite, α-FeOOH, with up to 8% H_2O content [3, 4]. Naturally occurring hydrohaematites usually contain 5.4 to 8% H_2O and show characteristic dehydration curves: a steady loss of water with rising temperature, apart from a slight inflection at about 129 to 150° C [4].

Hydrothermal transformation of amorphous ferric hydroxide gel results, in fact, in its simultaneous conversion into haematite and goethite, with its phase-equilibrium depending upon ageing conditions: increasing alkalinity favours goethite formation, whereas increasing temperature shifts the equilibrium towards haematite [5–9].

The transformation of amorphous iron hydroxide into crystalline products and the dehydration of goethite into haematite is much more complex than mentioned above. For example, recent investigations of the α-FeOOH dehydration process point to the existence of an intermediate crystalline phase, so-called "protohaematite", which has its own characteristic infrared spectrum, different from haematite [10]. Furthermore, the crystalline phase identified as haematite in the products of hydrothermal ageing of $Fe(OH)_3$, is strictly speaking, hydrohaematite, but if it is accompanied by goethite its detection by X-ray diffraction or by infrared spectroscopy is a very difficult task, and virtually impossible to realize [11]. Thus in order to investigate the structure of synthetic hydrohaematite, it was necessary to direct the transformation of

0022–2461/85 $03.00 + .12

amorphous $Fe(OH)_3$ towards hydrohaematite only. This can be done by adding 2 to 2.5 mol % Al^{3+} ions, which when substituting iron positions in the haematite lattice do not contaminate the system with another crystalline phase [11, 12]. Small quantities of unconverted $Fe(OH)_3$ present in hydrohaematite samples obtained at 373 K can be removed by warming them to 423 to 473 K [13].

It has been proved [14] that the infrared spectrum of hydrohaematite exhibits one distinct absorption band in the range 900 to 1000 cm^{-1} and a second one at about 630 cm^{-1}, manifesting itself as a shoulder on the lattice vibration band of Fe–O. On the basis of these two bands, assigned to OH-vibrations, hydrohaematite can be identified and distinguished from haematite. At the same time they prove the presence of hydroxyl groups, OH^-, in the α-Fe_2O_3 lattice. Replacing O^{2-} positions in the haematite lattice, they bring about cation deficiency which results in a lowering of the intensities of all X-ray reflections dependent on cation positions, which allows one to confirm the assumed defect structure of hydrohaematite by X-ray structural analysis [14].

New results are presented below regarding the hydrohaematite structure which support the model assumed earlier by Wolska [14]. Maintaining the basic technique of avoiding goethite phase formation, we improved the preparation method of hydrohaematite in order to obtain (1) full transformation of amorphous iron hydroxide and (2) preparations which eliminate the eventuality of dubious interpretation of their infrared spectra. A further purpose of this work is to clear up some discrepancies existing about spectroscopic features of haematite.

2. Experimental details

Samples of hydrohaematite were obtained by adding 1 M sodium hydroxide solution to 1 M Fe^{3+}- and Al^{3+}-nitrate solutions mixed in proportion to obtain $Fe_{1-z/2}Al_{z/2}(OH)_3$ gels (z = 0.04 to 0.05), until a pH of 10 to 11 in the mother liquor was reached. The suspensions were then put in palladium vessels and kept in an autoclave at 413 and 433 K (H_2O vapour pressure 3.61×10^5 and $6.18 \times 10^5\,N\,m^{-2}$, respectively) for 12 h. The products were washed with distilled water to get rid of concurrent nitrates, and dried at 373 K. For comparison purposes, a series of preparations was made in exactly the same way with the exception that the suspensions were kept in glass vessels instead of palladium ones. At all stages of the preparation procedure reagent grade chemicals were used. Samples of hydrohaematite obtained this way are well crystallized, giving X-ray reflections without any signs of the fine crystalline state.

Differential thermal analysis was performed with a Hungarian Q 1000 MOM model, infrared spectra were obtained using a Perkin-Elmer 180 spectrophotometer (KBr pellets in the 4000 to 300 cm^{-1} region and polyethylene discs in the 520 to 100 cm^{-1} region). Crystalline phase analysis and reflection intensity measurements were performed with X-ray diffraction unit employing Co$K\alpha$ radiation, equipped with an HZG (GDR) proportional counter spectrometer joined with counting components and an impulse printing unit.

The cation deficient character of the hydrohaematite lattice was confirmed by intensity measurements of the X-ray reflections: peaks from ($h\,k\,l$)-planes with even l, (i.e. depending on cation position in the lattice) show substantial subsidence in relation to the (1 1 3) reflection, the intensity of which depends exclusively on the anion sublattice. Calculations, based on these measurements, of relative intensities for (1 0 4)/(1 1 3) and (0 2 4)/(1 1 3) lines for hydrohaematite samples obtained here and for haematites formed after heating at 1173 K, are included in Table I. The lowering of intensities experimentally observed corresponds to the calculated values for hydrohaematite containing 2 to 2.5 mol % Al^{3+} ions and 2 to 2.5% H_2O in the form of hydroxyl groups. Assuming a cation deficiency model of the hydrohaematite lattice is valid [14], the value of x in the formula of hydrohaematite $Al_{z[1-(x/6)]}Fe_{(2-z)/[1-(x/6)]}(OH)_xO_{3-x}$ was calculated.

Results of differential thermal analysis, represented here in Fig. 1 by the DTA and TG curves for hydrohaematite samples 1, 2 and 3 of Table I, differ significantly from those obtained by low-temperature synthesis [13] and from naturally occurring hydrohaematites [4]. DTA curves do not display their characteristic endothermic peaks at 420 to 450 K and TG curves indicate a continuous weight loss for all samples between room temperature and 1150 K, except for a fair inflection at about 720 K.

To exemplify the individual character of

TABLE I Intensities of X-ray diffraction patterns observed in $Al_{z[1-(x/6)]}Fe_{(2-z)[1-(x/6)]}OH_xO_{3-x}$ samples

No.	Preparation conditions			H_2O content (wt %)	x	Relative X-ray intensities			
	Temp. (K)	pH	Al^{3+} (mol %)			(1 0 4)/(1 1 3)		(0 2 4)/(1 1 3)	
						hydrohaematite	haematite	hydrohaematite	haematite
1	433	10.5	2.0	2.08	0.3532	3.32	4.03	1.01	1.13
2	413	10.5	2.5	1.09	0.3234	3.30	3.88	0.98	1.10
3	413	10.5	2.0	1.94	0.3303	3.63	4.19	0.97	1.16
4	433	10.5	2.5	2.50	0.4208	3.24	4.07	0.98	1.19
5	413	10.0	2.0	2.36	0.3987	3.47	4.22	1.03	1.20
6	413	11.0	2.5	2.04	0.3464	3.26	3.83	1.01	1.16
7	433	10.0	2.0	1.75	0.2990	3.60	4.04	0.96	1.11

hydrohaematite infrared spectra, Fig. 2 shows spectrum 1 of sample 1 from Table I, spectrum 2 of the same sample after its preliminary dehydration at 473 K, and spectrum 3 of haematite obtained after heating sample 1 at 1173 K. Spectra 1 and 2 (practically identical) display six absorption bands from Fe–O vibrations and three bands brought about by the presence of OH-groups (3400, 950 and 630 cm^{-1}). The third spectrum of Fig. 2 contains only six lattice vibration bands characteristic of a haematite (see Table II).

Amorphous silica, present as a rule in natural hydrohaematites and which might in some preparative conditions be present in synthetic hydrohaematites, exerts an influence on the infrared spectra of these species. Fig. 3 shows the main frequency region of infrared spectra of $Al_{0.025}Fe_{0.975}(OH)_3$ gel submitted to a hydrothermal process at 433 K and pH 11 in palladium (spectrum I) and in glass (spectrum 2) vessels. Spectrum 3 belongs to a residue after evaporation of the 0.001 M NaOH (pH 11) solution, which underwent the same operations as preparation from spectrum 2. It is seen that the 950 cm^{-1} band, the most characteristic for hydrohaematite, in the spectrum 2 is partially overlapped by the band of amorphous silica at 1080 cm^{-1}. Spectrum 3 displays bands from amorphous silica only [15, 16].

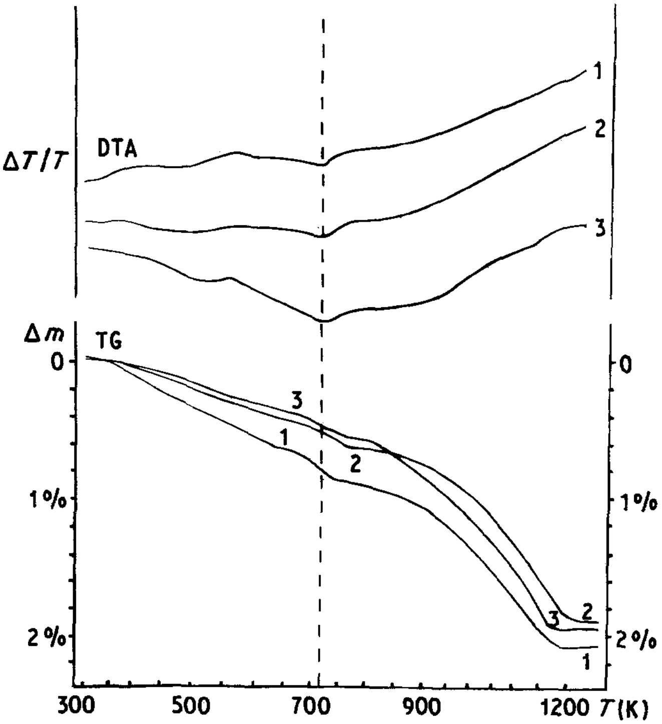


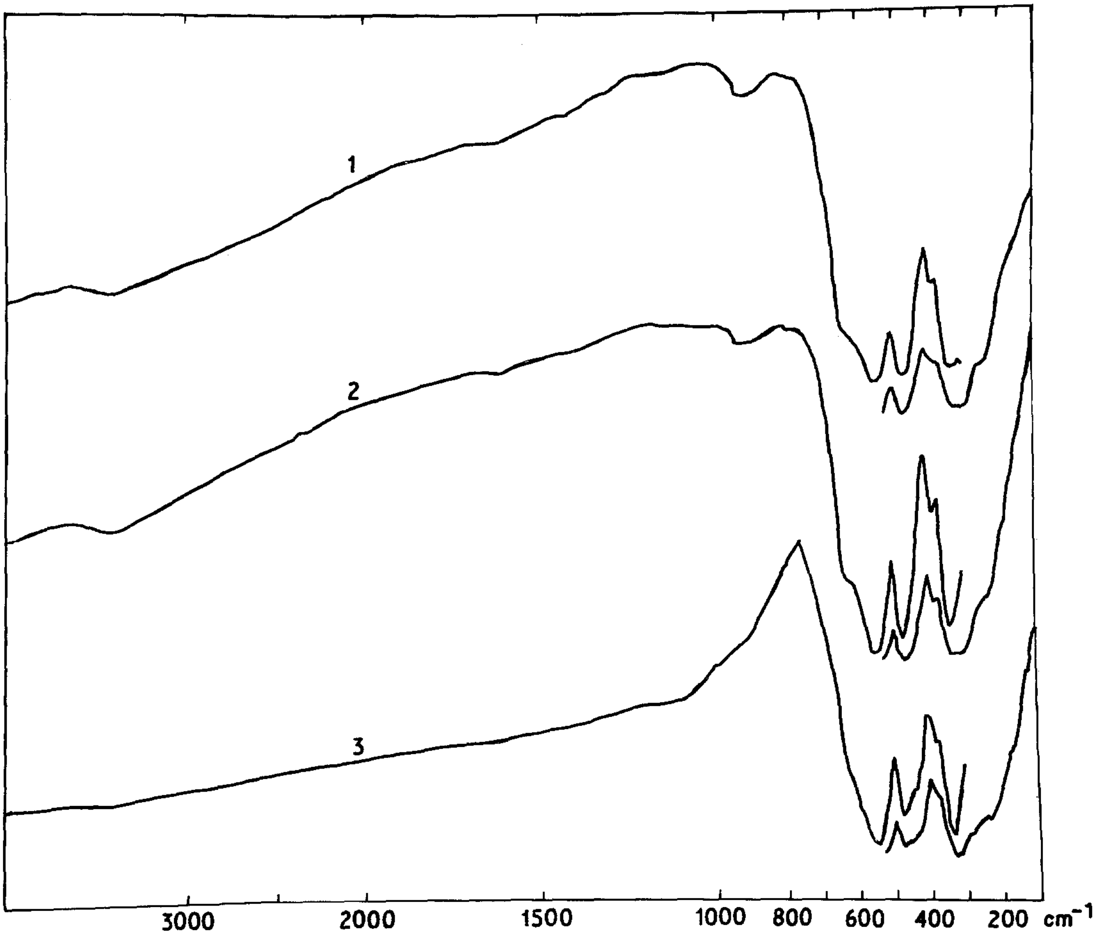
Figure 1 DTA and TG curves of synthetic hydrohaematites (samples 1, 2 and 3 from Table I).

TABLE II Infrared frequencies observed for hydrohaematite and haematite (comparison with references)

Mitsuishi *et al.* [18]	Onari *et al.*[19]	Yariv and Mendelovici [10]		Present work	
		Protohaematite	Haematite	Hydrohaematite	Haematite
				3400	
				950	
		~630		630	
571					
	526 A_{2u}	530	543	540	540
476	524 E_u		468	470	470
444	437 E_u	445			440
385		390	~380	385	385
323	299 A_{2u}		333	330	325
		308			
	286 E_u			300	
235	227 E_u	233	233–240	230	230

3. Discussion

The results above confirm earlier findings about the structure of hydrohaematite [14], additionally supporting them in an essential way. This was achieved due to a different preparation procedure: first, by applying autoclaves, it was possible to prepare samples at temperatures higher than 373 K (here 413 and 433 K) and by that to secure hydrohaematites free from "loosely bound water", evidence for which is the



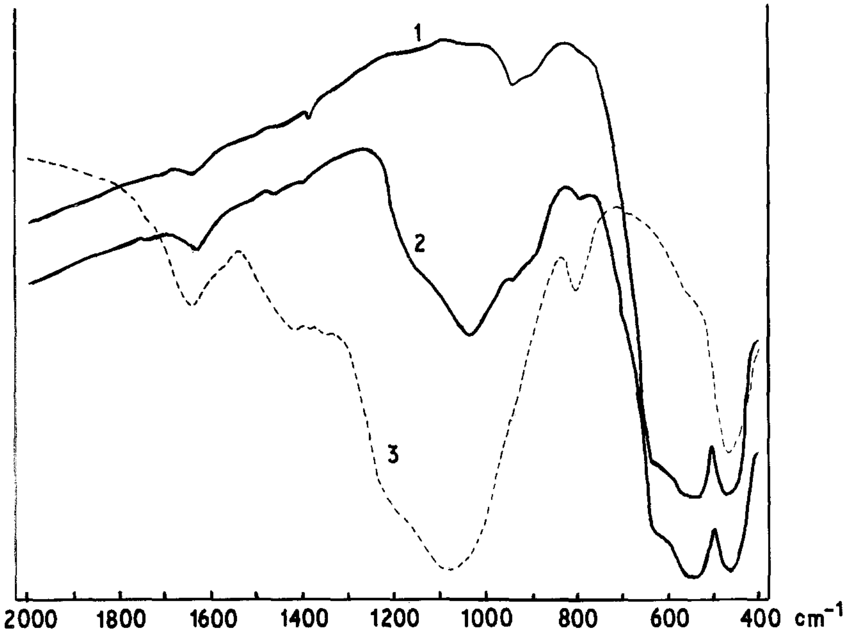


Figure 3 Infrared spectra of hydrohaematite samples obtained at 433 K (pH 11, $z = 0.05$) in palladium (spectrum 1) and glass containers (spectrum 2). Spectrum 3: residue after evaporation of 0.001 M NaOH (pH 11) heated at 433 K in a glass container.

lack of an endothermic effect at 400 to 450 K on the DTA curves (Fig. 1) and a residual infrared absorption band at 1630 cm^{-1} (Fig. 2); second, by replacement of glass vessels with palladium containers, which was necessary for the higher temperatures applied and high pH of the milieu (indispensable measures when well crystallized hydrohaematite is to be obtained) the effect of silica from laboratory glass on the formation of hydrohaematite was eliminated.

The fact that preparations without an endothermic effect on the DTA curves may be obtained, inclines us to conjecture that the mass loss registered during dehydration of the sample below 473 K should be ascribed to the decomposition of the remaining amorphous $Fe(OH)_3$ accompanying the low-temperature hydrohaematites, rather than to the loss of that "loosely bound water" or adsorbed water, practically removed when the sample is dried at 373 K. It seems that the lack of infrared absorption bands, characteristic of surface adsorbed water, supports that view.

The chemical formula for hydrohaematite has been drawn on the basis of the H_2O content in preparations after heating at 473 K and on the assumption that water leaving the species at higher temperatures stems from OH-groups occupying some oxygen anion positions in the haematite anionic sublattice. It is clear that the lowering of intensity of cation-dependent X-ray peaks in relation to (1 1 3) reflection intensity is a manifestation of a decrease in the number of Fe^{3+} ions in octahedral holes. Neutral molecules of water could not bring about the effect observed, nor would high temperatures be required to dislodge it from the species.

Like X-ray diffraction analysis, the spectroscopic method also proves the existence of hydroxyl groups in hydrohaematite. In the valence vibration region there is a distinct and durable band at 3400 cm^{-1}. Although this band grows smaller with the decline of the H_2O deformation band at 1630 cm^{-1}, during the first dehydration step (removing of H_2O and adsorbed OH-groups) it still exists even after the total disappearance of that band.

The assignment of the band at 3400 cm^{-1} to OH valence vibrations in the hydrohaematite lattice requires one to point out the OH-deformation band characteristic of the structure in question. In hydrohaematite preparations it is the band at 950 cm^{-1} which should be considered as the "fingerprint" of the species. It can be observed on the infrared spectra of haematites obtained by mild dehydration of amorphous iron(III) hydroxide, or hydrothermally, as described in this work, provided that the preparations do not contain goethite phase or silica. In the first case it is the OH-deformation vibration bands at 800 and 900 cm^{-1} [11], in the second one the usually large band from Si–O antisymmetric valence vibrations in silicates at 1080 cm^{-1}, which may completely screen the band at 950 cm^{-1}.

Within the region of the Fe–O lattice vibrations, the hydrohaematite spectrum exhibits six infrared bands ($2\,A_{2u} + 4\,E_u$) in accordance with factor group analysis for corundum structure [17], and an additional band at ~630 cm^{-1}, which disappears after full dehydration of the sample, thus proving its hydroxyl group origin, probably from Fe–OH vibrations. It has to be stressed, however that the Fe–O vibrations in haematite and hydrohaematite do not show a full coincidence on the frequency scale (see Table II). The most characteristic occurrence here is the simultaneous disappearance of the band at 300 cm^{-1} and the appearance of the band at 440 cm^{-1} after heating the hydrohaematite at 1173 K.

In Table II frequencies of infrared-active vibrations reported in some other papers [10, 18, 19] for natural haematite samples, synethetic haematite and so-called protohaematite [10] are presented. The specification largely suggests that the differences in positions of the bands should be attributed to the origin of samples, though lack of precise analytical data, particularly about the water and aluminium content, does not allow us to say more about the discrepancies. The effect of Al^{3+} substitution on the infrared band positions in a haematite discussed recently [20] has been observed as a displacement of the 470 cm^{-1} band for an aluminium concentration higher than 10 mol %. It seems that the band at 385 cm^{-1}, which disappears in the infrared spectra of a haematite containing 5 mol % Al^{3+} is far more sensitive [14]. We are therefore inclined to suppose that the lack of this band in the spectrum [19] might be explained by the presence of a very small quantity of aluminium in the natural haematite sample.

Although the data on infrared bands in the OH-vibration region of "protohaematite" are not available [10], our own results, as yet unpublished, indicate that products of mild dehydration of goethites exhibit all bands from OH-vibrations characteristic of hydrohaematite described in this work (at ~3400, 900 to 950 and 640 cm^{-1}).

These results suggest that the presence of hydroxyl groups in the haematite lattice is the major factor changing the pattern of its infrared spectrum, since by that the effect of the hydrogen bond, as well as the effect of cation deficiency in the lattice, is revealed. Determination of more thorough quantitative relations in the system discussed is a subject of further investigations.

References

1. H. STRUNZ, "Mineralogische Tabellen" (Academische Verlagsgesellschaft, Leipzig 1977) p. 536.
2. H. REMY, "Lehrbuch der anorganishchen Chemie" (Academische Verlagsgesellschaft, Leipzig, 1973) p. 358.
3. G. F. HÜTTIG and E. STROTZER, *Z. Anorg. Allg. Chem.* **226** (1936) 97.
4. N. S. KURNAKOW and E. J. RODE, *ibid.* **169** (1928) 57.
5. U. SCHWERTMANN, *ibid.* **298** (1959) 23.
6. R. R. ROBINS, *J. Inorg. Nucl. Chem.* **29** (1967) 431.
7. A. N. CHRISTENSEN, *Acta Chem. Scand.* **22** (1968) 1487.
8. J. TORRENT, R. GUZMAN and M. A. PARRA, *Clays Clay Miner.* **30** (1982) 337.
9. E. WOLSKA, *Mh. Chem.* **106** (1975) 905.
10. S. YARIV and E. MENDELOVICI, *Appl. Spectrosc.* **33** (1979) 410.
11. E. WOLSKA, *Mh. Chem.* **108** (1977) 819.
12. U. SCHWERTMANN, R. W. FITZPATRICK, R. M. TAYLOR and D. G. LEWIS, *Clays Clay Miner* **27** (1979) 105.
13. E. WOLSKA, *Mh. Chem.* **107** (1976) 349.
14. *Idem, Z. Kristallogr.* **154** (1981) 69.
15. U. SCHWERTMANN and H. THALMAN, *Clay Miner.* **11** (1976) 189.
16. J. HLAVAY, K. JONAS, S. ELEK and J. INCZEDY, *Clays Clay Miner.* **26** (1978) 139.
17. S. BHAGAVANTAM and T. VENKATARAYUDU, *Proc. Indian Acad. Sci.* **9A** (1939) 224.
18. A. MITSUISHI, H. YOSHINAGA, S. FUJITA and Y. SUEMOTO, *Jpn. J. Appl. Phys.* **1** (1962) 1.
19. S. ONARI, T. ARAI and K. KUDO, *Phys. Rev. B* **16** (1977) 1717.
20. S. A. FYSH and P. M. FREDERICKS, *Clays Clay Miner.* **31** (1983) 337.

*Received 25 September 1984
and accepted 10 January 1985*