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(Mg2)Al6(Si18O55)(BO3)(OH)2(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 Cr3+/V2+ 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 Si18 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, K0 = 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

INTRODUCTION

Tourmaline is a supergroup of minerals that is chemically complex and is divided into different varieties based on chemical composition (Hawthorne and Henry 1999; Henry et al. 2011). This group of minerals is so complex and chemically variable that an entire subcommittee on tourmaline nomenclature exists. These minerals are categorized using the generalized tourmaline structural formula XY2Z6(T4O16)(BO3)3VW where X = Na, Ca, K; Y = Fe, Mg, Mn, Al, Li; Z = Al, Fe, Mg, Cr; T = Si, Al; B = B; F = (OH), O, and W = (OH), O, F (Hawthorne and Henry 1999; Henry et al. 2011). From a compositional perspective, most of the variability occurs in the X, Y, and Z sites; more information on the classification of tourmaline supergroup minerals can be found in Hawthorne and Henry (1999) and Henry et al. (2011). Tourmaline is also highly sought after as a gemstone due to its high hardness and wide range of colors.

Tourmaline typically crystallizes in the rhombohedral crystal system with R3m symmetry (Hawthorne and Henry 1999; Henry et al. 2011), although other crystal systems have been reported (Akizuri et al. 2001; Shukunberg et al. 2007). It is typically considered a ring-silicate with six corner-shared TO4 tetrahedral sites that form a hexagonal ring, a ninefold X-site, two sixfold octahedral Y- and Z-sites, and a trigonal planar B-site (Fig. 1). Although the T-sites are dominantly occupied by Si, B, and Li substitution into them has been reported (Rosenberg and Foit 1979; Hughes et al. 2000). Interestingly, the first reported structure of tourmaline presented the Si18O46 ring as ditrigonal in symmetry (Hamburger and Buerger 1948). However, it was later shown to be hexagonal in symmetry (Ito and Sadanaga 1951), and all subsequent studies agree that the Si18O46 ring is hexagonal at ambient conditions.

Tourmaline is the most widespread borosilicate mineral in natural rocks and the dominant carrier of B in many rock types (Henry and Dutrow 1996) and is found in subduction zone environments (Nakano and Nakamura 2001; Bebout and