

INFRARED VIBRATIONS OF HEMATITE FORMED FROM AQUEOUS- AND DRY-THERMAL INCUBATION OF Si-CONTAINING FERRIHYDRITE

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Abstract—Ferrihydrite samples having Si/Fe molar ratios ranging from 0 to 1 were synthesized by the reaction of $\text{Fe}_2(\text{SO}_4)_3$ and Na_2SiO_3 with NaOH to an equilibrium pH of 8.2. Hematite formed by incubating the ferrihydrite (Si/Fe molar ratios ≤ 0.05) at pH 12.5 and 91°C for 36 hr had a globular morphology. Hematite formed from Si-free ferrihydrite gave infrared (IR) bands at 548, 471, 397, and 337 cm^{-1} , whereas, hematite formed from Si-containing ferrihydrite having 0.001 to 0.05 Si/Fe molar ratios gave broad IR bands at about 550, 450, and 330 cm^{-1} . Ferrihydrite having Si/Fe molar ratios ≥ 0.10 did not transform to hematite following the aqueous-thermal treatment.

The ferrihydrite samples were thermally treated for 2 hr at consecutive 100°C intervals from 100° to 800°C. The Si-free ferrihydrite transformed at 300°C to poorly crystalline hematite. Transmission electron microscopic analyses indicated that the hematite consisted of aggregates of spheroidal particles of 20–80 Å cross sections. Broad IR bands were observed at 529 and 452 cm^{-1} ; however, after heating the sample to 800°C, the particle cross sections increased to about 150–600 Å, and additional IR bands were present at 378 and 325 cm^{-1} . The differences in the IR patterns of hematite formed from ferrihydrite at 300° and 800°C were probably due to increases in particle size and aggregation and improved crystallinity of the hematite particles following the higher temperature treatment. The hematite formed by the thermal transformation of the ferrihydrite having a 0.01 Si/Fe molar ratio was also spheroidal, and IR vibrations were present at about 528 and 443 cm^{-1} . An increase in the temperature of the thermal treatment, however, did not result in additional IR bands.

Differences in the IR vibrations of hematite formed during aqueous- and dry-thermal treatments of the ferrihydrite samples were probably due to differences in the particle size and morphology of the product. The Si content, due to its effect on particle size of the precursor and the prevention of sintering and particle growth of hematite, influenced the IR pattern of the product. Particle morphology and IR spectroscopy may therefore be useful indicators of the precursor of hematite and the conditions of hematite formation in soil.

Key Words—Ferrihydrite, Hematite, Infrared spectroscopy, Morphology, Silicon, Thermal treatment.

INTRODUCTION

Feitknecht and Michaelis (1962) reported that conditions of synthesis that enhance aggregation of ferrihydrite also favor the transformation of ferrihydrite to hematite. In soils, the transformation of Fe oxides or oxyhydroxides to hematite is due primarily to internal dehydration and rearrangement of atoms within the aggregated structure (Schwertmann, 1988). In the laboratory, hematite may be formed by either of two processes: (1) the dry-thermal transformation of ferrihydrite, lepidocrocite, goethite, or maghemite; and (2) the aqueous-thermal incubation of ferrihydrite. The morphology and particle size of the hematite product is largely dependent on the conditions of synthesis and the specific Fe oxide from which it is synthesized (Matijevic and Scheiner, 1978; Barron *et al.*, 1984; Ozaki *et al.*, 1984; Serna *et al.*, 1987).

Sidhu (1988) observed that heating maghemite to 500°C for 3 hr produced sintered aggregates of hematite having only two major infrared (IR) bands, at 550 and 480 cm^{-1} . Fischer and Schwertmann (1975) observed

only three IR bands, at 557, 465, and 325 cm^{-1} , for ellipsoidal hematite formed by the aqueous incubation at 70°C of ferrihydrite at pH 6–7 in the presence of oxalate. Rendon and Serna (1981) found that hematite formed by the thermal transformation of goethite at 300°C gave IR bands at 650, 525, 440, and 300 cm^{-1} , and that the hematite formed by heating goethite at 600°C gave an additional band at 400 cm^{-1} . Serna *et al.* (1987), using classical theory of absorption of IR radiation by small particles, concluded that the differences in IR bands of hematite were largely dependent on particle morphology. Saraswat *et al.* (1980) reported the formation of an intermediate-phase pseudohematite upon heating ferrihydrite to 250° to 300°C, based on the comparison of the IR bands to those of well-crystallized hematite formed at temperatures $\geq 350^\circ\text{C}$. Corjeno (1987) also suggested the name pseudohematite for a product formed by heating ferrihydrite at 150°C for 24 hr.

The influence of particle size, morphology, and cationic substitution of Mn, Al, etc. on the IR vibrations

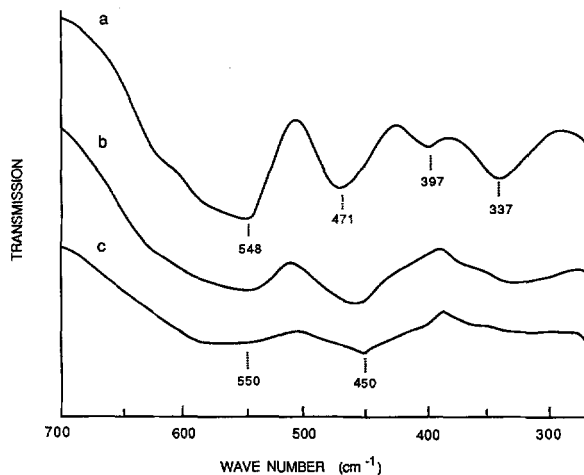


Figure 1. Infrared patterns of ferrihydrite samples after aqueous incubation at pH 12.5 and 91°C for 36 hr: (a) Si free; (b) 0.001 Si/Fe molar ratio; (c) 0.05 Si/Fe molar ratio.

of hematite needs to be thoroughly understood. Such studies may be useful in providing clues to the mineral precursor and condition of hematite formation. Limited information exists relating the IR vibrations to particle morphology and crystal size of hematite formed during transformations of ferrihydrite or Si-containing ferrihydrite. The specific objectives of the present investigation were to determine: (1) the influence of particle size and morphology on the IR spectra of hematite formed by aqueous- and dry-thermal incubation of ferrihydrite, and (2) the effect of temperature on the transformation of Si-containing ferrihydrites.

METHODS AND MATERIALS

Preparation of ferrihydrite and goethite

Ferrihydrite samples having Si/Fe molar ratios ranging from 0 to 1 were synthesized in the laboratory by the reaction of $\text{Fe}_2(\text{SO}_4)_3$ and Na_2SiO_3 with NaOH to an equilibrium pH of 8.2, according to the method of Vempati and Loeppert (1989). The properties and mechanisms of Si bonding of these samples were previously discussed by Vempati and Loeppert (1989) and Vempati *et al.* (1990).

Goethite was prepared by the rapid addition of 3 N KOH to 1 liter of 0.15 M $\text{Fe}(\text{NO}_3)_3$ to a final pH of ~ 11.2 . The product was aged at room temperature for 24 hr and then at 155°C in a Teflon pressure bomb for an additional 12 hr. All samples were dialyzed to remove excess salt and freeze dried.

Aqueous-thermal incubation

Ferrihydrite samples (25 mg) in 50 ml of H_2O in polypropylene bottles were adjusted to pH 12.5 using NaOH and incubated at 91°C for 36 hr in a water bath. The samples were washed three times with deionized water to remove excess Na and freeze dried.

Thermal transformation

Ferrihydrite samples were heated in a muffle furnace for 2 hr at 100°, 200°, 300°, 400°, 500°, 600°, 700°, and 800°C ($\pm 10^\circ\text{C}$). At each temperature increment, subsamples were taken for mineral analyses.

Mineral analyses

The freeze-dried samples were randomly oriented on double-adhesive tape on glass slides and analyzed by X-ray powder diffraction (XRD) using $\text{CuK}\alpha$ radiation from a Philips-Norelco diffractometer equipped with a graphite monochromator. For the IR study, KBr pellets were prepared by homogenizing 300 mg of ground KBr (dried at 110°C for 24 hr) with 3 mg of the oxide and pressing at 6.9×10^7 Pa. The IR spectra were recorded using a double-beam Perkin-Elmer 283 spectrophotometer. For transmission electron microscopic (TEM) analyses, the samples were dispersed in deionized water using a sonic bath, and a drop of suspension was air dried on a carbon-coated Cu grid. TEM micrographs and selected-area electron diffraction (SAD) patterns of the samples were obtained using a Philips 400T TEM operated at 60 kV.

RESULTS

Aqueous-thermal transformation

The products formed by the incubation of ferrihydrite with Si/Fe molar ratios ≤ 0.05 at pH 12.5 and 91°C for 36 hr consisted of hematite and smaller quantities of goethite. The hematite was electron dense and globular, having particle cross sections of about 200–1000 Å (Vempati and Loeppert, 1989). IR vibrations of hematite formed from the Si-free ferrihydrite were observed at 548, 471, 397, and 337 cm^{-1} (Figure 1a). For the Si-containing ferrihydrite samples having Si/Fe molar ratios ranging from 0.001 to 0.05, broad IR vibrations characteristic of hematite were observed at about 550, 450, and 330 cm^{-1} (Figures 1b and 1c); however, only a weak shoulder was observed near 397 cm^{-1} . The IR vibrations were broader with increasing Si/Fe molar ratio of the ferrihydrite. For ferrihydrite samples having Si/Fe molar ratios ≥ 0.10 , the transformation to hematite was not observed following the 36-hr aqueous-thermal treatment.

Dry-thermal transformation

The Si-free ferrihydrite sample transformed to hematite on heating for 2 hr at 300°C (Table 1). The width at half height (WHH) of the 104 XRD peak of hematite at 2.69 Å decreased from 0.64 to 0.40°2 θ as the temperature was increased from 300° to 800°C. Therefore, the product crystallinity increased, and/or the mean crystalline diameter decreased with increasing temperature of the heat treatment.

A direct relationship was noted between the Si/Fe molar ratio of the ferrihydrite and the temperature at

Table 1. Approximate temperatures of the thermal transformation of ferrihydrite having different Si/Fe molar ratios to hematite.

Si/Fe molar ratio	Temperature (°C)
0.0	300
0.01	400
0.05	500
0.10	600
0.25	800
0.50	¹
0.75	²

¹ Very poorly crystalline hematite, 800°C.

² No transformation product was observed at 800°C.

which hematite was first observed (Table 1). Herbillon and An (1969) reported similar results. No influence of Si on the XRD peak positions of the hematite products was noted, indicating that Si was not likely incorporated into the hematite structure. The ratios of WHH of the 104 and 110 XRD peaks, i.e., $(WHH_{104})/(WHH_{110})$, ranged from 1.04 to 1.44 (average value = 1.20). These results indicate that all hematite products produced during the dry-thermal incubation of ferrihydrite, exhibited a slight to moderate anisotropy (or deviation from sphericity) (Barron *et al.*, 1984). No trend of the influence of either initial Si content or incubation temperature on WHH ratio was noted, indicating that neither of these factors had a noticeable influence on the degree of anisotropy of the hematite.

The hematite particles, which formed by dehydration and reordering of the internal bonds of the ferrihydrite samples during the dry-thermal incubation, were spheroidal, irrespective of the Si/Fe molar ratio of the parent (Figure 2a). Hematite formed during thermal treatment of the Si-free ferrihydrite at 300°C gave broad IR bands centered at 529 and 452 cm^{-1} and a weak shoulder at about 325 cm^{-1} (Figure 3a). This hematite consisted of aggregates of spheroidal particles having individual diameters of about 20–80 Å, which was about the same as that of the untreated Si-free ferrihydrite. This particle diameter was about 10% of that of the globular hematite formed by the aqueous incubation of Si-free ferrihydrite at pH 12.5 and 91°C (Vempati and Loeppert, 1989). Electron diffraction patterns of the microcrystalline (i.e., <100 Å particle diameter) hematite contained weak spots, indicating that the product was poorly crystalline. With increasing temperature, the intensities of the 529- and 452- cm^{-1} bands increased, due apparently to the improved crystallinity of the hematite, which was also evident in XRD and electron diffraction patterns. Heating the Si-free ferrihydrite to 600°C produced an additional band at 378 cm^{-1} . Further heating to 800°C resulted in increased aggregation, increased electron density of the particles, increased particle size of the sintered hematite (to about 150–600 Å) (Figure 4a), and an additional IR band at 325 cm^{-1} (Figure 3b). The sharper electron diffraction

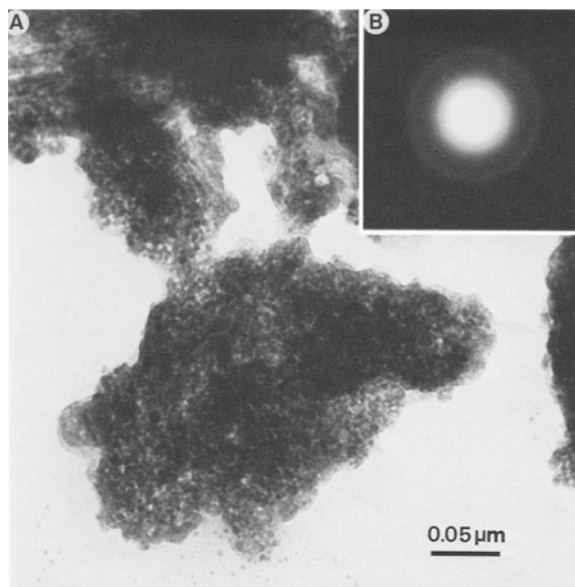


Figure 2. Transmission electron micrograph (A) and selected-area electron diffraction pattern (B) of hematite formed during the dry-thermal incubation of Si-free ferrihydrite at 300°C for 2 hr.

spot pattern following the high-temperature treatment also suggests a greater degree of crystallinity of the hematite (Figure 4b).

Hematite formed from the 0.01 Si/Fe molar-ratio ferrihydrite gave rise to only two broad IR bands at 528 and 443 cm^{-1} , following the 400°C thermal treatment. Further heating to 800°C produced no additional IR bands (Figure 5a). Also, the particle morphology and particle size did not change noticeably with the increase in incubation temperature from 400° to 800°C,

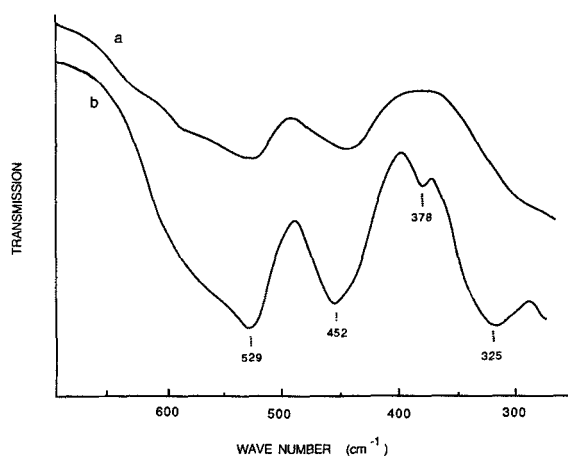


Figure 3. Infrared patterns of hematite formed from the dry-thermal incubation of Si-free ferrihydrite at (a) 300°C for 2 hr, and (b) 800°C for 2 hr.

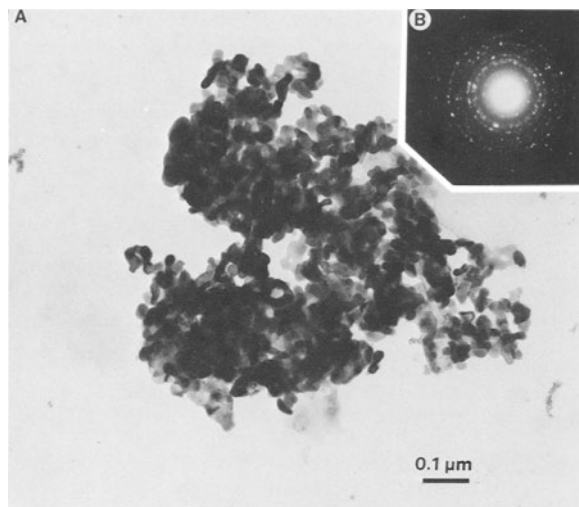


Figure 4. Transmission electron micrograph (A) and selected-area electron diffraction pattern (B) of hematite formed from the dry-thermal incubation of Si-free ferrihydrite at 800°C for 2 hr.

indicating that the Si may have prevented the formation of Fe–O–Fe bonds and the sintering of the hematite particles.

For the ferrihydrite having a 0.75 Si/Fe molar-ratio, IR vibrations attributable to Si–O stretching and bending were observed at 1050 and 459 cm^{-1} , respectively. The additional band at 789 cm^{-1} (Figure 5b), present after heating the 0.75 Si/Fe molar-ratio ferrihydrite to 800°C, was likely due to siloxane (Si–O–Si) vibrations (Hunt *et al.*, 1950), resulting from dehydroxylation of the silanol (Si–OH) groups. No IR bands characteristic of hematite were observed, even after the 800°C treatment.

In order for Si-containing ferrihydrite to transform to hematite, structural Fe–O–Si bonds must be broken prior to the formation of Fe–O–Fe bonds. With an increasing concentration of Si, higher temperatures were needed for the transformation of ferrihydrite to hematite. For the ferrihydrite having a 0.75 Si/Fe molar ratio, the 110 XRD peak was centered at 2.97 Å instead of the normally observed 2.54 Å for Si-free ferrihydrite (Vempati and Loepfert, 1989). The 2.97-Å peak did not shift after the sample had been heated at 800°C, suggesting that this temperature was insufficient to break the Fe–O–Si bonds or to alter the structure which was imposed by the presence of Si.

DISCUSSION

Assignment of infrared bands

Wilson *et al.* (1981), using an oriented deposit of a platy, hexagonal hematite, reported that the IR vibrations at 645 and 400 cm^{-1} were due to dipole moments parallel to the 'c' (A_{2u}) direction; whereas, the IR vi-

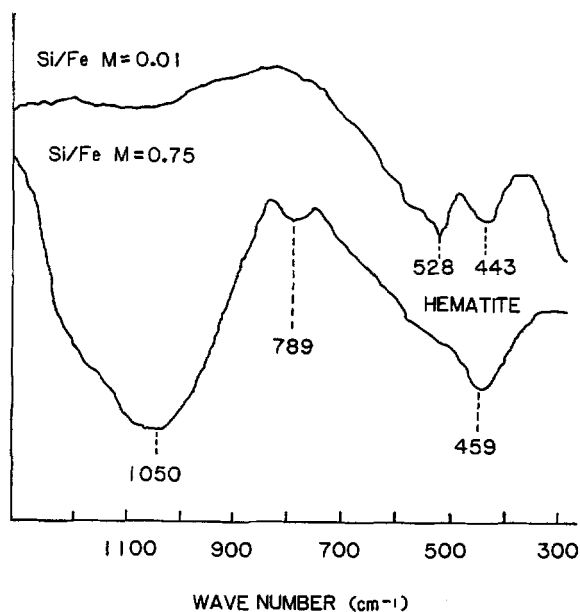


Figure 5. Infrared spectra of samples following dry-thermal treatment at 800°C for 2 hr: (a) hematite formed during the thermal transformation of ferrihydrite having a 0.01 Si/Fe molar ratio, and (b) ferrihydrite having a 0.75 Si/Fe molar ratio.

brations at 525, 440, and 300 cm^{-1} were due to dipole moments parallel to the 'ab' (E_u) plane (Rendon and Serna, 1981). Berreman (1963) noted that for a thin, flat film of cubic ionic crystals, the high-frequency modes are due to the longitudinal vibrations (ω_L); whereas, the low-frequency modes are due to the transverse vibrations (ω_T). For hematite crystals having a particle size smaller than the phonon wavelength, only the absorption bands due to surface modes are observed in the IR spectrum (Serna and Iglesias, 1986). The longitudinal (ω_L) vibrations should be observed for the A_{2u} representation, because the dipole moments are parallel to the 'c' direction; whereas, transverse (ω_T) vibrations should be observed for the E_u representation, because the dipole moments are parallel to the 'ab' plane.

In the present study, four IR bands corresponding to three ω_T vibrations (E_u) and one ω_L vibration (A_{2u}) were observed for the hematite formed by heating the Si-free ferrihydrite to 800°C (see Table 2). For the microcrystalline hematite formed at 800°C from Si-containing ferrihydrite or at $\leq 500^\circ\text{C}$ from the Si-free ferrihydrite, only two ω_T vibrations (E_u) and no ω_L vibrations (A_{2u}) were observed, due to the small particle size and poor degree of aggregation of the product. For the globular hematite formed during the aqueous-thermal incubation of the Si-free ferrihydrite, three ω_T vibrations (E_u) and one ω_L vibration (A_{2u}) were observed, but the wave numbers of the IR bands were different from those observed for the dry-thermally

Table 2. Infrared vibrations (cm^{-1}) of hematite formed during aqueous- and dry-thermal incubation of ferrihydrite or goethite.

D _g assignment	Crystal-line lattice vibration ¹	Precursor					
		Goethite		Ferrihydrite		Si-Ferrihydrite ²	
		Dry ³ (lath) ⁶	Aqueous ⁴ (globular) ⁶	Dry ³ (spheroidal) ⁶	Aqueous ⁴ (globular) ⁶	Dry ³ (spheroidal) ⁶	
A _{2u}	w _L	662	640	—	—	—	—
	w _T	526	—	—	—	—	—
E _u	w _L	622	—	—	—	—	—
	w _T	524	530	548	529	550	528
E _u	w _L	494	—	—	—	—	—
	w _T	437	440	471	452	450	443
A _{2u}	w _L	414	397	397	378	—	—
	w _T	299	—	—	—	—	—
E _u	w _L	386	—	—	—	—	—
	w _T	286	297	337	325	330	—
E _u	w _L	230	—	—	—	—	—
	w _T	227	230	—	—	—	—

¹ Tabulated by Rendon and Serna (1981).

² 0.01 Si/Fe molar ratio ferrihydrite from this study.

³ Heat treatment at 300°C.

⁴ Aqueous incubation at pH 12.5, 91°C for 36 hr.

⁵ Heat treatment at 800°C.

⁶ Particle morphology of the hematite product.

treated sample (Table 2). For the hematite formed during the aqueous-thermal incubation of Si-containing ferrihydrite, only three ω_T vibrations (E_u) were observed.

Implications

The aqueous and thermal incubation of Si-free and Si-containing ferrihydrite may yield hematite having very different particle morphologies and IR patterns. From the current study and other studies (Fischer and Schwertmann, 1975; Barron *et al.*, 1984; Serna and Iglesias, 1986; Serna *et al.*, 1987; Sidhu, 1988), the IR vibrations of hematite are dependent on the particle size and morphology of the product. The pseudohematite reported by Saraswat *et al.* (1980) and Cornejo (1987) may actually be a small particle size or less-crystalline hematite. The particle size and morphology of the hematite product of any transformation reaction is dependent on the precursor (including mineral form and the presence of coprecipitated or adsorbed phases) and the conditions of transformation. Therefore, differences in IR vibrations of hematite are directly attributable to particle size and morphology and to precursor and conditions of transformation. IR spectra and morphology of hematite particles may provide useful clues concerning the possible precursors and conditions of formation of hematite in soils.

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