

THE [9]-COORDINATED X-SITE IN THE CRYSTAL STRUCTURE OF TOURMALINE-GROUP MINERALS

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Tourmalines are complex aluminium borosilicates with strongly varying compositions because of isomorphous replacements (solid solutions). The tourmaline mineral group which crystallises in space group $R3m$ (No. 160; $Z = 3$) is chemically one of the most complicated groups of silicate minerals, with the general formula $X Y_3 Z_6 [T_6O_{18}] (BO_3)_3 V_3 W$ (HENRY *et al.*, 2011). The tetrahedral sites in tourmaline are primarily occupied by Si, and usually also by small amounts of Al and B. Planar rings of tetrahedra are linked by two types of octahedra, Z and Y , which share edges to form brucite-like fragments. The Z octahedra are relatively small, somewhat distorted, and are occupied predominantly by trivalent cations such as Al^{3+} , Fe^{3+} , Cr^{3+} and V^{3+} , but can contain significant amounts of the divalent cation Mg^{2+} . The Y site is a relatively regular octahedron occupied by a wide array of mono- or multivalent cations, most commonly Li^{1+} , Mg^{2+} , Fe^{2+} , Mn^{2+} , Cu^{2+} , Al^{3+} , Cr^{3+} , V^{3+} , Fe^{3+} , Mn^{3+} and Ti^{4+} . Most structural refinements indicate that a minor Y -site vacancy can exist. The X site is a nine-coordinated trigonal antiprism, located along the three-fold axis of symmetry. It is most commonly occupied by Na and Ca, or vacant, and in rare cases occupied by K. Recently Pb was also described on this site (ERTL *et al.*, 2007; LUSSIER *et al.*, 2011).

FOIT & ROSENBERG (1979) plotted a positive correlation between Na occupancy and the $\langle X-O \rangle$ distance in Ca-poor tourmalines (7 samples with ≤ 0.1 apfu Ca). Interestingly, they stated that, if the $\langle X-O \rangle$ distance is plotted against the effective radius of the cations occupying that site, no correlation can be observed. FOIT (1989) plotted the $\langle X-O \rangle$ distances in correlation to (Na + X -site vacancies) of 13 tourmaline samples with different chemistry. He found a positive correlation with $r = 0.83$. GRICE & ERCIT (1993) characterised 12 tourmaline samples of various composition and described a relatively high scatter between $\langle X-O \rangle$ and the arithmetic mean of the constituent radii which they attributed to the fact that the calculation of mean ionic radii cannot account for the effect of X -site vacancies. BOSI *et al.* (2005) mentioned that usually $\langle X-O \rangle$ is linearly correlated with the X -site vacancies, whereas it is almost constant in samples with OH at the O2 site. BOSI & LUCCHESI (2007) described that $\langle X-O \rangle$ decreases with Ca content and increases with Na and X -site vacancy contents, a fact that could of course be expected.

To learn more about the role of the X -site cations and vacancies in relation the $\langle X-O \rangle$ distance we investigated 81 tourmaline samples (from the literature) with different X -site occupation. These samples show strongly varying $\langle Y-O \rangle$ and $\langle T-O \rangle$ distances. In contrast to earlier statements in the literature this evaluation has clearly shown that the $\langle X-O \rangle$ distance, as could have been expected, is positively correlated to the average effective ionic radius of the X -site occupants ($r = 0.98$ for 81 tourmaline samples, with Al_6 at the Z site and $(OH)_3$ at the V site). X -site vacancies (up to ~ 0.7 apfu), as well as a significant variation of $\langle T-O \rangle$ and $\langle Y-O \rangle$ distances, do not seem to have a significant effect on the $\langle X-O \rangle$ distance.

Olenite and “oxy-rossmanite” samples, in which the V site is not completely occupied by OH, show a significant deviation to this correlation. Tourmalines of the elbaite-olenite-rossmanite series (with Al_6 at the Z site) show a positive correlation between the $\langle X-O \rangle$ and the $\langle Z-O \rangle$ distance ($r = 0.80$; 40 samples) due to inductive effects in the structure.

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