Temperature dependence of reflectance spectra and color values of hematite by in situ, high-temperature visible micro-spectroscopy

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ABSTRACT

We measured visible reflectance spectra and colors of hematite (α-Fe$_2$O$_3$) reagent powders and a natural feldspar grain containing dispersed hematite microcrystals from room temperature up to 800 °C using an in situ, high-temperature visible micro-spectrometer with dark field optics. The spectrum of room-temperature hematite powder is characterized by a nearly constant reflectivity in the range 400–550 nm, a shoulder near 620 nm, and a reflectivity maximum near 750 nm. The reflectance spectrum is similar to the diffuse reflectance spectra measured by a spectrophotometer and a conventional spectrometer with an integrating sphere. This result indicates that the dark field objective is suitable for measuring visible reflectance spectra of hematite powders with the visible micro-spectrometer. The reflectance of hematite powders in the longer wavelength region (>550 nm) decreases gradually with increasing temperature. The shoulder centered around 620 nm and the reflectance maximum near 750 nm also become indistinct at high temperatures. The calculated L* (dark-light), a* (red-green), and b* (blue-yellow) color values decrease with increasing temperature. This means that the red color of hematite becomes black with temperature increase. The calculated absorption intensities (Kubelka-Munk functions) suggest that this temperature dependence of the hematite powder-reflectance spectra can be mainly explained by a change in band gap absorption edges for a semiconductor (Urbach rule). The visible spectra and colors of a natural feldspar grain containing dispersed hematite microcrystals show a similar change with temperature, indicating that the temperature dependence can be observed under natural conditions at high temperatures, such as in volcanic eruptions.

Keywords: Visible micro-spectroscopy, dark field optics, hematite, visible reflectance spectra, L*a*b* color values, temperature dependence, Kubelka-Munk function

INTRODUCTION

Colors and visible spectra of volcanic materials at high temperatures change with time because transition metal ions such as Fe$^{2+}$ and Fe$^{3+}$ are oxidized/reduced and some oxidized products like hematite (α-Fe$_2$O$_3$) are formed. Color changes in volcanic materials have been used as indicators for their high-temperature oxidation (Tait et al. 1998; Miyagi and Tomiya 2002; Yamanoi et al. 2004). Yamanoi and Nakashima (2005) developed in situ, high-temperature visible micro-spectroscopy for monitoring visible spectral changes with time of the high-temperature oxidation of olivine at 600–800 °C. However, the spectral changes, which were obtained at high temperatures, included temperature dependence of visible spectra for heated materials (e.g., Burns 1993), besides the oxidation processes. Therefore, to quantitatively evaluate the oxidation processes and kinetics of volcanic materials, the temperature dependences at 600–800 °C of visible reflectance spectra of volcanic materials without oxidation have to be investigated first.

We have selected hematite as a representative oxidation product of volcanic materials. It was reported to be one of the causes of red coloring of a basaltic scoria (Yamanoi et al. 2004).

Hematite is stable at high temperatures [hematite does not change into maghemite (γ-Fe$_2$O$_3$) up to 1380 °C in air; Petras et al. 1998]. The temperature dependence of the visible spectrum of hematite has been reported in some previous studies (Marusak et al. 1980; Sherman et al. 1982; Morris et al. 1985, 1989, 1997; Mussella et al. 2002). Marusak et al. (1980) measured visible spectra of hematite at –173–7 °C. Sherman et al. (1982), Morris et al. (1985), and Morris et al. (1997) also measured visible spectra of hematite at 5 and 41 °C, –110 and 20 °C, and about –132, –63, and 27 °C, respectively. Morris et al. (1989) measured visible spectra of superparamagnetic (nanocrystalline) hematite at –100 and 20 °C. These data were taken at temperatures below 30 °C for simulating the martian surface. Mussella et al. (2002) measured spectral reflectivity of hematite from 510 to 860 nm up to about 900 °C. However, their spectra were affected by a notch filter artifact around 600 nm because a flash-lamp-pumped dry laser operating at 596 nm was used to heat samples.

In this study, we measured high-temperature visible reflectance spectra (400–800 nm) and colors of hematite reagent powders and those of mixtures of hematite and alumina powders at room temperature (about 27 °C) up to 800 °C by means of an in situ, high-temperature visible micro-spectrometer with dark field optics. In addition, a natural feldspar grain with dispersed hematite microcrystals was measured to confirm the temperature dependence under natural conditions. The focus of our work is...
investigating the origin of the temperature dependence on colors and visible spectral changes in hematite and its effect on oxidizing materials at high temperatures, comparable to the results reported by Yamanoi and Nakashima (2005).

**EXPERIMENTAL METHODS**

The measurements of visible reflectance spectra of hematite from room temperature to 800 °C were realized by adding a dark field objective to the high-temperature visible micro-spectrometer (Yamanoi and Nakashima 2005). A detailed configuration of the instrument is shown in the Appendix (Fig. 1).

Dark field reflectance spectra of hematite powders at high temperatures were measured by the following procedures. A dark spectrum was measured by closing the CCD detector shutter and was subtracted from all the spectra to remove CCD counts originating from dark current. About 0.05 g of hematite powder (Wako Pure Chemical Industries, Ltd., 99.9 wt%) was put on a platinum plate. A second electron image of the hematite obtained by a scanning electron microscope (SEM: JEOL JSM-5700LV) is shown in Fig. 1. The grain size distribution of the hematite powder measured by a laser-scattering particle size distribution analyzer (Shimazu SALD-3000S) at Kobe University showed a log-normal distribution, with the average grain size of about 0.4 µm. The hematite powder was set on the heating stage. As long known from pigment producing industries, the visible spectra and colors of hematite vary with particle size and shape (Kerker et al. 1979; Hund 1981; Morris et al. 1985; Torrent and Schwertmann 1987; Schwertmann 1993; Torrent and Barron 2003). Moreover, hematite color changed from red to purple because of increasing particle size during its heating to more than 800 °C (von Steinwehr 1969). Therefore, the hematite powder was first pre-heated on the heating stage to 800 °C and air-cooled to room temperature, to make a reproducible sample configuration.

The hematite powder was heated in air on the heating stage to 800 °C at a rate of 50 °C/min. The visible reflectance spectra of the sample were measured at every 100 °C from 800 to 1000 °C with a cooling rate of 50 °C/min and finally at room temperature (about 27 °C), with 10× accumulation of signals at an exposure time of 15 s, with an unexposed interval of 1 s. A thermal radiation spectrum of the sample was measured every 100 °C with the mechanical shutter closed to incident light. The same procedure was conducted on alumina (Al₂O₃) powders (Kanto Chemical Co., Inc., 99 wt%) as a white reference material at each temperature. The grain size distribution of the alumina powder measured by the laser-scattering particle size distribution analyzer showed a log-normal distribution, with the average grain size of about 50 µm. Pre-heating of the alumina powder was performed at 1000 °C.

Reflectance spectra of the sample at each temperature were calculated from the sample and reference reflection intensities and their thermal radiation intensities by Equation A1 in the Appendix. Errors in reflectance spectra were estimated by repeating measurements on alumina powders at 700 °C, with 60 spectra at an exposure time of 15 s, and were 0.02 (2 standard deviations; 2σ).

The previously reported visible reflectance spectrum of hematite powder is considered to result from the following absorption bands and an absorption edge due to a band gap (Fig. 2). Low reflectivities in the 400–550 nm range result from saturation by the combination of absorption bands in the ultraviolet (UV) region due to the O²⁻–Fe³⁺ charge transfer transition, and those around 400–450 nm due to a Fe²⁺–ligand field transition (Nagano et al. 2002). Reflectivity changes between 500 and 600 nm can be explained by the absorption edge of a band gap due to excitation of an electron from the valence band to the conduction band for semiconductors around 2.2 eV (570 nm) (Wang et al. 2005) and an absorption band of Fe³⁺–Fe²⁺ electron pair transition around 530 nm (Sherman and Waite 1985). The spectral feature near 650 nm may be due to a Fe²⁺–ligand field transition around 650 nm (Sherman and Waite 1985).

The L*a*b* color values at each temperature were calculated from the reflectance spectrum R at every 1 nm from 400 to 800 nm, which were averaged from reflectance spectra obtained at every 0.5 nm, by using Commission International de l’Eclairage (CIE) L*a*b* definitions (Wyszecki and Stiles 1982), to show quantitative color changes of hematite with temperature. The CIE recommended the CIE L*a*b* color system in 1976 as a standard for describing an objective color (Wyszecki and Stiles 1982; Nakashima et al. 1992). This color system can quantitatively and objectively describe a color that the CIE standard observer perceives under different conditions. The L* value is the psychometric brightness and corresponds to black (L* = 0) and white (L* = 100). The a* and b* values correspond to psychometric chromaticity. A positive a* value represents redness, and negative one greenness. A positive b* value corresponds to yellowness, and negative one blueness. We adopted a 10° viewing angle and CIE standard illuminant D₅₀ (a phase of natural daylight with a correlated color temperature of ~6500 K) as measurement conditions because these conditions are similar to observing natural rocks at field in the daytime. Errors of color values were estimated by 60% measurements of alumina powders at 700 °C and were 0.1 (2 standard deviations; 2σ).

To obtain quantitative absorption spectra of the hematite powder, Kubelka-Munk (KM) functions were applied to the sample reflectance spectra, R, using the following KM transformation (Kubelka and Munk 1931; Judd and Wyszecki 1975).

\[
\text{KM function} = \frac{(1 - R)^2}{2R}.
\]

Reflectance spectra and colors of mixtures of hematite and alumina powders (hematite contents were 0.1, 0.5, 1, 5, and 10 wt%) were measured by the above procedures. Temperature dependence of reflectance spectra and color values for alumina powders with low hematite contents simulating natural minerals were obtained. Moreover, we also measured a natural feldspar grain containing hematite microcrystals. This feldspar was from an altered granitic rock, Central Saga, Kyushu, Japan (Nakashima and Nagano 1989). These authors showed that white feldspars were colored red along a fracture and the reddish color is considered to be due to hematite and goethite by the diffuse reflectance spectra on the powders. Transmission electron microscopy (TEM) revealed the dissemination of at least two types of submicrometer iron minerals. Electron diffraction patterns on some
RESULTS AND DISCUSSION

Temperature dependence of visible reflectance spectra and color values of hematite powders

Reflectance spectra of the hematite powders with the dark field optics at high temperatures are shown in Figure 2. The spectrum at room temperature is characterized by a nearly constant reflectivity from 400 to 550 nm, a shoulder near 620 nm, and a reflectivity maximum near 750 nm. The reflectance spectrum of the hematite powder is consistent with reported spectra for hematite (e.g., Burns 1993; Mussella et al. 2002) and can be explained by the aforementioned absorption bands and absorption edge. Because our hematite grains are small (about 0.4 μm), the absorption due to the band gap may not be fully saturated and absorption bands at higher energies than the band gap such as electron pair transition can be partially observed.

The changes in reflectance with temperature were reversible, indicating that reproducible sample configurations could be obtained by pre-heating. As the temperature of hematite increases, reflectivities in the visible wavelength region longer than 550 nm mainly decrease gradually. The shoulder around 620 nm and the reflectance maximum around 750 nm become unclear. At 800 °C, the reflectance spectrum is almost flat in the whole visible wavelength region, with lower signal-to-noise (S/N) ratios. The decrease in reflectivities for 550–800 nm with increasing temperature is consistent with the results of Mussella et al. (2002).

The L* (dark-light), a* (red-green), and b* (blue-yellow) color values for hematite powders calculated from the reflectance spectra at high temperatures (Fig. 2) are shown in Figure 3 and Table 1. The L* and a* values are about 45 and 28 at room temperature, respectively. The b* value is about 13 at room temperature and decreases to nearly zero at 400 °C, and becomes negative values from 500 °C to 800 °C. This result clearly shows that the red color of hematite becomes black with increasing temperature. This quantitative change of color values with temperature is consistent with color changes perceived by the authors’ eyes.

Reflectance spectra of mixtures of hematite and alumina powders (hematite contents 0.1, 0.5, 1, 5, and 10 wt%) with the dark field optics at high temperatures were also obtained. All the spectra at room temperature have the same features as that of 100 wt% hematite (Fig. 2). These characteristic absorptions decrease with the contents of hematite in the mixtures. As the temperature of the mixtures increases, these features become unclear, and this result is similar to those of 100 wt% hematite (Fig. 2). The color values for the mixtures calculated from the reflectance spectra at high temperatures are given in Table 1. The a* values of all the mixtures decrease with increasing temperature. The increase in the value of a* with hematite content (Yokoyama and Nakashima 2005) becomes less pronounced at higher temperatures, especially for mixtures with hematite contents lower than 5 wt% (Table 1).

Origins of temperature dependence of visible reflectance spectra and color values of hematite

To represent quantitatively absorption intensities of hematite at high temperatures, their KM function values (KM spectra) are calculated as a function of energy (eV) (Fig. 4). The KM value (corresponding to absorbance) at room temperature is large at higher energy than 2.3 eV (shorter wavelength region than 550 nm) and shows a drastic decrease toward 2.1 eV (600 nm) and a gentler one down to 1.5–2 eV (600–800 nm). This is consistent with reported KM spectra for hematite (e.g., Nagano et al. 2002). The KM spectra at higher temperatures have lower S/N ratios due to intense thermal radiation in the visible region.

With increasing temperature, the absorbance of hematite increases in the whole visible range, in particular at the energy lower than 2.2 eV (wavelength region longer than 550 nm) (Fig. 4). The observed absorption edge appears to shift to the lower energy side with increasing temperature of hematite.

We first evaluate changes with temperature of the band gap absorption edge based on the Urbach rule (Urbach 1953). The change of absorption edge with temperature is given by Equation 2:

\[ A = A_0 \exp\left(-\frac{\sigma(E_0 - E)}{kT}\right) \]

where A is the absorption coefficient that is assumed to be proportional to the KM function here; \(A_0\), and \(\sigma\), empirical constants for hematite; \(E_0\), the band gap energy for hematite at 0 K; \(E\), the photon energy; \(k\), Bolzmann constant; \(T\), the absolute temperature (K). The exponential absorption edge is interpreted in terms of thermal fluctuations in the band gap energy (Skeettrup 1978). The main contribution to the temperature shift of the band gap energy...
is due to the temperature-dependent self-energies of the electrons and holes interacting with the phonons. Since the phonon number fluctuates in thermal equilibrium, the band gap energy also fluctuates, resulting in an exponential absorption tail below the average band gap energy. Fitting the absorption edge curves at different temperatures in Figure 4 by the Equation 2 gives \( E_0 \), \( \sigma \), and \( E_0 \) values, respectively.

The \( E_0 \) value of 2.33 eV is different from that of pure hematite (2.135 eV) (Monhanty and Ghose 1992). This difference is considered to be due to differences of sample preparation and purity of the samples. Since the visible spectra and colors of hematite vary with particle size and shape (Kerker et al. 1979; Hund 1981; Morris et al. 1985; Torrent and Schwertmann 1987; Schwertmann 1993; Torrent and Barron 2003), differences in sample preparation between this study and the previous study concerning band gap energy (Monhanty and Ghose 1992) may result in the \( E_0 \) difference. The \( E_0 \) value can be changed from 2.135 to 2.362 eV with an impurity of 0.10 wt% Mg in hematite (Monhanty and Ghose 1992). Therefore, the \( E_0 \) value of 2.33 eV might be associated with an impurity in our hematite samples (purity 99.9 wt%). The theoretical Urbach rule lines (black lines in Fig. 4) based on Equation 2 with the above parameters reproduce well the absorption edges, except for the data at 800 °C with low S/N ratios due to intense thermal radiation from the sample.

Second, we discuss the temperature dependence of absorption bands of Fe\(^{3+}\) electronic transitions such as the Fe\(^{3+}\) ligand field transition, the Fe\(^{3+}\)-Fe\(^{3+}\) electron pair transition and the O\(^2-\)-Fe\(^{3+}\) charge transfer transition. Burns (1993) summarized the temperature dependence of absorption bands of ligand field transitions. The absorption bands of ligand field transitions are expected to broaden and band centers to move to slightly longer wavelength due to thermal expansion with rising temperature. With increasing temperatures, absorption edges of O\(^2-\)-metal charge transfer transitions show red shifts, with increased absorption in the visible region in high-temperature spectra. The degree of red shift for the absorption band due to Fe\(^{3+}\) ligand field transition by thermal expansion can be estimated from reported change of Fe\(^{3+}\)-O\(^2-\) distance in hematite with temperature. The change of Fe\(^{3+}\)-O\(^2-\) distance by thermal expansion (the distance at 800 °C is larger than that at 20 °C by about 1% along the a axis; Saito 1965) will result in a red shift of about 20 nm to the higher wavelength (23 250 → 22 122 cm\(^{-1}\)) for the absorption band due to the Fe\(^{3+}\) ligand field transition at about 430 nm (23 250 cm\(^{-1}\)). The Fe\(^{3+}\)-Fe\(^{3+}\) electron-pair transition occurs at energies given approximately by the sum of two single ion Fe\(^{3+}\) ligand field transitions (Sherman and Waite 1985), and the red shift with temperature of the absorption band due to the Fe\(^{3+}\)-Fe\(^{3+}\) electron pair transition may be several tens of nanometers. In addition, an absorption tail in the UV region due to the O\(^2-\)-Fe\(^{3+}\) charge transfer transition might shift by about 100 nm from 300 to 1100 K, based on high-temperature spectra of olivine, which has an O\(^2-\)-Fe\(^{3+}\) charge transfer transition (Fukao et al. 1967). Therefore, these considerations imply that the red shifts of absorption bands of Fe\(^{3+}\) transitions with increasing temperature is no more than a few hundred nanometers.

Based on the above considerations, the observed temperature dependence of visible spectra (Fig. 2) and colors (Fig. 3) of hematite cannot be explained merely by the red shifts of absorption bands of Fe\(^{3+}\) transitions with increasing temperature, but must be mainly explained by the change of absorption edge with temperature (Fig. 4).

**Table 1. Summary of temperature dependence of color values of the mixtures of hematite and alumina powders and the natural feldspar grain calculated from their high-temperature reflectance spectra**

<table>
<thead>
<tr>
<th>Hematite content (wt%)</th>
<th>Temperature (°C)</th>
<th>Color values</th>
<th>Color values</th>
<th>Sample</th>
<th>Color values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L(^2) (dark-light)</td>
<td>a(^*) (red-green)</td>
<td>b(^*) (blue-yellow)</td>
<td>L(^*)</td>
<td>a(^*)</td>
</tr>
<tr>
<td>100</td>
<td>800</td>
<td>28.5</td>
<td>1.3</td>
<td>−1.6</td>
<td>54.5</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>29.4</td>
<td>2.7</td>
<td>−1.1</td>
<td>33.1</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>30.1</td>
<td>3.5</td>
<td>−0.7</td>
<td>60.1</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>31.0</td>
<td>4.9</td>
<td>−0.2</td>
<td>50.2</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>32.1</td>
<td>7.1</td>
<td>0.5</td>
<td>49.0</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>33.4</td>
<td>10.7</td>
<td>1.8</td>
<td>48.9</td>
</tr>
<tr>
<td></td>
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<td>35.2</td>
<td>15.8</td>
<td>4.1</td>
<td>49.9</td>
</tr>
<tr>
<td></td>
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<td>22.2</td>
<td>8.1</td>
<td>52.1</td>
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<tr>
<td></td>
<td>RT</td>
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<td>26.2</td>
<td>12.0</td>
<td>54.1</td>
</tr>
<tr>
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<td>1.1</td>
<td>0.0</td>
<td>90.5</td>
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<td>1.3</td>
<td>0.0</td>
<td>90.5</td>
</tr>
<tr>
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<td>2.0</td>
<td>0.3</td>
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<td>1.4</td>
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<td>7.7</td>
<td>2.5</td>
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<td>12.4</td>
<td>4.3</td>
<td>84.8</td>
</tr>
<tr>
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<td>18.6</td>
<td>7.2</td>
<td>84.3</td>
</tr>
<tr>
<td></td>
<td>RT</td>
<td>48.8</td>
<td>22.8</td>
<td>10.1</td>
<td>84.3</td>
</tr>
</tbody>
</table>

Note: RT = room temperature (about 27 °C).
Temperature dependence of visible reflectance spectra and color values of a natural feldspar with hematite microcrystals

To investigate the temperature dependence of visible spectra of hematite in natural minerals, we measured a natural feldspar grain containing dispersed hematite microcrystals. Reflectance spectra of the feldspar grain at room temperature up to 800 °C are shown in Figure 5a. The spectral changes with temperature were reversible, indicating that pre-heating cause a reproducible sample configuration. The spectrum at room temperature is characterized by a shoulder near 600 nm similar to the standard hematite powder (Fig. 2), indicating that the spectral features of this feldspar are mainly due to hematite microcrystals. With increasing temperature, reflectivities of the feldspar in the visible wavelength region longer than 550 nm decrease gradually. The shoulder around 600 nm becomes indistinct at higher temperatures. This temperature dependence of visible spectra of the natural feldspar is similar to that of hematite powders (Fig. 2).

The color values for the natural feldspar grain with dispersed hematite microcrystals calculated from the reflectance spectra at high temperatures are shown in Table 1. Changes in a* values from those at room temperature for the feldspar are shown in Figure 5b with those of mixtures of hematite and alumina powders. The a* value of the feldspar is about 6 at room temperature and decreases to about 2 at 800 °C (Table 1), and this a* value decrease of about 4 corresponds to that of hematite-alumina mixture with hematite content of 0.1 wt% (Fig. 5b). This is consistent with the reported iron impurity contents of some natural feldspars (0.04–0.19 wt% as FeO) (Hofmeister and Rossman 1984).

These results indicate that the temperature dependence of the visible spectra of hematite can be observed in some natural systems at high temperatures, such as in volcanic eruption processes. Volcanic materials can be held at high temperatures in a magma chamber, typically at above 750 °C (e.g., Spera 2000), and cooled down to ambient temperatures after eruption from a vent. When we observe volcanic materials that includes dispersed hematite microcrystals, the volcanic materials should appear black at high temperatures just after the eruption from the vent but should become red after cooling.

This dependence of hematite color on temperature will affect visible spectral changes shown by oxidizing materials at high temperatures, such as the results reported by Yamanoi and Nakashima (2005). However, visible spectral changes with time of volcanic materials at a given high temperature, obtained by means of in situ, high-temperature visible micro-spectroscopy, may not be affected by temperature in the same way as hematite. Therefore, in situ high-temperature visible micro-spectroscopy will be suitable for studying oxidized products except for hematite. A possible candidate for a suitable sample may be Fe$^{3+}$ ions in silicate mineral structures such as ferriolivine (Veblen

**Figure 4.** Calculated Kubelka-Munk (KM) spectra of the hematite powder from room temperature to 800 °C as a function of energy (gray curves). Black lines represent theoretical changes of the absorption edge with temperature obtained from the Urbach rule (Eq. 2).

**Figure 5.** (a) High-temperature reflectance spectra of a natural feldspar grain containing dispersed hematite microcrystals from room temperature to 800 °C. The spectra at room temperature, 300, 500, and 800 °C are shown. (b) Changes in a* (red-green) values from values at room temperature for the natural feldspar grain with dispersed hematite microcrystals and for the mixtures of hematite and alumina powders.
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Monhanty, S. and Ghose, J. (1992) Studies on some silicate mineral structures are not expected to show significant temperature dependence of their visible spectra and colors due to temperature dependence of the band gap for semiconductors (Urbach rule), observed here. Although further studies narrowing down applicable scope for in situ high-temperature visible microspectroscopy are needed, the methodology may be useful for tracing oxidation processes of minerals at high temperatures.

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Wavelength was calibrated by Hg emission lamp. To obtain high S/N ratio of reflectance spectra and homogeneous intensity distribution of incident light spectra in the 400–800 nm range, we removed the near-infrared (NIR) cut-off filter and placed HOYA HA-50, Olympus LB-200, and LBD filters in the light output path. We also used a HOYA HA-30 filter after the objective lens, to decrease intense thermal radiation from heated samples. We attached a mechanical shutter (UNIBLITZ) to the light source to obtain spectra of thermal radiation of samples by closing the shutter. An objective lens and a beam splitter for dark field were used because the dark field reflectance spectra collect diffusely scattered light reflected by the sample powders. The dark field optics uses different illumination from that of normal bright optics. The dark field optics have illumination with limited incident angles (about 20–25°) and receives vertical light from samples. The bright field optics vertically illuminate samples and measures reflected light from samples concentrically with the illumination. The core diameter of the output fiber was 100 µm, and a 5× dark field objective lens was used. A measurement spot size was about 100 µm. A heating stage was placed on the mechanical sample stage of the microscope. The heating cell is heated by Pt-PtRh heaters that are embedded around the sample chamber, and the sample on the heating stage is heated by thermal conduction. The temperature is controlled by a Pt-PtRh thermocouple just below the sample. Errors in temperature at the heating stage were estimated to be less than ±1 °C, based on the melting of Au (Suzuki and Nakashima 1999). Transparent glass windows can be set on the sample chamber of the heating stage, and inert gas can be flowed into the sample chamber for preventing sample oxidation at high temperatures.

Reflectance spectra of the sample at each temperature were calculated by the following relation from the sample and reference reflection intensities and their respective thermal radiation intensities:

$$R = \frac{I_{\text{sam}} - I_{\text{TR, sam}}}{I_{\text{ref}} - I_{\text{TR, ref}} / 0.8}$$

where $R$ is the reflectance of the sample at a temperature; $I_{\text{sam}}$, the reflection intensity of the sample at the temperature; $I_{\text{TR, sam}}$, the thermal radiation of the sample at the temperature; $I_{\text{ref}}$, the reflection intensity of the standard alumina powder at the temperature; $I_{\text{TR, ref}}$, the thermal radiation of the alumina powder at the temperature. Since the reflection intensity of alumina powder at room temperature measured by a conventional spectrophotometer is about 0.8, the reflection intensity of alumina powder obtained by the micro-spectrometer was divided by 0.8. Reflection intensity of alumina powder did not change significantly with temperature.

To check the validity of the dark field reflectance spectra measured by the visible micro-spectrometer and calculations of L*a*b* color values from the reflectance spectra, we measured diffuse reflectance spectra and determined color values of the same standard hematite powder by conventional methods of color measurements (Appendix Fig. 2). After white calibration by using a standard reference white material (a synthetic white opal) having known reflectance spectra, diffuse reflectance spectra at every 10 nm in the range 360–740 nm and color values of the hematite powder in a transparent glass container were measured by a spectrophotometer (KONICAMINOLTA CM2600d), which has an integrating sphere with diffuse lighting from the bottom of the glass containers (Appendix Fig. 2, curve c). The effective measurement diameter of the spectrophotometer was...
Specular reflection components were excluded at these measurements. The same color-measurement conditions (viewing angle and illuminant) as the dark field reflectance spectra measurements were adopted. Diffuse reflectance spectra of the same hematite powder at every 1 nm in the range 350–800 nm were also measured by a UV-Visible-NIR spectrometer (Jasco V570 with an integrating sphere attachment ISN-470) (Appendix Fig. 2, curve d). In addition, a reflectance spectrum of the hematite powder under normal bright field optics was also measured by the visible micro-spectrometer with bright field optics for comparing spectra by different lighting methods under the micro-spectrometer (Appendix Fig. 2, curve b).

Visible reflectance spectra and color values under dark field optics

The visible reflectance spectrum of the hematite powder at room temperature was measured under the visible micro-spectrometer with dark field reflection optics (Appendix Fig. 2, curve a). The shape of the reflectance spectrum of the hematite powder under dark field optics is different from that with the bright field optics (Appendix Fig. 2, curve b) and similar to those of the diffuse reflectance spectra (Appendix Fig. 2, curves c and d). The dark field optical setup is therefore suitable for measuring diffuse reflectance spectra of the hematite powder with the visible micro-spectrometer. However, absolute reflectance values of dark field and diffuse reflectance spectra are different. This difference partially results from the reflectance of the reference material (alumina powder) under dark field optics, which is taken as just 0.8 in the visible wavelength region. In fact, the reflectance values of alumina powder are not exactly 0.8; they start at about 0.7 at 350 nm and increase gradually to about 0.85 at 750 nm. The dark field setup has limited incident angles (about 20–25°), while the diffuse lighting by the integrating sphere has whole lighting angles without specular reflection components. This difference of illumination may partially affect the reflectance differences.

The L*, a*, and b* color values of the hematite powder at room temperature calculated from the microscopic dark field spectrum are 40.3, 26.2, and 12.0, respectively (cf. Table 1). The L*a*b* values for the same hematite powder measured by the spectrophotometer are 34.7, 23.2, and 14.4, respectively. The difference in these color values originates from the above differences in measurements of reflectance spectra and wavelength interval, and regions used for calculating color values (every 1 nm from 400 to 800 nm for the visible micro-spectrometer with dark field optics and every 10 nm from 360 to 740 nm for the spectrophotometer). Despite these differences, color values obtained under the microscopic dark field optics are considered to be useful for representing color change trends of hematite.