

Mn-bearing “oxy-rossmanite” with tetrahedrally coordinated Al and B from Austria: Structure, chemistry, and infrared and optical spectroscopic study

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ABSTRACT

Pink, Mn-bearing “oxy-rossmanite” from a pegmatite in a quarry near Eibenstein an der Thaya, Lower Austria, has been characterized by crystal structure determination, chemical analyses (EMPA, SIMS), and optical absorption and infrared spectroscopy. Crystal structure refinements in combination with the chemical analyses give the optimized formulae $X(\square_{0.53}\text{Na}_{0.46}\text{Ca}_{0.01})^Y(\text{Al}_{2.37}\text{Li}_{0.33}\text{Mn}_{0.25}^{2+}\text{Fe}_{0.04}^{2+}\text{Ti}_{0.01}^{4+})^Z\text{Al}_6^T(\text{Si}_{5.47}\text{Al}_{0.28}\text{B}_{0.25})\text{O}_{18}(\text{BO}_3)_3^V[(\text{OH})_{2.85}\text{O}_{0.15}]^W[\text{O}_{0.86}(\text{OH})_{0.10}\text{F}_{0.04}]$, with $a = 15.8031(3)$, $c = 7.0877(3)$ Å, and $R = 0.017$ for the sample with 2.05 wt% MnO, and $X(\square_{0.53}\text{Na}_{0.46}\text{Ca}_{0.01})^Y(\text{Al}_{2.35}\text{Li}_{0.32}\text{Mn}_{0.28}^{2+}\text{Fe}_{0.04}^{2+}\text{Ti}_{0.01}^{4+})^Z\text{Al}_6^T(\text{Si}_{5.51}\text{Al}_{0.25}\text{B}_{0.24})\text{O}_{18}(\text{BO}_3)_3^V[(\text{OH})_{2.80}\text{O}_{0.20}]^W[\text{O}_{0.86}(\text{OH})_{0.10}\text{F}_{0.04}]$ for a sample with $a = 15.8171(3)$, $c = 7.0935(2)$ Å, $R = 0.017$, and 2.19 wt% MnO. Although the structure refinements show significant amounts of ¹⁴B, the <T-O> bond-lengths (~1.620 Å) mask the incorporation of ¹⁴B because of the incorporation of ¹⁴Al. The <T-O> distances, calculated using the optimized T site occupancies, are consistent with the measured distances. This “oxy-rossmanite” shows that it is possible to have significant amounts of ¹⁴B and ¹⁴Al in an Al-rich tourmaline. The “oxy-rossmanite” from Eibenstein has the highest known Al content of all natural tourmalines (~47 wt% Al₂O₃; ~ 8.6 apfu Al). The near-infrared spectrum confirms both that hydroxyl groups are present in the Eibenstein tourmaline and that they are present at a lower concentration than commonly found in other lithian tourmalines. The integrated intensity (850 cm⁻²) of the OH bands in the single-crystal spectrum of “oxy-rossmanite” from Eibenstein is distinctly lower than for other Li-bearing tourmaline samples (970–1260 cm⁻²) with OH contents >3.0 pfu. These samples fall on the V site = 3 (OH) line in the figure defining covariance of the relationship between the bond-angle distortion (σ_{oct}^2) of the ZO₆ octahedron and the <Y-O> distance. On a bond-angle distortion-<Y-O> distance diagram “oxy-rossmanite” from Eibenstein lies between the tourmalines that contain 3 (OH) at the V site, and natural buergerite, which contains 0.3 (OH) and 2.7 O at the V site. No H could be found at the O1 site by refinement, and the spherical electron density in the difference-Fourier map around the O1 site supports the conclusion that this site is mainly occupied by O. The pink color comes from the band at 555 nm that is associated with Mn³⁺ produced by natural irradiation of Mn²⁺. This is the first time a tourmaline is described that has a composition that falls in the field of the previously proposed hypothetical species “oxy-rossmanite”.