

High-pressure single-crystal study of dravite

Earl O'Bannon¹, Martin Kunz², Christine Beavers², and Quentin Williams¹

¹Department of Earth & Planetary Sciences, University of California Santa Cruz

²Advanced Light Source, Lawrence Berkeley National Lab

Tourmaline ($XY_3Z_6[T_6O_{18}][BO_3]_3V_3 \cdot W$, X=Ca, Na; Y=Li, Mg, Fe, Al; Z=Mg, Al, Fe, T=Si, Al; V=OH; and W=OH, F) is a well-known piezoelectric material that has a wide range of industrial applications. The high pressure and temperature decomposition of tourmaline has been studied extensively. However, high-pressure experiments at ambient temperature are scarce, and its high-pressure polymorphism is unknown. Here we use luminescence spectroscopy of V^{2+}/Cr^{3+} impurities and single-crystal diffraction to study the high-pressure behavior of dravite tourmaline (Na, Mg endmember) to pressures of ~ 16 GPa. We observe two emission bands: the first exhibits a pressure shift of 0.38 ± 0.02 nm/GPa throughout the entire pressure range while the second shows an unusual shift of 0 nm/GPa up to ~ 8.5 GPa followed by a monotonic shift of 0.22 ± 0.03 nm/GPa to the highest pressure measured. The change in pressure shift observed by luminescence is indicative of either the presence of a phase transition or a change in compression mechanism of the V^{2+}/Cr^{3+} site associated with this emission band. In high-pressure single-crystal diffraction experiments, dravite can be indexed to a rhombohedral unit cell up to 15.4 GPa, the upper pressure limit of these measurements. It shows highly anisotropic compression with the *c*-axis being more compressible than the *a*-axis. We fit the pressure volume data to a 3rd order Birch-Murnaghan equation of state and get an isothermal bulk modulus, K_0 , of 90(3) GPa with a pressure derivative, K_0' , of 11(1) GPa. The origin of the very novel zero pressure shift of one of the two emission bands is correlated to changes in site volume as a function of compression, and a potential high-pressure isosymmetric phase transition is discussed. Our pressure volume results are also compared to previous studies on uvite (Ca, Mg endmember) and schorl (Na, Fe endmember) tourmaline. This study demonstrates the power of luminescence spectroscopy and single-crystal x-ray diffraction to investigate subtle changes in atomic positions as a function of pressure, which can be difficult when using other techniques at high pressure such as powder diffraction.