

Electron paramagnetic resonance spectroscopic study of synthetic fluorapatite: Part I. Local structural environment and substitution mechanism of Gd³⁺ at the Ca₂ site

NING CHEN,¹ YUANMING PAN,^{1,*} AND JOHN A. WEIL²

¹Department of Geological Sciences, University of Saskatchewan, Saskatoon, SK S7N 5E2, Canada

²Department of Chemistry, University of Saskatchewan, Saskatoon, SK S7N 5C9, Canada

ABSTRACT

Gd-doped fluorapatite (1.2 ± 0.2 wt% Gd₂O₃), synthesized from CaF₂-rich melts, has been investigated as single crystals and powder samples by using X-band (~9.4 GHz) electron paramagnetic resonance (EPR) spectroscopy at ~295 and 120 K. The well-resolved X-band EPR spectra yielded a previously unreported type of Gd³⁺ center “a” ($S = 7/2$) and also suggested the possible presence of a second and partly resolved type of Gd³⁺ center “b.” In particular, the single-crystal X-band EPR spectra of center “a” from three orthogonal-rotation planes allowed determination of the spin-Hamiltonian parameters, including the spin terms of type BS (matrix **g**) and S² (matrix **D**) and the parameters associated with the high-spin terms of type S⁴ and S⁶ as well as BS³ and BS⁵. The validity of the parameters has been confirmed by agreement between observed and simulated EPR spectra for both single crystals and powder samples.

The principal values of the matrices **g** and **D** indicate that the local symmetry of center “a” in the X-band EPR spectra is rhombic. The principal axis directions of the **D** suggest that this Gd³⁺ center arises from a substitution of Gd³⁺ ion into the Ca₂ type of site. This assignment is supported by the results of a pseudo-symmetry analysis using the S⁴ parameters, e.g., the calculated twofold pseudo-symmetry axis coincides with the twofold rotoinversion axis of the Ca₂ site. The local structural environment of this Gd³⁺ ion suggests that the ion is incorporated via the mechanism $\text{Gd}^{3+} + \text{O}^{2-} \leftrightarrow \text{Ca}^{2+} + \text{F}^-$.