Vanadium-induced coloration in grossite (CaAl$_4$O$_7$) 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 [M1 (D$_{5h}$), M4 (C$_4$), and M5 (C$_4$)], one M3 tetrahedron (C$_5$), and one unusual fivefold-coordinated trigonal bipyramid M2 (D$_{3d}$). Possible locations of vanadium ions in grossite (CaAl$_4$O$_7$) are limited to two crystallographically distinct sites (T1 and T2, both C$_5$) 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 M4 face-sharing octahedral and M2 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 M4 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 M4 and M2 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 T2 site.

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

**INTRODUCTION**

The importance of calcium-aluminum oxide compounds and mineralogical analogs evenly spans Materials Science and Earth Sciences. Hibonite (ideal formula CaAl$_{12}$O$_{19}$) and grossite (ideal formula CaAl$_4$O$_7$) are common constituents of calcium aluminate cements (CACs), which are a special type of cement commonly used in refractory concrete production. Along with aluminate cements (CACs), which are a special type of cement

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