

## **Influence of the octahedral cationic-site occupancies on the framework vibrations of Li-free tourmalines, with implications for estimating temperature and oxygen fugacity in host rocks**

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### **ABSTRACT**

Tourmalines,  $XY_3Z_6T_6O_{18}(BO_3)_3V_3W$ , are excellent petrogenetic indicators as they capture the signature of the host-rock bulk composition. Raman spectra of tourmalines can be used as fingerprints for species identification and crystal-chemical analysis. While Li-bearing species are directly distinguishable by the shape of the OH-stretching vibrations, the discrimination of Mg- and Fe-dominant species can be hindered by the coexistence of at least two types of octahedrally coordinated  $R^{n+}$  cations.

Thirty Li-free tourmaline samples comprising 14 different species were studied by Raman spectroscopy and electron microprobe. All nine  $Fe^{3+}$ -bearing samples were also analyzed by single-crystal X-ray diffraction and Mössbauer spectroscopy. The Raman scattering analysis shows that Mg-dominant species can be immediately distinguished from Fe-dominant species by the shape of the vibrational modes at  $\sim 200$ – $240\text{ cm}^{-1}$  arising from the  $YO_6$  vibrations. Trivalent Fe can be observed and quantified by shifts of the framework vibrations toward lower wavenumbers. The position of the main  $ZO_6$  vibrational mode ( $275$ – $375\text{ cm}^{-1}$ ) can be used to determine the  ${}^2Fe^{3+}$  content, while the  ${}^YFe^{3+}$  content can be inferred from the position of the peak at  $\sim 315\text{ cm}^{-1}$ . Fits to the data points indicate that the homovalent substitution of  $Fe^{3+}$  for  $Al^{3+}$  leads to a considerably larger downward shift of the  $ZO_6$  vibrational mode than the heterovalent substitution  $Mg^{2+}$  for  $Al^{3+}$ . The intensity ratio of the two major  $YO_6$  vibrational modes ( $200$ – $240\text{ cm}^{-1}$ ) of the fully characterized  $Fe^{3+}$ -bearing samples reflects the amount of Y-site Mg and thus can be used to deduce the site-occupancy disorder of Mg over the Y and Z site for tourmaline species with  $Mg \leq 2\text{ apfu}$ .

By combining the information from framework and OH-stretching vibrations, Raman spectroscopy alone can be used as a micrometer-scale sensitive non-destructive method for the analysis of tourmaline crystal chemistry including trivalent Fe, which is the major tracer for oxygen fugacity and central for intersite geothermometry.

**Keywords:** Tourmaline, Raman spectroscopy, framework vibrations, trivalent iron