

Limitations of Fe²⁺ and Mn²⁺ site occupancy in tourmaline: Evidence from Fe²⁺- and Mn²⁺-rich tourmaline†

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ABSTRACT

Fe²⁺- and Mn²⁺-rich tourmalines were used to test whether Fe²⁺ and Mn²⁺ substitute on the Z site of tourmaline to a detectable degree. Fe-rich tourmaline from a pegmatite from Lower Austria was characterized by crystal-structure refinement, chemical analyses, and Mössbauer and optical spectroscopy. The sample has large amounts of Fe²⁺ (~2.3 apfu), and substantial amounts of Fe³⁺ (~1.0 apfu). On basis of the collected data, the structural refinement and the spectroscopic data, an initial formula was determined by assigning the entire amount of Fe³⁺ (no delocalized electrons) and Ti⁴⁺ to the Z site and the amount of Fe²⁺ and Fe³⁺ from delocalized electrons to the Y-Z ED doublet (delocalized electrons between Y-Z and Y-Y): ${}^X(\text{Na}_{0.9}\text{Ca}_{0.1}){}^Y(\text{Fe}_{2.0}\text{Al}_{0.4}\text{Mn}_{0.3}\text{Fe}_{0.2}^{3+}){}^Z(\text{Al}_{4.8}\text{Fe}_{0.8}^{3+}\text{Fe}_{0.2}^{2+}\text{Ti}_{0.1}^{4+}){}^T(\text{Si}_{5.9}\text{Al}_{0.1})\text{O}_{18}(\text{BO}_3)_3{}^V(\text{OH})_3{}^W[\text{O}_{0.5}\text{F}_{0.3}(\text{OH})_{0.2}]$ with $a = 16.039(1)$ and $c = 7.254(1)$ Å. This formula is consistent with lack of Fe²⁺ at the Z site, apart from that occupancy connected with delocalization of a hopping electron.

The formula was further modified by considering two ED doublets to yield: ${}^X(\text{Na}_{0.9}\text{Ca}_{0.1}){}^Y(\text{Fe}_{1.8}\text{Al}_{0.5}\text{Mn}_{0.3}\text{Fe}_{0.3}^{3+}){}^Z(\text{Al}_{4.8}\text{Fe}_{0.7}^{3+}\text{Fe}_{0.4}^{2+}\text{Ti}_{0.1}^{4+}){}^T(\text{Si}_{5.9}\text{Al}_{0.1})\text{O}_{18}(\text{BO}_3)_3{}^V(\text{OH})_3{}^W[\text{O}_{0.5}\text{F}_{0.3}(\text{OH})_{0.2}]$. This formula requires some Fe²⁺ (~0.3 apfu) at the Z site, apart from that connected with delocalization of a hopping electron. Optical spectra were recorded from this sample as well as from two other Fe²⁺-rich tourmalines to determine if there is any evidence for Fe²⁺ at Y and Z sites. If Fe²⁺ were to occupy two different 6-coordinated sites in significant amounts and if these polyhedra have different geometries or metal-oxygen distances, bands from each site should be observed. However, even in high-quality spectra we see no evidence for such a doubling of the bands. We conclude that there is no ultimate proof for Fe²⁺ at the Z site, apart from that occupancy connected with delocalization of hopping electrons involving Fe cations at the Y and Z sites.

A very Mn-rich tourmaline from a pegmatite on Elba Island, Italy, was characterized by crystal-structure determination, chemical analyses, and optical spectroscopy. The optimized structural formula is ${}^X(\text{Na}_{0.6}\square_{0.4}){}^Y(\text{Mn}_{7.3}^{2+}\text{Al}_{1.2}\text{Li}_{0.5}){}^Z\text{Al}_6{}^T\text{Si}_6\text{O}_{18}(\text{BO}_3)_3{}^V(\text{OH})_3{}^W[\text{F}_{0.5}\text{O}_{0.5}]$, with $a = 15.951(2)$ and $c = 7.138(1)$ Å. Within a 3σ error there is no evidence for Mn occupancy at the Z site by refinement of Al ↔ Mn, and, thus, no final proof for Mn²⁺ at the Z site, either.

Oxidation of these tourmalines at 700–750 °C and 1 bar for 10–72 h converted Fe²⁺ to Fe³⁺ and Mn²⁺ to Mn³⁺ with concomitant exchange with Al of the Z site. The refined ⁵⁷Fe content in the Fe-rich tourmaline increased by ~40% relative to its initial occupancy. The refined ⁵⁵Fe content was smaller and the <Y-O> distance was significantly reduced relative to the unoxidized sample. A similar effect was observed for the oxidized Mn²⁺-rich tourmaline. Simultaneously, H and F were expelled from both samples as indicated by structural refinements, and H expulsion was indicated by infrared spectroscopy. The final species after oxidizing the Fe²⁺-rich tourmaline is buergerite. Its color had changed from blackish to brown-red. After oxidizing the Mn²⁺-rich tourmaline, the previously dark yellow sample was very dark brown-red, as expected for the oxidation of Mn²⁺ to Mn³⁺. The unit-cell parameter *a* decreased during oxidation whereas the *c* parameter showed a slight increase.

Keywords: Mn²⁺-rich tourmaline, Fe²⁺-rich tourmaline, Mössbauer, crystal structure, lower Austria, Elba Island, Italy, site occupancy

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