

MID-IR OPTICAL CONSTANTS OF SIX IRON OXIDE/OXYHYDROXIDE MINERALS. Timothy D. Glotch¹, ¹Stony Brook University, Stony Brook, New York 11784. tglotch@notes.cc.sunysb.edu

Introduction: Optical constants of geologic materials are useful for modeling of remote sensing data from Mars and other solar system bodies. To date, derivation of the visible and IR optical constants of iron oxides/oxyhydroxides have been limited to hematite and magnetite [1-3]. Iron oxides/oxyhydroxides are important components of the globally homogenous Martian fines and some basalts [4-5]. Extensive deposits of crystalline hematite also occur at several locations on the Martian surface [6-8]. In addition, iron oxides/oxyhydroxides have been suggested to occur on some asteroids and in the interplanetary dust [9-11]. Thus, the derivation of the mid-IR optical constants of iron oxide/oxyhydroxide minerals is highly desirable for interpretation of the surface mineralogy of Mars and outer solar system airless bodies as well as cosmic dust and perhaps discs around young stars.

In this work, we examine six iron oxides/oxyhydroxides—single crystals of hematite (α -Fe₂O₃) and magnetite (Fe₃O₄), and pressed pellets of maghemite (γ -Fe₂O₃), goethite (α -FeOOH), akaganéite (β -FeOOH), and lepidocrocite (γ -FeOOH). The hematite sample is from Brumado, Bahia, Brazil, and the magnetite sample is from Cerro Huañaquino, Bolivia. The maghemite is a synthetic powder manufactured by ISK Magnetics, and the other three samples are also synthetic powders described by [12-13].

Methods: Both the hematite and magnetite crystals were polished using successively finer grits, until they displayed optical specular reflection. The hematite crystal was cut perpendicular to the (001) face. Following [3], polarized spectra were acquired of surfaces perpendicular to the [001] and [100] axes to isolate the O and E rays. As magnetite is isotropic, its spectral character does not vary with direction, so a spectrum was acquired of one of the sample's natural crystal faces. Each of the synthetic powders was pressed at 18,000 psi using a Carver hydraulic press resulting in a 13 mm diameter compact pellet.

Bidirectional reflectance spectra of each of the six samples were acquired on Caltech's Nicolet Nexus 870 FTIR spectrometer and Stony Brook University's Nicolet 6700 FTIR spectrometer. Single crystal spectra were acquired from 400-4000 cm⁻¹ (2.5-25 μ m) using a KBr beamsplitter and DTGS detector with a KBr window, and from 50-600 cm⁻¹ (17-200 μ m) using a Solid Substrate beamsplitter and a DTGS detector with a polyethylene window. The spectra were merged to create a spectrum extending from 50-4000 cm⁻¹. Pressed pellet spectra were acquired from 400-2000

cm⁻¹ (5-25 μ m) and 100-600 cm⁻¹ (17-100 μ m) using the same apparatus.

All optical constants were determined from the reflectance spectra described above using Lorentz-Lorenz dispersion theory. Dispersion theory [14-15] is a mathematical formulation that represents the vibration of a crystal lattice as the sum of the vibrations of two or more harmonic oscillators. The vibration of each oscillator creates a dipole moment, which in turn produces the radiation that is measured in an infrared spectrum. Each oscillator is defined by three parameters: ν , $4\pi\rho$, and γ , which represent the center frequency of the oscillation, the band strength, and damping coefficient, respectively. An additional term, ϵ_0 , is the high frequency dielectric constant, which is a bulk mineral property rather than an oscillator-dependent property. Dispersion equations vary slightly in the literature, but we adopt the formulation of [16], which is widely used. As described by [16], dispersion theory relates these properties of the oscillators in a mineral to the optical constants, n and k by the following equations:

$$n^2 - k^2 = \epsilon_0 + \sum_j \frac{4\pi\rho_j \nu_j^2 (\nu_j^2 - \nu^2)}{(\nu_j^2 - \nu^2)^2 + (\gamma_j^2 \nu_j^2 \nu^2)}$$

$$nk = \sum_j \frac{2\pi\rho_j \nu_j^2 (\gamma_j \nu_j \nu)}{(\nu_j^2 - \nu^2)^2 + (\gamma_j^2 \nu_j^2 \nu^2)}$$

where n is the real index of refraction, k is the imaginary index of refraction, and j represents the j th oscillator. The derived values for the optical constants are inserted into the Fresnel equations to calculate modeled reflectivity as a function of wavelength for specular surfaces:

$$R_r = \frac{R_{\perp}^2 + R_{\parallel}^2}{2},$$

where

$$R_{\parallel}^2 = \frac{(\cos\theta - u)^2 + \nu^2}{(\cos\theta + u)^2 + \nu^2},$$

$$R_{\perp}^2 = \frac{[(n^2 - k^2)\cos\theta - u]^2 + (2nk\cos\theta - \nu)^2}{[(n^2 - k^2)\cos\theta + u]^2 + (2nk\cos\theta + \nu)^2}$$

$$u = \left(\frac{n^2 - k^2 - \sin^2 \theta + [(n^2 - k^2 - \sin^2 \theta)^2 + 4n^2 k^2]^{\frac{1}{2}}}{2} \right)^{\frac{1}{2}}$$

$$v = \left(\frac{-(n^2 - k^2 - \sin^2 \theta) + [(n^2 - k^2 - \sin^2 \theta)^2 + 4n^2 k^2]^{\frac{1}{2}}}{2} \right)^{\frac{1}{2}}$$

and θ is the angle of incident radiation measured from the surface normal (20° for Caltech and 30° for Stony Brook). R_{\perp} and R_{\parallel} are amplitudes, and must be squared to get the fractional intensities, which are the measured parameters. If desired, reflectivity may be converted to emissivity according to Kirchhoff's Law:

$$\varepsilon = 1 - R$$

Dispersion analysis is performed by iteratively adjusting the oscillator parameters until the best possible fit (minimum root mean square error) is achieved between the modeled spectrum and the spectrum measured in the laboratory.

Results and Future Work: The spectral variability of iron oxide minerals, and therefore their optical constants, is great. Examples of simple (magnetite) and complex (maghemite) oxide spectra and their derived optical constants are shown in Figures 1 and 2. The derived optical constants in both graphic and tabular form, as well as the oscillator parameters used to derive them are available online in the growing Stony Brook Optical Constant Database at http://ms.cc.sunysb.edu/~tglotch/optical_constants.htm. Although it would be ideal to determine oriented optical constants for each of the minerals described in this study, goethite, lepidocrocite, maghemite, and akaganéite most often occur as finely crystalline powders or macroscopically as crystal masses, making isolation of specific orientations very difficult. These pressed pellets are also less reflective than single crystals making acquisition of their spectra at the shortest and longest wavelengths difficult. Future work will involve extending the spectral (and optical constant) coverage of the pressed pellets out to 50 cm^{-1} at the low wavenumber end of the spectrum using the new Nicolet 6700 FTIR spectrometer at Stony Brook University.

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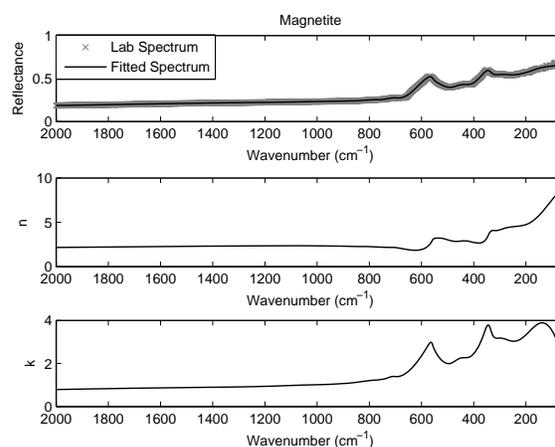


Figure 1. Measured and modeled spectra, n , and k of a single magnetite crystal. Data are displayed from $50\text{-}2000 \text{ cm}^{-1}$ but are available from $50\text{-}4000 \text{ cm}^{-1}$.

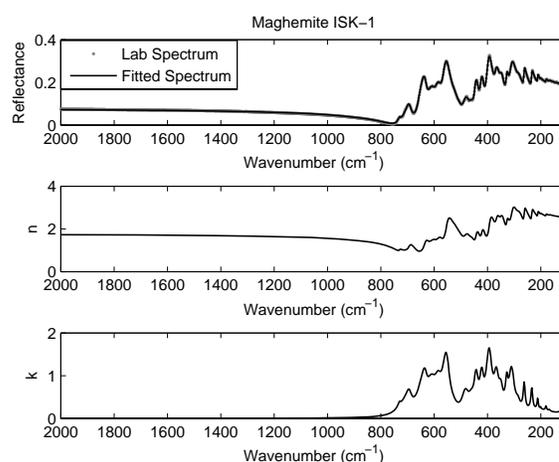


Figure 2. Measured and modeled spectra, n , and k of a pressed pellet of maghemite.