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

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ABSTRACT

The 3.65 Å phase [MgSi(OH)₆] is a hydrous phase that is predicted to be stable in a simplified MgO-SiO₂-H₂O (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., $b_{\text{lattice}} > 0$. In contrast, the hydroxyl region softens, i.e., $b_{\text{OH}} > 0$. 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

INTRODUCTION

Water exerts a significant influence on the dynamics of the solid Earth. For instance, water is known to lower melting temperatures (Hirschmann 2006) and affects transport properties including the rheology of the mantle (Karato 2010). Thus, considerable research has been done to understand how water is transported into the deep Earth and how much water is stored in the deep Earth. The efficiency of the transport of water is related to the thermodynamic stability of mineral phases including hydrous minerals and nominally anhydrous minerals. It is well known that hydrous phases often have limited thermal stabilities and hence they tend to dehydrate releasing water. The released aqueous fluids affect the surrounding mantle, which eventually leads to the melting of the overlying mantle wedge and is known to trigger earthquakes (Iwamori 1998, 2004, 2007; Kawamoto 2006). However, a part of the water is retained in dense hydrous phases which are efficient in transporting water to greater depths. Hence, significant research has been conducted to quantify the phase stabilities of hydrous phases (Kawamoto 2006; Pawley et al. 2007). Recent experimental studies on the simplified ternary system for hydrated mantle lithosphere, i.e., the MgO-SiO₂-H₂O (MSH) system have documented the existence of 3.65 Å phase— a thermodynamically stable form of MgSi(OH)₆ with a structure characterized by lattice plane spacing of 3.65 Å (Wunder et al. 2011, 2012; Koch-Müller et al. 2021) at pressures of 9–10 GPa. This phase is formed from the breakdown of the 10 Å phase [Mg₃Si₄O₁₀(OH)₂·nH₂O] with $n=7$ (Pawley et al. 2011; Wunder et al. 2011, 2012; Koch-Müller et al. 2021). The 3.65 Å phase could potentially transport ~35 wt% water, bound in its crystalline lattice, into the deep interior.

How much water is efficiently transported and sequestered in the deep Earth can be better understood if we can map the degree of mantle hydration. Thus it is crucial to have better constraints on the elastic and transport properties of these hydrous phases and nominally anhydrous phases and relate these constraints on the physical properties of the mineral aggregates with the geophysical observables. A key issue is that these hydrous phases often have high compressibility than that of nominally anhydrous phases, and it is quite important to have a better understanding...