Vanadium-induced coloration in grossite (CaAl₄O₇) and hibonite (CaAl₁₂O₁₉)

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ABSTRACT

High concentrations of vanadium cause very unusual coloration in hibonite (purple) and grossite (light violet) crystals in an exotic mineral assemblage from Sierra de Comechingones (Argentina). In the hibonite (CaAl₁₂O₁₉) structure vanadium ions, in various valence states (divalent, trivalent, and tetravalent), may be distributed over five crystallographic sites with coordinations corresponding to different polyhedra, namely, three unequal octahedra [M1 (D_{3d}), M4 (C_{3v}), and M5 (C_s)], one M3 tetrahedron (C_{3v}), and one unusual fivefold-coordinated trigonal bipyramid M2 (D_{3h}). Possible locations of vanadium ions in grossite (CaAl₄O₇) are limited to two crystallographically distinct sites (T1 and T2, both C₁) in tetrahedral coordination.

The combination of single-crystal X-ray diffraction and absorption spectroscopy techniques aided by chemical analyses has yielded details on the nature of the vanadium-induced color in both hibonite and grossite crystals. In hibonite, both *M*4 face-sharing octahedral and *M*2 trigonal bipyramid sites of the *R*-block are partially occupied by V³⁺. Strongly polarized bands recorded at relatively low energies in optical absorption spectra indicate that V²⁺ is located at the *M*4 octahedral site of the hibonite *R*-block. Chemical analyses coupled with an accurate determination of the electron densities at structural sites in hibonite suggest that the vanadium ions occupy about 10 and 5% of the *M*4 and *M*2 sites, respectively. For grossite, polarized optical absorption spectra reveal no indications of V²⁺; all observed absorption bands can be assigned to V³⁺ in tetrahedral coordination. Although not evident by the observed electron densities at the *T* sites of grossite (due to the low-V content), longer bond distances, and a higher degree of polyhedral distortion suggest that V³⁺ is located at the *T*2 site.

Keywords: Calcium aluminates, hibonite, grossite, optical absorption spectroscopy, single-crystal X-ray diffraction, vanadium