

An UV/Vis/NIR optical absorption spectroscopic and color investigation of transition-metal-doped gahnite (ZnAl₂O₄ spinel) crystals grown by the flux method

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ABSTRACT

Synthetic flux-grown end-member gahnite, ZnAl₂O₄, and several different colored crystals doped with one or more transition metals including Mn, Ni, Cr, Co, and Fe were studied by electron microprobe methods and UV/Vis/NIR single-crystal optical absorption spectroscopy. The first major objective was to measure and assign the various electronic absorption features. The second was to analyze quantitatively the crystal colors using the experimental spectra and the CIE 1931 color-space-chromaticity diagram. The microprobe results show that the doped gahnites have transition metal concentrations between about 0.001 and 0.1 cations per formula unit. The spectrum of colorless, nominally pure ZnAl₂O₄ displays no absorption in the visible region. Microprobe analysis of a light-blue gahnite crystal reveals small amounts of Ni and Mn. The UV/Vis/NIR spectrum does not indicate any dd-electronic transitions relating to Mn. All absorption features also cannot be fully interpreted using Tanabe-Sugano diagrams for Ni²⁺ in either octahedral or tetrahedral coordination. A series of seven slightly different colored gahnites with differing concentrations of Cr³⁺ and most also containing smaller amounts of Ni was investigated. The spectrum of a one pink crystal shows two intense absorption features in the visible region. They are assigned to spin-allowed ⁴A_{2g} → ⁴T_{2g} (⁴F) and ⁴A_{2g} → ⁴T_{1g} (⁴F) transitions of ^{VI}Cr³⁺. Other spectra display additional weak bands and lines that are most probably spin-forbidden dd-transitions of Ni²⁺. These gahnites with Ni and Cr show varying purple colorations depending on the concentrations of both metals. Two more deeply blue gahnites contain Co²⁺ as demonstrated by their UV/Vis spectra but not by microprobe analysis. Two intense absorption features at ~7440 and ~16 850 cm⁻¹ are observed and assigned to the spin-allowed transitions ⁴A₂ → ⁴T₁ (⁴F) and ⁴A₂ → ⁴T₁ (⁴P) of Co²⁺, respectively. Complex absorption fine structure, caused by spin-orbit and/or vibronic interactions, is also observed. Three different gahnites with yellow to orange colorations contain measurable Mn. Their spectra are similar in appearance and display several weak ^{IV}Mn²⁺ spin-forbidden transitions located above 20 000 cm⁻¹. The spectra of two green gahnites show several Fe spin-forbidden electronic transitions arising from single, isolated ^{IV}Fe²⁺ and ^{VI}Fe³⁺ cations between 10 000 and 25 000 cm⁻¹. The intensities of some of the ^{VI}Fe³⁺-related bands can be increased through exchange-coupled interactions with next nearest ^{IV}Fe²⁺ neighbors. The colors of various doped gahnites and the end-member galaxite are analyzed using their single-crystal absorption spectra in the visible region. Their dominant wavelength, λ_k, and hue saturation, p_c, values are given on the CIE 1931 color-space-chromaticity diagram and are discussed. The Hex colors of all crystals are calculated and can be compared to those of the studied crystals.

Keywords: Spinel, gahnite, microprobe analysis, optical absorption spectroscopy, electronic d-d transitions, crystal color, transition metal