

SPECIAL COLLECTION: ADVANCES IN ULTRAHIGH-PRESSURE METAMORPHISM

## Tetrahedral boron in natural and synthetic HP/UHP tourmaline: Evidence from Raman spectroscopy, EMPA, and single-crystal XRD

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### ABSTRACT



Olenitic tourmaline with high amounts of tetrahedral B (up to 2.53 <sup>[4]</sup>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 × 150 μm) 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. Tourmalines with radial acicular habit are zoned in <sup>[4]</sup>B-concentration [core: 2.53(25) <sup>[4]</sup>B pfu; rim: 1.43(15) <sup>[4]</sup>B pfu], whereas columnar crystals are chemically homogeneous [1.18(15) <sup>[4]</sup>B pfu]. An amount of 1.4(1) <sup>[4]</sup>B pfu was found in the columnar tourmaline by single-crystal structure refinement (SREF) ( $R = 1.94\%$ ). The EMPA identify  ${}^{[T]}\text{Si}_{-1}{}^{[V,W]}\text{O}_{-1}{}^{[T]}\text{B}_1{}^{[V,W]}(\text{OH})_1$  as the main and  ${}^{[X]}\square_{-1}{}^{[T]}\text{Si}_{-1}{}^{[X]}\text{Na}_1{}^{[T]}\text{B}_1$  as minor exchange vectors for <sup>[4]</sup>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<sup>-1</sup>) are unambiguously assigned to a specific cation arrangement. We found the sum of the relative integrated intensity ( $I_{\text{rel}}$ ) of two low-frequency bands at 3284–3301 cm<sup>-1</sup> (ν<sub>1</sub>) and 3367–3390 cm<sup>-1</sup> (ν<sub>2</sub>) to positively correlate with the <sup>[4]</sup>B concentrations:  ${}^{[4]}\text{B} [\text{pfu}] = 0.03(1) \times [I_{\text{rel}}(\nu_1) + I_{\text{rel}}(\nu_2)]$ . 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 <sup>[4]</sup>B-bearing tourmaline from the Koralpe, Austria. This work shows the potential for Raman spectroscopy as a non-destructive method for the chemical classification of (precious) natural tourmaline, and as a tool to rapidly characterize chemical zonation of tourmalines in thin section.

**Keywords:** Tourmaline, tetrahedral boron, high-pressure synthesis, single-crystal XRD, polarized Raman spectra, Koralpe tourmaline, Invited Centennial article