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Radiation-induced defects in montebrasite: An electron paramagnetic resonance study of O^- hole and Ti^{3+} electron centers

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Abstract

Montebrasite is a lithium aluminum phosphate mineral with the chemical formula $LiAlPO_4(F_x,OH_{1-x})$ and considered a rare gemstone material when exhibiting good crystallinity. In general, montebrasite is colorless, sometimes pale yellow or pale blue. Many minerals that do not have colors contain hydroxyl ions in their crystal structures and can develop color centers after ionization or particle irradiation, examples of which are topaz, quartz, and tourmaline. The color centers in these minerals are often related to O^- hole centers, where the color is produced by bound small polarons inducing absorption bands in the near UV to the visible spectral range. In this work, colorless montebrasite specimens from Minas Gerais state, Brazil, were investigated by electron paramagnetic resonance (EPR) for radiation-induced defects and color centers. Although γ irradiation (up to a total dose of 1 MGy) did not visibly modify color, a 10 MeV electron irradiation (80 MGy) induced a pale greenish-blue color. Using EPR, O^- hole centers were identified in both γ- or electron-irradiated montebrasite samples showing superhyperfine interactions with two nearly equivalent ^{27}Al nuclei. In addition, two different Ti^{3+} electron centers were also observed. From the γ irradiation dose dependency and thermal stability experiments, it is concluded that production of O^- hole centers is limited by simultaneous creation of Ti^{3+} electron centers located between two equivalent hydroxyl groups. In contrast, the concentration of O^- hole centers can be strongly increased by high-dose electron irradiation independent of the type of Ti^{3+} electron centers. From detailed analysis of the EPR angular rotation patterns, microscopic models for the O^- hole and Ti^{3+} electron centers are presented, as well as their role in the formation of color centers discussed and compared to other minerals.

Keywords: Montebrasite, EPR, irradiation, electron-hole center, O^- hole center, Ti^{3+}, color enhancement