

Linking Mössbauer and structural parameters in elbaite-schorl-dravite tourmalines

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ABSTRACT

Accurate crystal-chemical analysis of complex minerals such as tourmalines belonging to the elbaite-schorl-dravite series was obtained by combining Mössbauer spectroscopy (MS) and structural information. Well-defined relationships were established between the two approaches, leading to a close match of results obtained and a strong link between observed parameters.

Although MS information is a powerful tool for quantifying the amount of Fe²⁺ and Fe³⁺, it is not always useful in determining their site distribution. In particular, both for Fe³⁺ and for (Fe²⁺-Fe³⁺) interactions structural information is still essential. Fe³⁺ MS doublets were identified and assigned to iron in *Y* and *Z* sites on the basis of structural information. In a few spectra, Fe³⁺ doublets with very low parameters ($\delta \sim 0.2$ mm/s) were observed and, in contrast with the *T*-site assignment of previous works, were assigned to Fe³⁺ in octahedral coordination. Electron delocalization between Fe²⁺ and Fe³⁺ was observed and related to three different interactions (*Y*-*Y*, *Y*-*Z*, and *Z*-*Z*). Notably, MS hyperfine parameters of Fe²⁺ were self-consistent and particularly reliable in determining Fe²⁺ site partitioning. Fe²⁺ at *Y* was modeled by three doublets ($\Delta E_Q = 2.45, 2.19,$ and 1.72 mm/s). The sum of their absorption areas perfectly matches the ⁵⁷Fe²⁺ populations derived from structural data ($r^2 = 0.97$). The fourth doublet observed ($\Delta E_Q = 1.38$ mm/s) is consistent with Fe²⁺ at *Z*, which is an octahedron smaller and less distorted than *Y* ($\lambda_Z = 1.014, \lambda_Y = 1.024$). The absorption area of this doublet is highly correlated with the amount of ⁵⁷Fe²⁺ obtained from site-occupancy refinement ($r^2 = 0.95$).

For ⁵⁷Fe³⁺ a link between the quadrupole splitting parameter ΔE_Q and variations in the chemical/structural environment surrounding Fe nucleus was observed. The ΔE_Q of ⁵⁷Fe³⁺ increases with ZO_6 volume ($r^2 = 0.84$) and is linked to the variation of electrical field gradient generated by the ²⁷R²⁺ → ²⁷Al substitution. Since the *Z* skeleton completely surrounds *Y* islands, ΔE_Q of ⁵⁷Fe³⁺ shows much more susceptibility to inductive effects from the second rather than the first coordination sphere.

Keywords: Tourmaline, Mössbauer spectroscopy, structural formula, Fe disorder