High-pressure behavior of 3.65 Å phase: Insights from Raman spectroscopy

Abhisek Basu[1,*], Mainak Mookherjee[1,†], Christelle Bucag[1], Sergey Tkachev[2], and Bernd Wunder[3]

[1]Earth Materials Laboratory, Earth, Ocean and Atmospheric Science, Florida State University, Tallahassee, Florida 32306, U.S.A.
[2]Center for Advanced Radiation Sources, University of Chicago, Chicago, Illinois 60637, U.S.A.
[3]Deutsches GeoForschungsZentrum GFZ, Section 3.6, Telegrafenberg, 14473 Potsdam, Germany

Abstract

The 3.65 Å phase [$MgSi(OH)_6$] is a hydrous phase that is predicted to be stable in a simplified MgO-SiO_2-H_2O (MSH) ternary system at pressures exceeding 9 GPa. Along cold subduction zones, it is likely to transport water, bound in its crystalline lattice, into the Earth's interior. The 3.65 Å phase consists of Mg and Si octahedral sites attached to the hydroxyl group that forms a hydrogen bond and is predicted to undergo pressure-induced symmetrization of the hydrogen bond. Therefore, in this study, we investigate the high-pressure behavior of the 3.65 Å phase using Raman spectroscopy. We have conducted five distinct compressions up to ~60 GPa using two different pressure-transmitting media—alcohol mixture and neon. At ambient conditions, we identified vibrational modes using complementary first-principles simulations based on density functional perturbation theory. Upon compression, we note that the first derivative of the vibrational modes in the lattice region stiffens, i.e., $b_i^{lattice} > 0$. In contrast, the hydroxyl region softens, i.e., $b_i^{OH} > 0$. This is indicative of the strengthening of hydrogen bonding upon compression. We noticed a significant broadening of vibrational modes related to hydroxyl groups that are indicative of proton disorder. However, within the maximum pressures explored in this study, we did not find evidence for pressure-induced symmetrization of the hydrogen bonds. We used the pressure derivative of the vibrational modes to determine the ratio of the bulk moduli and their pressure derivative. We note that the smaller bulk moduli of hydrous phases compared to the major mantle phases are compensated by significantly larger pressure derivatives of the bulk moduli for the hydrous phases. This leads to a significant reduction in the elasticity contrast between hydrous and major mantle phases. Consequently, the detection of the degree of mantle hydration is likely to be challenging at greater depths.

Keywords: Subduction zone, hydrous mineral phases, 3.65 Å phase, high-pressure Raman spectroscopy, diamond-anvil cell (DAC), hydrogen bonding