

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 ~ 200 – 240 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 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 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