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Tetrahedrally coordinated boron in tourmalines from the liddicoatite-elbaite series from Madagascar: Structure, chemistry, and infrared spectroscopic studies

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ABSTRACT

Four colorless tourmalines of the liddicoatite-elbaite series from pegmatites from Anjanabonoina, Madagascar, have been characterized by crystal-structure determination and by chemical analyses. Optimized formulae range from $^{X}(Ca_{0.57}Na_{0.29}\square_{0.14})$ $^{Y}(Al_{1.41}Li_{1.33}Mn^{2+}_{0.07}\square_{0.19})$ $^{Z}Al_6$ $^{T}(Si_{5.86}B_{0.14})O_{18}(BO_3)_3$ $^{V}(OH)_{3.00}$ $^{W}[F_{0.76}(OH)_{0.24}]$ [$a = 15.8322(3)$, $c = 7.1034(3)$ Å] to $^{X}(Na_{0.46}Ca_{0.30}\square_{0.24})$ $^{Y}(Al_{1.82}Li_{0.89}Fe^{2+}_{0.01}Mn^{2+}_{0.01}\square_{0.27})$ $^{Z}Al_6$ $^{T}(Si_{5.56}B_{0.44})O_{18}(BO_3)_3$ $^{V}(OH)_{3.00}$ $^{W}[(OH)_{0.50}F_{0.50}]$ [$a = 15.8095(9)$, $c = 7.0941(8)$ Å] (R = 1.3–1.7%). There is a high negative correlation ($r^2 = 0.984$) between the <T-O> bond-lengths (~1.618–1.614 Å) and the amount of ^{IV}B (from the optimized formulae). Similar to the olenites (from Koralpe, Austria) the liddicoatite-elbaite samples show a positive correlation between the Al occupancy at the Y site and ^{IV}B ($r^2 = 0.988$). Short-range order configurations show that the presence of ^{IV}B is coupled with the occupancy of (Al_2Li) and $(Al_2\square)$ at the Y site. The structural formulae of the Al-rich tourmalines from Anjanabonoina, Madagascar, show ~$\square_{0.2}$ (vacancies) on the Y site. We believe that short-range order configurations with $^{Y}(Al_2\square)$ are responsible for these vacancies. Hence, an oft-used calculation of the Li content by difference on the Y site may be problematic for Al-rich tourmalines (olenite, elbaite, rossmanite). Fourier transform infrared (FTIR) spectra were recorded from the most ^{IV}B-rich tourmaline sample. The bands around 5195 and 5380 cm^{-1} can be assigned to H_2O. Because these bands still could be observed in FTIR spectra at temperatures from –150 to +600 °C, it seems unlikely that they result from H_2O in fluid inclusions. Interestingly, another FTIR spectrum from a dravite in which the X site is filled completely with Na, does not show bands at ~5200 and ~5400 cm^{-1}. Although not definitive, the resulting spectra are consistent with small amounts of H_2O at the X site of the elbaite. The rare-earth element (REE) pattern of the B-rich elbaite (ΣREE: ~150 ppm) demonstrates that this sample is strongly enriched in LREEs compared to HREEs and exhibits a negative Eu anomaly. This sample shows the strongest enrichment of LREEs and a high La_N/Yb_N ratio of ~351, which seems to confirm an important role of the fractional crystallization process.

Keywords: Liddicoatite-elbaite, tetrahedrally coordinated boron, Madagascar, structure, chemistry