

EFFECT OF ALUMINUM SUBSTITUTION ON VISIBLE AND NEAR-IR OPTICAL PROPERTIES OF HEMATITE WITH IMPLICATIONS FOR MARTIAN SPECTRAL DATA. Richard V. Morris, Code SN4, NASA-JSC, Houston, TX 77058, and Howard V. Lauer, Jr., LEMSCO, Houston, TX.

#### INTRODUCTION

Hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) formed in the terrestrial weathering environment can exhibit substantial aluminum substitution. The degree of substitution is determined by comparing certain properties characteristic of the oxide component to those for synthetic, Al-substituted hematites whose physicochemical properties are known. Al substitution in hematite is accompanied by a decrease in size of the unit cell, inhibition of growth along the crystallographic z-axis which promotes a platy morphology, a decrease in the temperature of the Morin transition, a decrease in magnitude of the Mossbauer internal field strength, and shifts to higher energies of the positions of vibration bands in the mid-IR [e.g., 1-3]. Use of these data to determine Al contents of hematite in natural systems is in general not straightforward because there is often more than one way to produce the same result. For example, both Al substitution and particle morphology (which is also influenced by aluminum substitution) produce shifts in positions of vibration bands in the mid-IR. Similarly, both Al substitution and small particle diameter (superparamagnetic particles) cause a reduction in the Mossbauer internal field strength. The degree of substitution achieved by natural process is generally less than the maximum achievable (~33 mole % Al) by synthetic procedures [1,2].

Based on a study of pigmentary hematite supported on silica gel, [4] concluded that hematite as pigmentary particles is likely a mineralogical constituent of the martian surface. In particular, the 860-870 nm band characteristic of martian bright regions [5] is attributed to pigmentary hematite particles that are larger than ~10 nm in diameter. This is a consequence of the observation that a resolved band in the region 846-870 nm is present for hematite particles larger than ~10 nm in diameter but not for hematite particles smaller than that diameter [4,6]. It may be possible to infer the degree of aluminum substitution in martian hematite if the dependence of the position of the ~860 nm band on aluminum content is known.

The band in hematite is due to the electronic transition from the ferric ground state ( ${}^6\text{A}_1$ ) to the least energetic level of the first excited state ( ${}^4\text{T}_{1g}$ ). The corresponding transition in ferric-doped corundum ( $\alpha\text{-Al}_2\text{O}_3$ ) occurs near 1100 nm. This implies Al substitution in hematite should be accompanied by a longward shift in the position of the  ${}^4\text{T}_{1g}$  band. Based on Mossbauer measurements to estimate aluminum contents, [7] report that this is the case for a set of hematites produced in the terrestrial weathering environment. They found that the band position ranged from 860 to 877 nm as aluminum substitution ranged from 2 to 19 mole %. Use this data to infer Al contents from spectral data implies that the position of the  ${}^4\text{T}_{1g}$  band for unsubstituted hematite is essentially equal to 858 nm, which is not the case. As stated above, [6] report a range from 846 to 870 nm for a set of synthetic and essentially aluminum-free hematites. In order to better understand the relationship between band position and aluminum content, we obtained optical (visible and near-IR), Mossbauer, and XRD data for a set of synthetic Al-substituted hematites. Low-temperature optical data were obtained to determine if temperature is a significant effect with respect to interpretation of martian spectral data. The samples were prepared using a modification of a procedure given by [8].

## RESULTS AND DISCUSSION

Because we have not yet obtained compositional data, we used  $H_{int}$  determined from Mossbauer spectra at 293 K as a measure of the degree of Al substitution. The XRD data indicate that the reduction in  $H_{int}$  that can occur for sufficiently small particles is not an important factor for these samples. Figure 1 shows spectral data for representative samples of the Al-substituted hematites arranged in order of increasing Al content as indicated by the values of  $H_{int}$ . Sample 1 is unsubstituted, and Sample 4, according to the data of [2] has ~21 mole % Al. The vertical dashed line is at 865 nm, the  ${}^4T_{1g}$  minimum for Sample 1. Figure 2 is a plot of the position of the  ${}^4T_{1g}$  band minimum at 293 K as a function of  $H_{int}$  for all samples. In agreement with [7], the longward shift is ~15 nm for ~21 mole % Al. The magnitude of the shift is not much larger than experimental error and is less than the 25 nm range observed for unsubstituted hematites [6]. Between 293 and 173 K, the  ${}^4T_{1g}$  band shifted by ~10 nm to shorter wavelengths for all samples.

The relatively small shift (<15 nm) due to Al substitution together with the relatively large range (25 nm) found for unsubstituted hematites means that estimates of Al contents of hematites from spectral data alone is inherently imprecise for geologically reasonable amounts of Al (<20 mole %).

For Mars, location of the  ${}^4T_{1g}$  band in the region 860-870 nm tends to favor the presence of Al-free hematite, but up to ~10 mole % Al is not inconsistent with the data. For remote sensing of Mars, the temperature dependence of the  ${}^4T_{1g}$  is inconsequential.

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