High-pressure study of dravite tourmaline: Insights into the accommodating nature of the tourmaline structure

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ABSTRACT

The high-pressure behavior of dravite tourmaline [$Na(Mg_3)Al_6(Si_6O_{18})(BO_3)_3(OH)_3(OH)$] has been studied using luminescence spectroscopy and synchrotron-based single-crystal diffraction up to ~65 and ~24 GPa, respectively. Two emission bands associated with Cr^{3+}/V^{2+} substitution are constant in energy up to ~9.0 GPa, and they shift to longer wavelength at higher pressures, suggesting that a change in compressional mechanism could occur at this pressure. Single-crystal diffraction data show subtle changes in ring ditrigonality occur near 9.0 GPa, which could cause the observed change in luminescence. Near 15 GPa, a splitting of one of the emission bands is observed, suggesting that a phase transition occurs at this pressure and that two unique octahedral sites are present in the high-pressure phase. Hysteresis is not observed on decompression, which indicates that this is a second-order transition, and the high-pressure structure appears to be metastable up to ~65 GPa. Single-crystal diffraction measurements show that a phase transition from rhombohedral $R3m$ to rhombohedral $R3$ occurs at pressures near 15.4 GPa. The high-pressure phase is characterized by a distorted Si_6O_{18} ring (e.g., the Si-Si-Si angles deviate from 120°), and the Si, Al, O6, O7, and O8 sites of the low-pressure phase split, implying that the high-pressure phase of tourmaline is a higher entropy phase. The large X-site exerts the primary control on compressibility, and the substitution of larger cations into this site will likely lower the pressure at which this transition occurs. Dravite tourmaline shows anisotropic compression with the c-axis being more compressible than the a-axis. The pressure and volume data up to ~15.4 GPa were fit with second- and third-order Birch-Murnaghan equations of state. We obtain a bulk modulus, $K_0 = 109.6(3.2)$ GPa, and a pressure derivative, $K_0' = 4.6(8)$ GPa, and with the pressure derivative set to 4, a bulk modulus of 112.0(1.0) GPa is derived. Moreover, our high-pressure results show that massive overbonding of the X and Y sites can be accommodated by the tourmaline structure. This unexpected result may explain the extraordinary structural tolerance with respect to chemical substitution on the X, Y, and Z sites.

Keywords: Dravite, high-pressure, single-crystal diffraction, luminescence, phase transitions