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Electron paramagnetic resonance spectroscopic study of synthetic fluorapatite: Part III. Structural characterization of sub-ppm-level Gd and Mn in minerals at W-band frequency

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ABSTRACT

Room-temperature, single-crystal W-band (~94 GHz) electron paramagnetic resonance (EPR) spectra of a flux-grown fluorapatite (AP30-0) containing 0.8(1) ppm Gd and 0.9 ppm Mn disclose the presence of two even-isotope Gd^{3+} centers (electron spin number S = 7/2 and nuclear spin number I = 0) and a $^{55}Mn^{2+}$ center (S = I = 5/2). The relative abundance of the two Gd^{3+} centers (corresponding to recently established centers "a" and "b" containing Gd^{3+} ions at the Ca2 and Ca1 sites, respectively) in AP30-0 has been estimated to be 0.20, indicating that "a" in this sample arises from the presence of ~0.2 ppm Gd at the Ca2 site. In addition, high-resolution W-band spectra of this sample at ~120 and ~77 K disclose the ^{155}Gd and ^{157}Gd spectra of "a," in which these isotopes (I = 3/2) are only ~0.02 ppm in abundance. To the best of our knowledge, this is the first-ever demonstration of structural characterization of sub-ppm-level trace elements in minerals and their synthetic analogs. Moreover, the fact that the Gd^{3+} and $^{55}Mn^{2+}$ centers in AP30-0 are detected despite the multiplicity of lines arising from their complex fine structures, hyperfine structures, and magnetic-site splittings, suggests that the W-band EPR technique is potentially capable of characterizing trace elements with a single unpaired electron (S = 1/2) and zero nuclear spin (I = 0) at even lower concentrations.

The spin-Hamiltonian parameters of the $^{55}Mn^{2+}$ center, including matrices **g**, **D**, **A**, and **P**, and high-spin term of type S^4, have been determined by optimization using the single-crystal W-band EPR spectra of a Gd-doped fluorapatite containing 3.0(4) ppm Mn. The principal-axis directions of **D** and the pseudo-symmetry axes calculated from the S^4 parameters confirm that this center corresponds to occupancy of $^{55}Mn^{2+}$ ions at the Ca1 site. Also, the optimized parameters suggest that the Mn^{2+}-substituted Ca1 site in the flux-grown fluorapatite has rhombic (i.e., triclinic) local symmetry [e.g., $D/g_e\beta_e$ = 436.2(6) G, $E/g_e\beta_e$ = 1.1(1) G], slightly different from the trigonal symmetry of the ideal Ca1 site.