

HIGH TEMPERATURE CRYSTAL FIELD SPECTRA OF TRANSITION METAL-BEARING MINERALS: RELEVANCE TO REMOTE-SENSED SPECTRA OF PLANETARY SURFACES

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Introduction. Transition metal ions in silicate minerals and glasses contribute to the visible-near infrared spectral profiles of planetary surfaces. The 0.4-2.5 μ m region of the Moon, Mercury and Mars, in particular, is dominated by crystal field and intervalence charge transfer transitions within and between cations of Fe and Ti, the more abundant transition elements on these planets. Weaker spectral features from less abundant Cr and Mn ions might be resolvable, however. Recently, temperature-induced variations of the electronic spectra of heated ferromagnesian silicate minerals and Fe-Ti bearing glasses were described, and changes documented of energies and intensities of Fe²⁺ crystal field bands in olivines and pyroxenes [1,2,3]. We report here results of high temperature crystal field spectral measurements of a variety of heated minerals containing Cr³⁺, Mn²⁺ and Fe³⁺ ions, and correlate the temperature-induced variations with those previously observed for Fe²⁺-bearing silicates.

Background. Two trends emerging from early studies [4] of temperature variations of crystal field spectra of transition metal compounds were: first, absorption bands shift to slightly longer wavelengths (lower energies) with rising temperature due to changes (expansion) of cation coordination sites; and second, intensities of absorption bands increase as temperature rises due to vibronic coupling (changes in population of vibrational and electronic energy levels of the cation). These trends, however, were found not to be generally applicable to spin-allowed crystal field transitions in octahedrally coordinated Fe²⁺ ions in common ferromagnesian silicates. For example, high temperature absorption spectral measurements of olivines [1,5,6] revealed that the 1.04-1.08 μ m band (γ -polarization) due to Fe²⁺ on the M2 site not only moved to lower wavelengths with rising temperature, but its intensity also decreased at elevated temperatures. These changes contrasted with the olivine 0.8 μ m and 1.2 μ m bands (due to Fe²⁺ on the M1 site) which increased in intensity and shifted to longer wavelengths at elevated temperatures. Spectra of pyroxenes revealed that whereas the absorption band at 0.9 μ m intensified and moved to longer wavelengths, the 1.8 μ m band in orthopyroxenes and pigeonites did not shift in energy and decreased in intensity [1]. These results for octahedrally coordinated Fe²⁺ ions in olivines and pyroxenes suggested a need to examine temperature variations of the crystal field spectra of other transition metal ions [7], including spin-allowed transitions in Cr³⁺ and spin-forbidden transitions in Mn²⁺ and Fe³⁺, in well-characterized rock-forming minerals.

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Results. Polarized absorption spectra at temperatures between 25°C and 400°C were measured on crystals of ruby [Cr³⁺-corundum, Al₂O₃], emerald [Cr³⁺-beryl, Be₃Al₂Si₆O₁₈], andradite [Fe³⁺-garnet, Ca₃Fe₂(SiO₄)₃], epidote [Ca₂(Fe³⁺, Al) (Al₂O(SiO₄)₂(Si₂O₇)OH)], spessartine [Mn²⁺-garnet, Mn₃Al₂(SiO₄)₃] and rhodonite [(Mn²⁺, Fe, Ca)₅Si₅O₁₅].

Ruby. Cr³⁺ ions occur in a six-coordinated symmetry C_{3v} site.

Spin-allowed bands at approx. 18,000 cm⁻¹ (⁴A₂→⁴E, ⁴A₁) and 25,700 cm⁻¹ (⁴A₂→⁴E, ⁴A₂) shifted to lower energies by 330-430 cm⁻¹ over the temperature range 20-400°C, broadened, and intensified.

Emerald. Cr³⁺ ions occur in a six-coordinated, symmetry D₃ site. Spin-allowed bands at approx. 16,000 cm⁻¹ (⁴A₂→⁴E, ⁴A₁) and 24,000 cm⁻¹ (⁴A₂→⁴E, ⁴A₂) shifted to lower energies by 260-410 cm⁻¹ between 20°C and 300°C. The band widths and integrated intensities both increased. The spin-forbidden band at 14,600 cm⁻¹ (⁴A₂→²E) also shifted to lower energy by 150 cm⁻¹ and greatly decreased in intensity.

Andradite. Fe³⁺ ions occur in a slightly distorted octahedron. The broad, weak spin-forbidden bands at 17,000 cm⁻¹ (⁶A_{1g}→⁴T_{2g}) and 11,700 cm⁻¹ (⁶A_{1g}→⁴T_{1g}) shifted to higher energies by 200-300 cm⁻¹ between 20°C and 400°C, broadened significantly, and intensified. The crystal field-independent transitions ⁶A_{1g}→⁴E_g, ⁴A_{1g} consisting of a narrow band at 22,670 cm⁻¹ and a slightly broader band at 22,900 cm⁻¹, shifted by approx. 150 cm⁻¹ to lower energies between 20°C and 300°C and their intensities decreased sharply.

Epidote. Fe³⁺ ions occupy the very distorted six-coordinated, symmetry C_s site. The sharp field-independent (⁶A₁→⁴A₁, ⁴E) peaks at 21,800 cm⁻¹ and 21,000 cm⁻¹ shifted to lower energies by 200-300 cm⁻¹, broadened, and decreased in integrated intensity between 20°C and 200°C. The broad field-dependent (⁶A₁→⁴T₁; ⁶A₁→⁴T₂) bands, which are strongly polarization dependent in epidote, showed negligible or small decreases in energy at elevated temperatures.

Spessartine. Mn²⁺ ions occur in eight-fold coordination in the garnet structure. All three spin-forbidden transitions (⁶A₁→⁴A₁, ⁴E at 24,500 cm⁻¹; ⁶A₁→⁴T₂ at 23,300 cm⁻¹; and ⁶A₁→⁴T₁ at 20,000 cm⁻¹) decreased in intensity between 20°C and 400°C. The 24,500 cm⁻¹ band shifted to higher energies by about 200 cm⁻¹, while the other two bands moved 500 cm⁻¹ to lower energies.

Rhodonite. Mn²⁺ ions occupy all five cation sites. Field-independent bands at 29,120 cm⁻¹ (⁶A₁→⁴E(D)) and 24,460 cm⁻¹ and 24,180 cm⁻¹ (⁶A₁→⁴A₁, ⁴E(G)) decreased in intensity and shifted approx. 200 cm⁻¹ to lower energies between 20°C and 400°C. Field-dependent bands at 27,800 cm⁻¹ (⁶A₁→⁴T₂(D)) and 23,600 cm⁻¹ (⁶A₁→⁴T₂(G)) decreased in energy and intensity with increased temperature, whereas that at 18,500 cm⁻¹ (⁶A₁→⁴T₁(G)) exhibited very little change in position or intensity.

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Discussion. Changes of spectral parameters with temperature can be correlated with crystal structural changes, primarily, and with changes in the character of the cation-oxygen bond in the heated minerals [1,7]. Overall results indicate energy shifts of the crystal field bands towards the free ion state, the shifts being correlated with the thermal expansion of the cation site and the degree of distortion of the coordination polyhedra in the few minerals (e.g. olivines, pyroxenes, garnets, beryl) for which high temperature crystal structure refinements are available. Changes in the intensity of spin-allowed crystal field bands with temperature can be attributed to increases of vibronic coupling and changes of site distortion with temperature. The marked decrease in intensity of field-independent spin-forbidden bands of Fe^{3+} , Mn^{2+} and Cr^{3+} is poorly understood.

Applications. High temperature absorption spectra of transition metal-bearing minerals, not only provide crystallographic information on the nature and extent of distortion and expansion of cation sites in heated minerals, but also enable the positions of diagnostic bands to be calibrated as a function of temperature. Electronic spectral features due to crystal field transitions in Fe^{2+} , Fe^{3+} and Ti^{3+} ions and to intervalence charge transfer transitions in $\text{Fe}^{2+}\rightarrow\text{Ti}^{4+}$, $\text{Ti}^{3+}\rightarrow\text{Ti}^{4+}$ and $\text{Fe}^{2+}\rightarrow\text{Fe}^{3+}$ clusters are likely to dominate the spectra of widely dispersed regolith materials on most planetary surfaces. However, the possibility always exists that these and other transition metal ions may be identifiable by their crystal field spectra in gossans overlying ore deposits on planetary surfaces, particularly those (e.g. Venus) showing evidence of crustal plate movements. In such cases, metallogenic provinces near subduction zones and spreading centers may occur. In anticipation of very high resolution (i.e. the ability to focus on small areas of planetary surfaces and to detect elements in low concentrations) remote-sensed spectra by future space-probes orbiting hot and cold planetary bodies, the present study initiates the acquisition of a broad data-base of diagnostic crystal field bands for transition metal ions in a variety of minerals over a range of temperatures [8].

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