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# Spectroscopic characterization of transition metal impurities in natural montebrasite/amblygonite

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## Abstract

Natural single-crystal specimens of the montebrasite/amblygonite series from Brazil, with general formula $LiAlPO_4(F,OH)$, were investigated by electron microprobe, Raman spectroscopy, X-ray diffraction, and infrared absorption. Since little is known about impurities and their local symmetries, electron paramagnetic resonance (EPR) was applied. Six different paramagnetic impurities and radiation defects were detected by EPR. Three of them, all substituting for $Al^{3+}$ ions, namely, iron ($Fe^{3+}$), vanadium ($V^{4+}$), and niobium ($Nb^{4+}$) impurities were characterized in this work. The $Fe^{3+}$ ($3d^5$)-related EPR spectra and angular dependencies show occupation of low-symmetry sites that are revealed in the high asymmetry parameter of the electronic fine structure, $E/D = 0.27$. Vanadium and niobium impurities are identified through their typical strong hyperfine interactions. Both form interesting examples for which the properties of $3d^1$ ion ($V^{4+}$) and $4d^1$ ion ($Nb^{4+}$) in the same host matrix can be compared. It is shown that both ions form complex defects of type $VO^{2+}$ (vanadyl) and $NbO^{2+}$ (niobyl), showing superhyperfine interaction with two equivalent hydrogen ions and not to fluorine. The EPR rotation patterns are analyzed in detail for three mutually perpendicular crystal planes. Spin Hamiltonian parameters are calculated and discussed.

**Keywords:** EPR, montebrasite, amblygonite, Fe, Nb, niobyl, V, vanadyl