

Structural behavior of $C2/m$ tremolite to 40 GPa: A high-pressure single-crystal X-ray diffraction study

JASON N. OTT^{1,2,*}, BORA KALKAN^{1,3}, MARTIN KUNZ³, GENESIS BERLANGA¹, ALI F. YUVALI¹,
AND QUENTIN WILLIAMS¹

¹Department of Earth and Planetary Sciences, University of California, Santa Cruz, California 95064, U.S.A.

²Department of Earth and Space Sciences, Box 351310, University of Washington, Seattle, Washington 98195, U.S.A.

³Advanced Light Source, Lawrence Berkeley National Lab, 1 Cyclotron Road, Berkeley, California 94720, U.S.A.

ABSTRACT

The high-pressure structure and stability of the calcic amphibole tremolite $[\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2]$ was investigated to ~40 GPa at 300 K by single-crystal X-ray diffraction using synchrotron radiation. $C2/m$ symmetry tremolite displays a broader metastability range than previously studied clinoamphiboles, exhibiting no first-order phase transition up to 40 GPa. Axial parameter ratios a/b and a/c , in conjunction with finite strain vs. normalized pressure trends, indicate that changes in compressional behavior occur at pressures of ~5 and ~20 GPa. An analysis of the finite strain trends, using third-order Birch-Murnaghan equations of state, resulted in bulk moduli (K_{0T}) of 72(7), 77(2), and 61(1) GPa for the compressional regimes from 0–5 GPa (regime I), 5–20 GPa (II), and above 20 GPa (III), respectively, and accompanying pressure-derivatives of the bulk moduli (K'_{0T}) of 8.6(42), 6.0(3), and 10.0(2). The results are consistent with first-principle theoretical calculations of tremolite elasticity. The axial compressibility ratios of tremolite, determined as $\beta_a:\beta_b:\beta_c = 2.22:1.0:0.78$ (regime I), 2.12:1.0:0.96 (II), and 1.03:1.0:0.75 (III), demonstrate a substantial reduction of the compressional anisotropy of tremolite at high pressures, which is a notable contrast with the increasingly anisotropic compressibility observed in the high-pressure polymorphs of the clinoamphibole grunerite. The shift in compression-regime at 5 GPa (I–II) transition is ascribed to stiffening along the crystallographic a -axis corresponding to closure of the vacant A-site in the structure, and a shift in the topology of the a -oriented surfaces of the structural I-beam from concave to convex. The II–III regime shift at 20 GPa corresponds to an increasing rate of compaction of the Ca-polyhedra and increased distortion of the Mg-octahedral sites, processes which dictate compaction in both high-pressure compression-regimes. Bond-valence analyses of the tremolite structure under pressure show dramatic overbonding of the Ca-cations (75% at 30 GPa), with significant Mg-cation overbonding as well (40%). These imply that tremolite's notable metastability range hinges on the calcium cation's bonding environment. The eightfold-coordinated Ca-polyhedron accommodates significant compaction under pressure, while the geometry of the Ca-O polyhedron becomes increasingly regular and inhibits the reorientation of the tetrahedral chains that generate phase transitions observed in other clinoamphiboles. Peak/background ratio of diffraction data collected above 40 GPa and our equation of state determination of bulk moduli and compressibilities of tremolite in regime III, in concert with the results of our previous Raman study, suggest that $C2/m$ tremolite may be approaching the limit of its metastability above 40 GPa. Our results have relevance for both the metastable compaction of tremolite during impact events, and for possible metastable persistence of tremolite within cold subduction zones within the Earth.

Keywords: Tremolite, single-crystal X-ray diffraction, high-pressure, metastability, equation of state, synchrotron, diamond anvil cell