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Vanadium-induced coloration in grossite ($CaAl_4O_7$) and hibonite ($CaAl_{12}O_{19}$)

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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 ($CaAl_{12}O_{19}$) 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 [*M*1 (D_{3d}), *M*4 (C_{3v}), and *M*5 (C_s)], one *M*3 tetrahedron (C_{3v}), and one unusual fivefold-coordinated trigonal bipyramid *M*2 (D_{3h}). Possible locations of vanadium ions in grossite ($CaAl_4O_7$) are limited to two crystallographically distinct sites (*T*1 and *T*2, both C_1) 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 V^{3+}. Strongly polarized bands recorded at relatively low energies in optical absorption spectra indicate that V^{2+} 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 V^{2+}; all observed absorption bands can be assigned to V^{3+} 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 V^{3+} is located at the *T*2 site.

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