American Mineralogist, Volume 84, pages 454–464, 1999

Vibrational spectra of dense, hydrous magnesium silicates at high pressure: Importance of the hydrogen bond angle

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ABSTRACT

Changes in configuration and hydrogen bonding are inferred from the complex responses of peak parameters (frequency, width, height, and area) to compression for various hydroxyl groups in dense, hydrous magnesium silicates (DHMS). Stretching frequencies (ν_i) depend not only on both O-H...O bond length but also bond angle, which suggests a need to re-examine frequency-structure relationships at 1 atm. For phase B [$Mg_{12}{}^{VI}Si^{IV}Si_3O_{19}(OH)_2$], ν of the most intense OH^- peak determined from IR spectra at nearly hydrostatic pressures (P) decreases to a minimum at 5 GPa, and then rises to a broad maximum near 35 GPa, whereas ν of the other intense peak decreases to a broad minimum near 30 GPa. This behavior shows that compression of phase B initially moves O19 toward H2 on O21 and rotates H1 about O20 away from O19 and toward O21 inside the triangle of O atoms, thus increasing the H1-O20-O19 bond angle (from 12 to 21° at 37 GPa). H-H repulsion rotates H2 outside of the triangle by 11° at 37 GPa. Changes in O-O bond length and H-O-O angle calculated from the trends of OH frequency with increasing pressure are consistent with the relatively incompressible layer of SiO_4 tetrahedra. Widths, areas, and heights of the hydroxyl peaks also increase with P (whereas areas of the lattice modes are constant), with H1 being much more affected: This response suggests that the H1 bond bends further with compression. Raman spectra of stoichiometric OH^- modes in superhydrous phase B [$Mg_{10}{}^{VI}Si^{IV}Si_2O_{14}(OH)_4$] roughly parallel these trends, consistent with similarly paired hydroxyls with bent bonds. For phase A [$Mg_7{}^{IV}Si_2O_8(OH)_6$], the Raman OH^- bands depend linearly on P, and with constant peak height with slopes similar to those observed for weak stretching modes of trace H in phase B. This behavior is common and is associated with linear hydrogen bonds and unpaired OH^- groups. Combining our data with previous results reveals systematic, linear relationships of $d\nu/dP|_{i0}$ with ν that suggest high-polyhedral bulk moduli for DHMS.

Most frequencies of 31 mid-IR lattice modes for phase B depend linearly on curvature is seen for several modes. Raman frequencies of lattice modes from superhydrous phase B (shyB) and phase A depend linearly on P.