

SPINELS RENAISSANCE: THE PAST, PRESENT, AND FUTURE OF THOSE UBIQUITOUS MINERALS AND MATERIALS

Optical absorption spectroscopy study of the causes for color variations in natural Fe-bearing gahnite: Insights from iron valency and site distribution data[†]

ROSA ANNA FREGOLA^{1,*}, HENRIK SKOGBY², FERDINANDO BOSI^{2,3}, VERONICA D'IPPOLITO³, GIOVANNI B. ANDREOZZI³ AND ULF HÅLENIUS²

¹Dipartimento di Scienze della Terra e Geoambientali, Università di Bari Aldo Moro, via E. Orabona 4, I-70125 Bari, Italy

²Department of Geosciences, Swedish Museum of Natural History, SE-10405 Stockholm, Sweden

³Dipartimento di Scienze della Terra, Sapienza Università di Roma, Piazzale Aldo Moro 5, I-00185 Roma, Italy

ABSTRACT

Four gahnite single crystals with variable colors from pale blue to green have been studied by a multi-analytical approach with the aim to evaluate existing assignments of optical absorption bands. Combined information from electron microprobe analyses, Mössbauer spectroscopy, IR-spectroscopy, single-crystal X-ray structure refinements, and optical absorption spectroscopy confirms the conclusions of earlier studies that the absorption bands recorded in the visible spectral region up to ~540 nm (above ~18 500 cm⁻¹) are related to electronic *d-d* transitions in tetrahedrally coordinated Fe²⁺. It also demonstrates that a set of absorption bands between ~550–625 nm (~16 000–18 200 cm⁻¹) are caused by spin-allowed and spin-forbidden *d-d* transitions in tetrahedrally coordinated Co²⁺. Two absorption bands at higher wavelengths (~680 and ~800 nm, i.e., ~14 700 and ~12 500 cm⁻¹) are assigned to electronic transitions in exchange coupled ^{VI}Fe³⁺-^{IV}Fe²⁺ pairs and a band at ~950 nm (~10 500 cm⁻¹) is assigned to a spin-allowed electronic transition in ^{VI}Fe²⁺. Low-Fe gahnite crystals owe their blue color to traces of cobalt at concentration levels in the order of 200 ppm and less, while the green color of gahnite crystals with higher Fe-contents is due to a combination of electronic ligand-metal transitions causing strong UV-absorption and electronic transitions in exchange coupled Fe²⁺-Fe³⁺ cation pairs that absorb in the red region of the visible spectrum. A detailed characterization of samples that includes cation site occupancy and iron valency data is demonstrated to be crucial for interpreting optical absorption spectra. Also electronic transitions in trace element chromophores below the detection limit of electron microprobe may participate to light absorption. All this information contribute to the comprehension of the causes of crystal color of minerals, gemstones, and ceramic pigments.

Keywords: Crystal structure, site occupancy, optical absorption spectra, Mössbauer spectra, spinel, gahnite