

Exploring the potential of Raman spectroscopy for the determination of tourmaline chemistry

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Tourmalines, $XY_3Z_6(T_6O_{18})(BO_3)_3V_3W$, are complex ring silicates that can be classified into 3 primary groups with several subgroups containing about 40 species. Due to the incorporation of critical light elements (H, Li, F, and B) and the varying oxidation state of transition elements (Fe, Mn), tourmalines are commonly incompletely chemically characterized [1], which leads to difficulties in the proper classification of the tourmaline species.

In this study, we explore the potential of Raman spectroscopy for the first non-destructive distinction of tourmaline species and for the quantitative determination of the content of the major elements on the X-, Y-, and Z positions: Na, Ca, Li, Fe^{2+} , Mn^{2+} , Mg, and Al.

We have measured Raman spectra of 45 natural tourmaline samples belonging to 10 major tourmaline species in the range from 15 to 4000 cm^{-1} . Of particular interest is the spectral range of the OH bond stretching between 3300 and 3900 cm^{-1} . The thorough analysis of band positions and integrated intensities allowed for a distinction between vibrations originating from OH in the V and the W position. Using the mean ionic radii of various elements in tourmaline from [2], we set up an enhanced model based on one- and two-mode behaviour of mixed crystals to assign certain chemical species to the observed vibrations. The 3 V-anions with their linkage to one Y-cation and 2 Z-cations are taken individually into account, whereas the W-anion is linked to 3 Y-cations. Using this assignment, we have calculated Y-cation contents from the integrated intensities of the Raman bands and compared them to data obtained by electron microprobe analysis and laser-ablation inductively-coupled-plasma mass spectrometry. The results show good agreement for $(Fe+Mn)^{2+}$, Mg, and Li, and satisfactory correspondence for Al. By considering the one-mode behaviour of the $(OH)^V$ stretching bond regarding the X-site occupancy, the contents of Na, Ca, and X-site vacancy can also be estimated.

[1] Henry *et al.* (2011) *Am. Min.* **96**, 895-913. [2] Bosi and Lucchesi (2007) *Am. Min.* **92**, 1054-1063.