

## The crystal chemistry of Li in gadolinite

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### ABSTRACT

This paper describes a multi-technique approach to the complete crystal-chemical characterization of a gadolinite-(Y) sample found in a volcanic holocrystalline ejectum near the Vico lake (Latium, Italy). Gadolinite-(Y) occurs as poly-twinned crystals forming rounded short-prismatic aggregates (generally 0.1–0.3 mm in size, with the largest ever found >1 mm), associated with zircon, thorite, danburite, betafite, and tourmaline.

Both the chemical and the structural characterization of gadolinite-(Y) from Vico required non-standard procedures. After correction for (100) twinning, the structure of a crystal with unit-cell dimensions  $a = 4.7708(4)$  Å,  $b = 7.6229(7)$  Å,  $c = 9.8975(9)$  Å,  $\beta = 90.017(7)^\circ$ , and  $V = 359.95(6)$  Å<sup>3</sup> was refined in the  $P2_1/c$  space group down to  $R = 2.3\%$ . Electron microprobe (EMP) analyses failed to give accurate quantification of major elements, due to the presence of light and volatile elements as well as of rare earth elements (REE) and actinides. Secondary ion-mass spectrometry (SIMS) analysis done with accurate calibrations on well-characterized minerals allowed quantification of light, volatile, REE, and actinide elements, and also of Ca and Si. The derived chemical composition was interpreted with reference to the site-scattering values obtained from single-crystal structure refinement. The resulting unit formula is  $(\text{Ca}_{0.81}\text{REE}_{0.66}\text{Y}_{0.39}\text{Th}_{0.13}\text{U}_{0.02})_{\Sigma 2.01}(\text{Fe}_{0.29}^{2+}\text{Li}_{0.14}\text{Fe}_{0.12}^{3+}\text{Mn}_{0.02}\text{Mg}_{0.01})_{\Sigma 0.58}(\text{Si}_{1.98}\text{Be}_{1.09}\text{B}_{0.81}\text{Li}_{0.12})_{\Sigma 4.00}\text{O}_8(\text{O}_{1.20}\text{F}_{0.51}\text{OH}_{0.29})_{\Sigma 2.00}$ , which yields a calculated density of 4.267 g cm<sup>-3</sup>.

Fourier transform infrared spectroscopy (FTIR) single-crystal spectrum of gadolinite-(Y) shows several absorptions in the OH-stretching region that can be assigned to the different local configurations involving Ca and (REE, Y) at the A site and Be, B, and Li at the Z site.

Lithium incorporation in gadolinite-group minerals is proposed to occur according to the exchange vectors: (1)  ${}^X\text{Fe}^{2+} + {}^4\text{Y} \rightarrow {}^X\text{Li} + {}^4(\text{Th} + \text{U})$  and (2)  ${}^Z\text{Be} + {}^X\text{Fe}^{2+} \rightarrow {}^Z\text{Li} + {}^X\text{Fe}^{3+}$ ; the maximum amount of Li allowed in the gadolinite structure is 1.0 apfu.

This work provides the first evidence that Li is a significant component in gadolinite-group minerals, particularly in geochemical environments enriched in actinides. This conclusion suggests that materials having the composition of Li-rich gadolinite may be considered as possible forms for radioactive waste disposal.

**Keywords:** Gadolinite, lithium, single crystal XRD, EMPA, SIMS, IR spectroscopy