

RELATION OF INFRARED, CRYSTALLOCHEMICAL, AND MORPHOLOGICAL PROPERTIES OF Al-SUBSTITUTED HEMATITES

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Abstract—Synthetic Al-hematites prepared from ferrihydrites, at low (~100°C) and high (400° and 800°C) temperatures were studied for their morphological, crystallochemical, and infrared (IR) characteristics. Low-temperature Al-hematites had a platy morphology (the plate thickness was inversely related to amount of Al substitution), and the high temperature Al-hematites showed a poorly defined morphology due to interparticle sintering. In the low-temperature Al-hematites shifts in the IR mode frequencies were noted and could be partly explained by a shape factor that was deduced from particle morphology. The intrinsic effect of Al substitution, however, was to produce shifts of as much as 10–15 cm⁻¹ for the highest Al substitution (~16%). Similar shifts were observed for the high-temperature hematites in which morphology was not appreciably affected by Al substitution.

Key Words—Aluminum, Hematite, Infrared spectroscopy, Iron oxides, Morphology, Unit-cell parameters.

INTRODUCTION

Hematite (α -Fe₂O₃) is present in many soils and sediments (Schwertmann and Taylor, 1977) and, similar to other iron oxides, can show substantial Al substitution (Janot and Gibert, 1970; Schwertmann *et al.*, 1977; Bigham *et al.*, 1978; Torrent *et al.*, 1980). Although as much as 16 mole % Al substitution has been found in synthesis experiments at low (70°C) (Schwertmann *et al.*, 1979) and high temperatures (~1000°C) (e.g., von Steinwehr, 1967), natural hematites are less Al-rich.

Al-substituted hematites have an a_0 value that decreases with increasing Al substitution (although there is a marked deviation from Vegard's rule) and may show inhibited growth in the crystallographic z -direction at substitutions >3–4 mole % Al (Schwertmann *et al.*, 1979). Al substitution also affects the infrared (IR) spectrum of hematite; Schwertmann *et al.* (1979) found that for hematites synthesized at low temperature (<100°C), absorption bands shifted to lower frequencies with Al substitution, probably because the smaller Al cation attracts oxygen atoms from neighboring FeO₆-octahedra thereby lengthening the Fe–O bond. In contrast, Mendelovici and Yariv (1981), in a study of lateritic bauxites from Venezuela, observed a shift to higher absorption values for Al-hematites heated at high temperatures (600°–1000°C). Rendón and Serna (1981) demonstrated that the IR spectrum of hematite microcrystals depends on the shape of the particles, an effect that can be accounted for by the use of a pure phonon theory (Serna *et al.*, 1982). Because

Al induces morphological changes in hematite, the objective of the present study was to elucidate the influence of Al substitution on IR spectra *per se*, as well as indirectly through morphological changes.

EXPERIMENTAL

Three series of hematites were examined. Series A ("low temperature") was prepared for coprecipitating 10 mmole of Fe + Al nitrates (mole % Al = 0–16%) with 2 M KOH to a final volume of 200 ml and pH 9. Na-citrate was then added to a final concentration of 2×10^{-5} M. The pH was readjusted to 9, if necessary, and the suspension was kept at about 100°C in polypropylene bottles and shaken occasionally by hand. After 8 days, the resulting products were treated with pH 3 NH₄-oxalate to remove any residual noncrystalline material. The salts were removed by washing at pH 8 to obtain good flocculation, and the solid products were dried at 60°C and gently crushed. In series B1 and B2 ("high temperature"), ferrihydrite was prepared as in series A, but by precipitating with a 13% NH₃ solution to a final pH of 7 and a final suspension volume of 150 ml. The suspension was dialyzed against deionized water, and the salt-free solid product was freeze dried. Hematite products from series B1 and B2 were obtained by heating the precipitates to 400° and 800°C, respectively. Noncrystalline material was removed and the products were treated as for series A.

The hematite products were identified by X-ray powder diffraction, and their unit-cell parameters were determined using the 104 and 110 lines (with PbNO₃ as

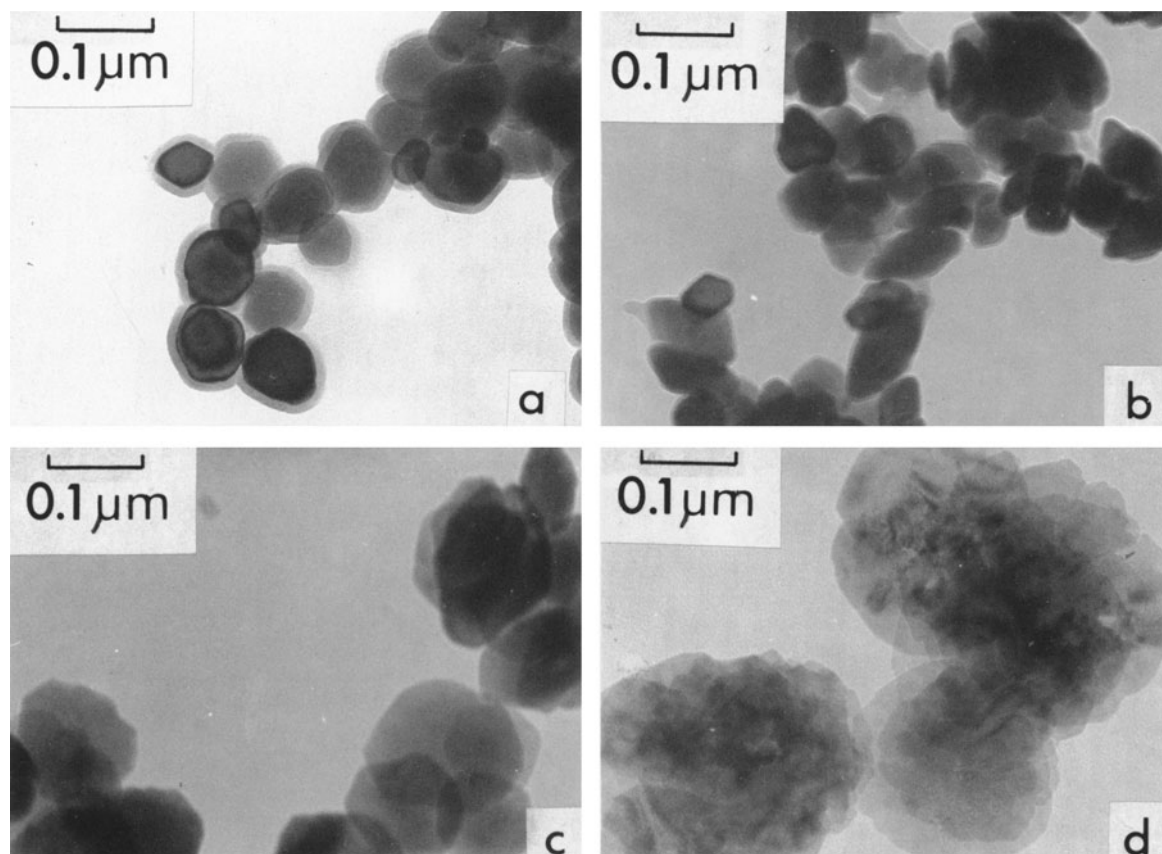


Figure 1. Electron micrographs of “low-temperature” hematites differing in Al substitution. 1a = 0.1 mole %; 1b = 4.3 mole %; 1c = 12.8 mole %; 1d = 16.0 mole %.

internal standard). The ratio $\text{Al}/(\text{Al} + \text{Fe})$ was determined by atomic absorption after dissolving the hematites in cold 11 M HCl. Electron micrographs (Philips EM 300 electron microscope) were obtained after dispersing the sample in acetone and evaporating a drop of the suspension on a carbon-coated copper grid. The IR spectra of the samples were recorded from KBr disks using a Perkin-Elmer 580B spectrophotometer. The precision was better than 2 cm^{-1} .

RESULTS AND DISCUSSION

Crystallochemical and morphological characteristics

Under the transmission electron microscope (TEM) the low-temperature hematites exhibited a platy morphology (Figure 1). At low Al substitution, the plates were hexagonal, about 500 \AA in diameter and relatively thick. As Al substitution increased the plates seemed to be thinner and to have a roughly circular outline; their diameter increased to $>1500 \text{ \AA}$ at Al substitutions greater than 12–13%. Aluminum substitution appeared, therefore, to promote anisotropic growth, as previously observed by Schwertmann *et al.* (1979). This anisotropic growth could be estimated from the X-ray

powder diffractograms of hematites, by measuring the widths of half height (WHH) of the 104 and 110 lines which are, respectively, a measure of crystal thickness normal to a near basal plane, and to a nonbasal plane. For series A WHH(104) increased by a factor of about 3 from unsubstituted to highly substituted hematites and WHH(110) decreased by a factor of about 1.3, i.e., the particles tended to be thinner and larger, in agreement with TEM observations. This trend can be expressed by the WHH(104)/WHH(110) ratio which is an estimate of the diameter/thickness ratio of the crystals and which increased with Al substitution (Table 1).

High-temperature hematites, regardless of their degree of substitution, had a poorly defined morphology (Figure 2) which is characteristic of sintering processes. Their WWW(104)/WHH(110) ratios were usually close to 1, excluding, thus, any substantial anisotropic growth (Table 1).

In all series, the a_0 and c_0 values decreased with increased Al content (Table 1). Most of these values were higher than those calculated by Vegard's rule, although the deviation was more marked for series A. These deviations may be related to the presence of

Table 1. Crystallochemical characteristics of synthetic hematites.¹

Sam- ple	a_0 (Å)	c_0 (Å)	$\frac{WHH(104)^2}{WHH(110)}$	Al/(Fe + Al) (mole %)
A1	5.034	13.760	1.43	0.1
A2	5.032	13.747	1.45	1.2
A3	5.030	13.740	1.65	2.4
A4	5.026	13.729	1.91	4.3
A5	5.022	13.723	2.78	6.1
A6	5.020	13.716	2.61	8.7
A7	5.019	13.714	3.33	12.8
A8	5.012	13.710	3.28	16.0
B11	5.033	13.745	1.46	0.1
B12	5.029	13.726	1.33	3.3
B13	5.027	13.721	1.39	3.6
B14	5.019	13.705	1.23	6.4
B15	5.011	13.659	1.22	11.2
B16	5.005	13.657	1.14	14.3
B17	5.000	13.652	1.01	16.0
B21	5.033	13.734	1.35	0.3
B22	5.026	13.706	1.00	3.6
B23	5.027	13.715	0.84	3.8
B24	5.019	13.682	1.19	6.6
B25	5.011	13.659	0.93	12.3
B26	5.012	13.662	0.88	12.9
B27	5.013	13.660	1.00	13.5

¹ See text for synthesis conditions of series A, B1, and B2. Within each series the only variable was Al substitution.

² WHH = width at half height of XRD lines.

bound water in the hematite structure (Wolska, 1981). Thus, the amount of extra water seemed to be inversely related to the temperature of formation. In any case, the relationship between the cell parameters and the amount of Al substitution varied, as is also evident from the data of von Steinwehr (1967), Caillere *et al.* (1960), Wolska (1976), and Schwertmann *et al.* (1979).

Infrared absorption spectra

Because the IR spectrum of powdered hematite depends on particle shape (Rendón and Serna, 1981; Ser-

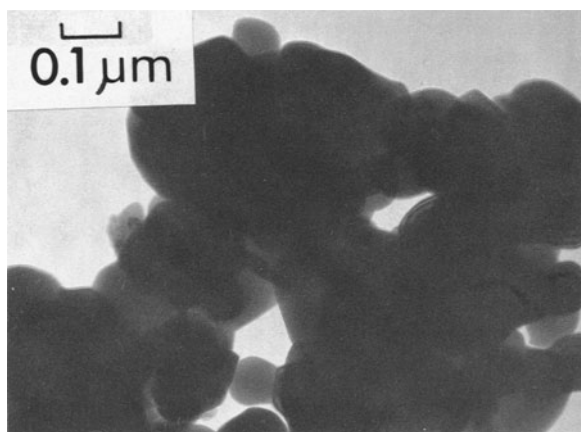


Figure 2. Electron micrograph of sample B21 (a "high-temperature" hematite) showing a poorly defined morphology.

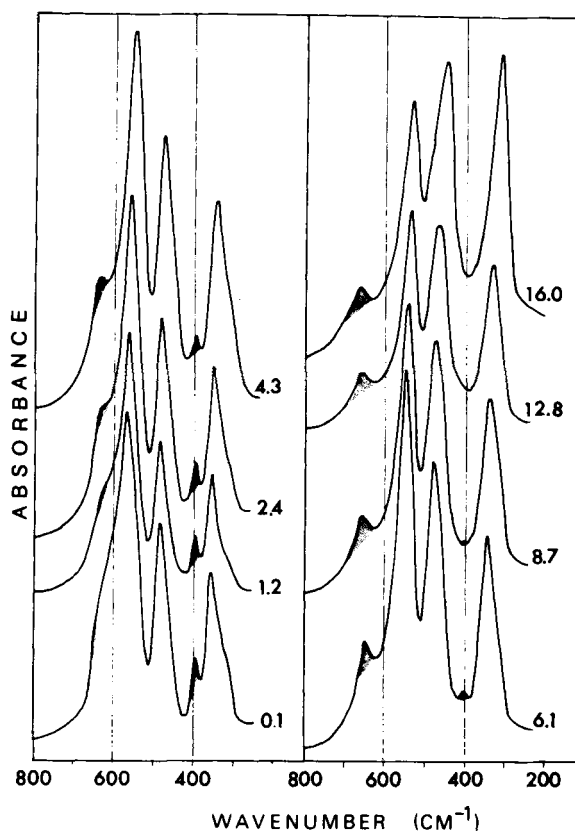


Figure 3. Infrared absorption spectra of series A (low-temperature) hematites for different values of Al substitution. The bands adscribed to the A_{2u} modes ($E||C$) have been shaded. Numbers in spectra refer to mole % Al.

na *et al.*, 1982), marked differences in the IR spectra of our samples were expected, irrespective of the intrinsic effect of aluminum. Hematite (D_{3d}^5 symmetry) gives 6 IR-active vibrations, two A_{2u} ($E||C$) and four E_u ($E\perp C$), in the 30–1000- cm^{-1} range. For particles much smaller than the radiation wavelength, however, as with the hematites in the present investigation, absorptions due to "surface modes" should appear for each mode between their crystal transverse (W_T) and longitudinal (W_L) frequencies (Ruppini and Englman, 1970).

The IR spectra of the low-temperature Al-hematites are shown in Figure 3 and the absorption maxima in Table 2. The absorption band at 230 cm^{-1} was not observed when KBr pellets were used. In agreement with their platy morphology (as seen by the TEM), the IR spectra of the low-temperature hematites showed a relative intensity greater for the E_u modes ($E\perp C$) than for the A_{2u} modes ($E||C$). In addition, as theoretically expected, with decreasing particle thickness (increasing Al content), the A_{2u} modes shifted to higher frequencies, whereas the E_u modes shifted to lower ones. Thus, A_{2u} approached W_L as the E_u modes approached W_T .

Table 2. Infrared absorption maxima (cm^{-1}) for the low-temperature ($\sim 100^\circ\text{C}$) synthetic Al-hematites.

Sample	Al/(Fe + Al) (mole %)	$A_{2\mu}(E C)^\dagger$ (cm^{-1})	$E_{\mu}(E \perp C)^\dagger$ (cm^{-1})			
A1	0.1	~ 620	390	565	482	352
A2	1.2	~ 625	392	564	482	352
A3	2.4	~ 630	394	562	482	351
A4	4.3	638	396	555	480	347
A5	6.1	649	398	549	480	343
A6	8.7	655	400	542	477	337
A7	12.8	658	—	535	468	332
A8	16.0	662	—	535	450	315

[†] Infrared-active vibrations.

For hematite and other corundum-type microcrystals, IR maxima depend on a shape factor, G , of the particle (Serna *et al.*, 1982). G varies between 0 and 1 depending on the axial ratios of the ellipsoid such that $G_1 + G_2 + G_3 = 1$, where the subscripts refer to each principal axis. For a revolution ellipsoid, two of the axial ratios are equal and $G_1 + 2G_2 = 1$, or $G_1 + 2G_{\perp} = 1$. For series A, the $G_{||}$ and G_{\perp} values, determined by the method of Serna *et al.* (1982, Figure 4), depended on the amount of Al substitution (Figure 4). As Al increased, G_{\perp} decreased and $G_{||}$ increased, a result that can be interpreted as a decrease in particle thickness along the z -direction, in agreement with the XRD data and the TEM observations. In series B1 and B2 no clear trends for the $A_{2\mu}$ and E_{μ} modes (data not shown) were noted due probably to the absence of a unique morphology in these samples, as evidenced by TEM observations. Although the contribution from each morphology to the total IR spectrum of a powder sample can be evaluated (Serna *et al.*, 1982), the values obtained for $G_{||}$ and G_{\perp} were adjusted reasonably well to the spectra. Thus, for series B1, the G values ranged between 0.74 and 0.56, and for series B2, between 0.56 and 0.40. These values indicate a better development

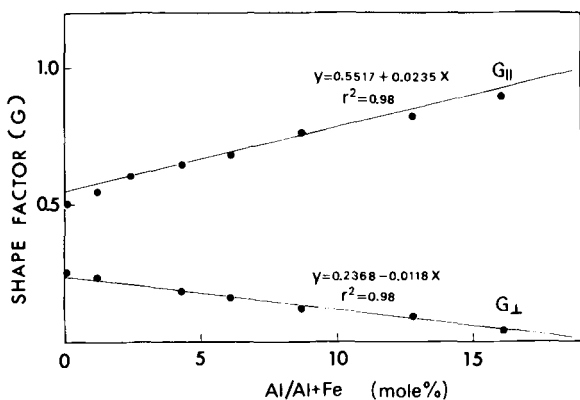


Figure 4. Relationships between the shape factor, G , and the Al substitution for low-temperature hematites (series A).

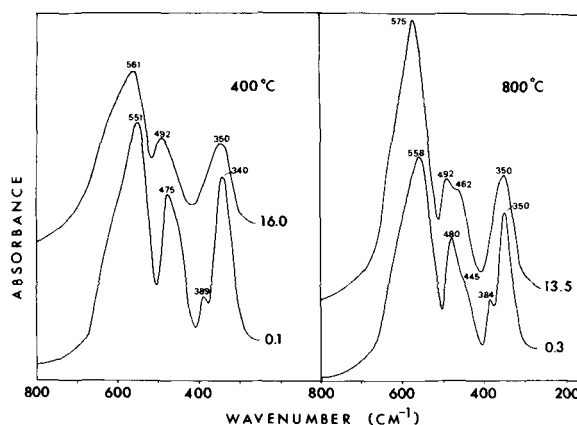


Figure 5. Infrared absorption spectra of unsubstituted and highly Al-substituted hematites from series B1 and B2 (high temperature).

of the crystal z -direction due to particle sintering at elevated temperature (Rendón and Serna, 1981; Rendón *et al.*, 1983).

Because the presence of aluminum did not apparently produce morphological changes in the high-temperature hematites, the intrinsic contribution of Al to the IR spectrum of hematite was then estimated. For the IR spectra of series B1 and B2, frequency differences of 10–15 cm^{-1} (depending on the mode) were observed between the unsubstituted and highly substituted samples (Figure 5). In addition, all of the modes were shifted to higher frequencies, i.e., they shifted towards the corundum ($\alpha\text{-Al}_2\text{O}_3$) modes, as expected. Similar behavior, in direction and magnitude, was observed for the lattice vibrations of Al-substituted goethites (Fey and Dixon, 1981).

Further evidence of the intrinsic effect of Al on the vibrational modes of hematite came from series A. It should be noted that the IR spectrum of the hematite with the highest substitution (16 mole % Al) was rather similar to that of the hematite obtained by heating goethite at 250°C , a hematite of platy morphology (Rendón and Serna, 1981). Here again, the modes were shifted as much as 10–15 cm^{-1} to higher frequencies for the Al-hematite with respect to unsubstituted hematite. If corundum is the end member of the substitution of Al for Fe in hematite, differences in frequency for the corresponding modes range from 100 to 150 cm^{-1} . Therefore, the observed frequency differences between pure and Al-hematites were as expected from linear interpolation between the IR frequencies of hematite and corundum.

In summary, the effect of Al substitution *per se*, on the IR spectra of hematites is to produce shifts in the mode frequencies of as much as 10–15 cm^{-1} for the greatest Al substitution ($\sim 16\%$). For those hematites having Al-induced, platy morphology, however, shifts can be higher as a result of the combined effect of morphology and Al substitution.

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Резюме—Синтетические Al-гематиты, полученные из ферригидритов при низких (~100°C) и высоких (400° и 800°C) температурах, исследовались для определения их морфологических, кристаллическо-химических и инфракрасных (ИК) характеристик. Низко-температурные Al-гематиты имели пластинчатую морфологию (толщина пластинок была обратно пропорциональна количеству замещенного Al), а высоко-температурные Al-гематиты указывали на плохо определенную морфологию в результате внутри-частичной агломерации. В случае низко-температурных Al-гематитов наблюдались сдвиги ИК частот, которые могут быть частично объяснены параметром формы, который определялся по морфологии частиц. Однако, результатом внутреннего эффекта замещения Al были сдвиги, достигающие величины 10–15 см⁻¹ для самого большого замещения Al (~16%). Подобные сдвиги наблюдались в случае высоко-температурных гематитов, для которых замещение Al не влияло значительно на морфологию частиц. [E.G.]

Resümee—Synthetische Al-Haematite, die aus Ferrihydrit bei niedrigen (etwa 100°C) und hohen (400°–800°C) Temperaturen hergestellt wurden, wurden im Hinblick auf ihre Morphologie, Kristallchemie und Infrarot (IR) Charakteristika untersucht. Niedrigtemperatur-Al-Haematite hatten eine tafelige Morphologie (die Tafeldicke war umgekehrt proportional zum Anteil der Al-Substitution), die Hochtemperatur-Al-Haematite zeigten eine schlecht zu definierende Morphologie aufgrund von Sinterung zwischen den einzelnen Partikeln. Bei den Niedrigtemperatur-Al-Haematiten zeigten sich Verschiebungen bei den IR-Frequenzen, die zum Teil durch einen Formfaktor erklärt werden konnten, der aus der Partikelmorphologie abgeleitet wurde. Der eigentliche Effekt der Al-Substitution war jedoch die Verschiebung von bis zu 10–15 cm⁻¹ für die höchste Al-Substitution (etwa 16%). Ähnliche Verschiebungen wurden bei den Hochtemperatur-Haematiten beobachtet, bei denen die Morphologie nicht wesentlich durch die Al-Substitution beeinflusst wurde. [U.W.]

Résumé—On a étudié des hématites-Al synthétiques préparées à partir de ferrihydrites, à des températures basses (~100°C) et élevées (400 et 800°C) pour déterminer leurs caractéristiques morphologiques, cristallochimiques, et infra-rouges (IR). Les hématites-Al de basse température avaient une morphologie à plaques (l'épaisseur de la plaque était inversement apparentée à la quantité de substitution d'Al), et les hématites de température élevée montraient une morphologie pauvrement définie à cause de la fusion interparticule due à la chaleur. Des déplacements de fréquences de mode d'IR dans les hématites-Al de température basse ont été remarqués et ont été partiellement expliqués par un facteur de forme déduit de la morphologie de particule. L'effet intrinsèque de la substitution d'Al, cependant, était de produire des déplacements d'autant que 10–15 cm⁻¹ pour la substitution d'Al la plus élevée (~16%). Des déplacements semblables ont été observés pour les hématites de température élevée dans lesquelles la morphologie n'a pas été appréciablement affectée par la substitution d'Al. [D.J.]