Dense hydrous magnesium silicates (DHMS) are important potential carriers of water into deep parts of the Earth’s mantle due to their high-pressure stability and large hydrogen content. They can play an especially relevant role for the water cycle in regions related to deep subduction. Therefore, knowledge of their structure, stability, and physical properties is necessary to constrain the hydrogen budget in the Earth’s interior.

The DHMS 3.65 Å phase is named after the d-value of its most prominent X-ray reflection and was first synthesized by Sclar and Morzenti (1971) at 9 GPa and temperatures below 500 °C. Recently, Wunder et al. (2011) determined the composition of the 3.65 Å phase to be MgSi(OH)₆, characterized its IR and Raman properties, phase relations, and structure. The crystals of the 3.65 Å phase are too small for structure determination by single-crystal X-ray diffraction analyses. Therefore, constraints were placed on its structure by Rietveld refinement with powder XRD, using the structure of δ-Al(OD)₃ (Dachille and Gigl 1983; Komatsu et al. 2007; Matsui et al. 2011) as a starting model, and replacing the octahedral Al by Mg and Si according to the substitution 2[6]Al⁴⁺ = [10]Mg²⁺ + [10]Si⁴⁺. Accordingly, its structure can be considered as a modified hydrous A-site defective perovskite. From crystal chemical considerations the structure of the 3.65 Å phase is of great interest, as it represents the second DHMS with exclusively sixfold-coordinated Si beside phase D. Wunder et al. (2011) suggested two different structural models for the 3.65 Å phase: (1) by analogy with δ-Al(OD)₃, after Komatsu et al. (2007) four different H exist, which are arranged in the empty A-site positions of perovskite. This structural model with disordered H-positions has the symmetry of space group Pnam. (2) The second model with space group P2₁2₁2₁, is derived from the structure determination of δ-Al(OD)₃, after Matsui et al. (2011). In this structural model, hydrogen atoms are ordered and occupy three different positions within the vacant A site of perovskite. Octahedral tilt angles differ strongly in the two models. Wunder et al. (2011) assumed disordered (MgSi) configuration at the octahedral positions of both these structures. Rietveld refinements could not resolve the ambiguity about (MgSi) ordering.

In this study, we present results of DFT-calculations that were performed to constrain the symmetry and the positions of the hydrogen atoms of the 3.65 Å phase from lattice energy minimization. Furthermore, we performed low-T IR spectroscopy and computed the frequency-dependent dielectric response function as an independent verification of the proposed crystal structure. Adapting the structural parameters of the DFT-determined low-energy configuration we improved significantly the previous Rietveld refinement of the powder XRD pattern of the 3.65 Å phase.