OPTICAL SPECTRA AND BAND ASSIGNMENTS FOR THE HEMATITE (α-Fe₂O₃)-
CORUNDUM (α-Al₂O₃) SERIES. Richard V. Morris, SN4/NASA Johnson Space Center,
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Introduction: The assignment of absorption bands due to interelectronic
transitions of ferric iron in the optical spectra of hematite (α-Fe₂O₃) has
generally been done (e.g., 1,2,3) with reference to the energy-level diagrams
for ferric iron in a crystal field having cubic symmetry (e.g., 4). In this
representation, the band minimum near 0.87 μm in reflectance spectra is
assigned to 6A₁→4T₁, the shoulder near 0.62 μm to 6A₁→4T₂, and the edge near
0.55 μm to a wing of 6A₁→(4E, 4A). However, hematite actually has a trigonal
structure (e.g., 5), and group-theoretical considerations show that, while the above four transitions from the ground 6S state to the first
excited ⁴G state are permitted for cubic symmetry, six transitions are per-
mitted for the case of trigonal symmetry (e.g., 4). Thus, the above assign-
ments implicitly assume that the trigonal field for hematite can effectively
be regarded as cubic with a trigonal perturbation such that the effect of re-
duced symmetry is, at most, band broadening. There are certain potential
difficulties, however, in reconciling this view to the work of (6,7) on
ferric-doped corundum (α-Al₂O₃) where the crystal field also has a trigonal
symmetry. They observed too many bands to be consistent with the cubic
energy level diagram and suggested that lower symmetry may be the reason.

In order to determine if the cubic representation and derived assign-
ments are adequate for hematite, we determined the optical properties of
compounds having compositions intermediate between those of hematite and
corundum. This permitted us to follow positions of the bands in iron-dope
and corundum where the band assignments are easier to establish to hematite where
the cubic assignments are suspect.

Methods: Compounds compositionally intermediate between hematite and
corundum were prepared by precipitation from iron and aluminum sulfate aque-
ous solutions followed by dehydration at high temperature. The exact proce-
dure varied from composition to composition. X-ray diffraction was used to
verify hematite and corundum solid solutions. The diffuse reflectance spec-
tra were recorded on a Cary-14 configured with an integrating sphere.

Results and Discussion: Figure 1 shows the absorption spectrum of (7)
for a corundum solid solution having Al/Fe = 515 and our reflectance spectra
for solid solutions having Al/Fe = 6.5, 0.7, 0.3, 0.04, and 0.0. The band
assignments of (7) for their absorption spectrum are indicated in the figure.
There is a one-to-one correspondence in the position and number of bands
between the absorption spectrum and our reflectance spectrum with Al/Fe =
6.5. The dashed lines between the spectra connect individual bands which we
believe are reasonably assigned to the same transition in each case. The
bands at high energy become undetectable in our reflectance spectra for low
values of the Al/Fe ratio because the reflectance is too low (cf. 8).

It is clear that the assignment scheme for hematite in Figure 1 is very
different from the previously published scheme (1,2,3) discussed above. The
band at 0.86 μm is still associated with the cubic ⁶A₁→⁴T₁ transition, al-
though the knee near 1.03 μm is evidence that this band is actually a compo-
site one involving transitions to the levels of ⁴T₁ split by the trigonal
crystal field. The band manifest by the shoulder near 0.62 μm and the one
whose wing defines the 0.55 μm absorption edge are now assigned to transi-
tions to different levels of the split cubic ⁴T₂ level.
In conclusion, we suggest that for hematite the trigonal crystal field is sufficiently strong that it cannot be adequately represented by the cubic energy-level diagram and that previous band assignments for hematite spectra based on that diagram appear to be erroneous. An alternate scheme consistent with the data is that the 0.86 μm band is the envelope of the transitions from $^6A_1$ to the split components of the cubic $^4T_1$ level and that the shoulder near 0.62 μm and absorption edge near 0.55 μm are due to transitions from $^6A_1$ to the split components of the cubic $^4T_2$ level. The transitions from $A$ to the split components of the cubic ($^4E$, $^4A$) level would occur at higher energies, conceivably around 0.45 μm as in ferric-doped corundum.


Figure 1: Absorption spectrum of (7) for ferric-doped corundum and reflectance spectra of this study for hematite-corundum solid solutions. The parameter Al/Fe is the atomic ratio.