# Tetrahedrally coordinated boron in synthetic high-pressure olenite: Towards Raman spectroscopy as a chemical probe for tourmaline

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Olenitic tourmaline with high amounts of tetrahedral B (up to 2.53 $^{[4]}$B pfu) has been synthesized in a piston-cylinder press at 4.0 GPa/700 °C and a run duration of 9 days. Crystals are large enough (up to 30 x 150 $\mu m^2$) to allow for reliable and spatially resolved quantification of B by electron microprobe analysis (EMPA), single-crystal X-ray diffraction, and polarized single-crystal Raman spectroscopy. Tourmaline with radial acicular habit is zoned in $^{[4]}$B-concentration (core: 2.53(25) $^{[4]}$B pfu; rim: 1.43(15) $^{[4]}$B pfu) whereas columnar crystals are chemically homogeneous (1.18(15) $^{[4]}$B pfu). A similar amount of 1.4(1) $^{[4]}$B pfu was found in the columnar tourmaline by single-crystal structure refinement (SREF) ($R$ = 1.94%). The EMPA identify $^{[T]}Si_{-1}{}^{[V,W]}O_{-1}{}^{[T]}B_1{}^{[V,W]}(OH)_1$ as the main and $^{[X]}\square_{-1}{}^{[T]}Si_{-1}{}^{[X]}Na_1{}^{[T]}B_1$ as minor exchange vectors for $^{[4]}$B incorporation, which is supported by the SREF. Due to the restricted and well-defined variations in chemistry, Raman bands in the OH-stretching region (3000 - 3800 $cm^{-1}$) are unambiguously assigned to a specific cation arrangement. We found the sum of the relative integrated intensity ($I_{rel}$) of two low frequency bands at 3284 - 3301 $cm^{-1}$ (ν1) and 3367 – 3384 $cm^{-1}$ (ν2) to positively correlate with the $^{[4]}$B concentrations: $^{[4]}$B [pfu] = 0.03(1) * [$I_{rel}$ (ν1) + $I_{rel}$ (ν2)]. Hence, those bands correspond to configurations with mixed Si/B occupancy at the T site. Our semi-quantitative correlation also holds for well-characterized natural $^{[4]}$B-bearing tourmaline from the Koralpe, Austria.

This study contributes to promote Raman spectroscopy as a fast and non-destructive tool for the chemical classification of (precious) natural tourmaline.