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 \([4]B\) 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 × 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 \([4]B\)-concentration \([\text{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]\). An amount of 1.4(1) \([4]B\) pfu was found in the columnar tourmaline by single-crystal structure refinement (SREF) \((\chi = 1.94\%\)) of the EMPA identify \([7]Si_{1}^{[V,W]O}[7]B_{1}^{[V,W]}(OH)\), as the main and \([8]Si_{1}^{[V,W]}Na_{1}^{[X]}B_{1}\), 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 \((3000–3800 \text{ cm}^{-1})\) unambiguously assigned to a specific cation arrangement. We found the sum of the relative integrated intensity \((I_{r})\) of two low-frequency bands at 3284–3301 cm\(^{-1}\) (v1) and 3367–3390 cm\(^{-1}\) (v2) to positively correlate with the \([4]B\) concentrations: \([4]B\) [pfu] = 0.03(1) \(I_{r}(v1) + I_{r}(v2)\). 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 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

**INTRODUCTION**

Tourmaline has an enormous potential for petrogenetic studies and has successfully been used as a geochemical recorder of temperature (e.g., van Hinsberg and Schumacher 2007), pressure (Berryman et al. 2015b), and fluid composition (e.g., von Goerne et al. 2001). Taking into account its wide stability field ranging from sub-surface (Henry et al. 1999; Moore et al. 2004) to ultra-high-P conditions (Krosse 1995), and that tourmaline preserves its composition throughout its P-T history due to low-element diffusivities (Henry and Dutrow 1996), tourmaline is considered with good reason “an ideal indicator of its host environment” (van Hinsberg et al. 2011).

The reason for the widespread occurrence of tourmaline is its flexible crystal structure, which can accommodate a large variety of site occupants. Its general formula is written as

\[([9]X^{[4]}Y_{1}^{[6]}Z_{2}^{[6]}T_{1}^{4}O_{6}^{[5]}BO_{3})_{3}V_{3}W\] (Henry et al. 2011), where the most common ions (or vacancy, \(\square\)) at each site are \(X = Na^{+}, Ca^{2+}, K^{+}\); \(Y = Fe^{2+}, Mg^{2+}\); \(Z = Al^{3+}, Fe^{3+}, Mg^{2+}\); \(T = Si^{4+}, Al^{3+}\); \(V = OH^{3+}, O^{2-}\); and \(W = OH^{3+}, F^{-}, O^{2-}\). The olenite end-member stoichiometry is \(NaAl_{3}Si_{6}O_{18}(BO_{3})_{3}O_{4}(OH)\), a Mg-Fe free tourmaline with full occupation of the X-site and only one OH-group per formula unit (pfu).

Tourmaline is the most important carrier of B in crustal rocks and its B isotope composition extends the applicability of tourmaline to a geochemical tracer for geological mass transfer (e.g., Marschall et al. 2006) and metasomatic processes (Trumbull et al. 2009; Bast et al. 2014). B isotope fractionation between tourmaline and fluid is not only T-dependent (Meyer et al. 2008) but also strongly affected by the structural bonding environment of B (Kowalski et al. 2013). Thus, for a thorough interpretation of B isotope data, the quantification of accurate B concentrations at the two structural positions \([3]B\) and \([4]T\) is essential.

In most tourmalines, B is exclusively threefold coordinated,