

The 3.65 Å phase, MgSi(OH)₆: Structural insights from DFT-calculations and *T*-dependent IR spectroscopy

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ABSTRACT

First-principles calculations based on density-functional theory (DFT) and low-*T* IR spectroscopy were performed to gain more insight into the structure of the so-called 3.65 Å phase, a high-pressure phase of the composition MgSi(OH)₆. DFT-calculations predict a monoclinic symmetry with ordered sixfold-coordinated Mg and Si and six unique hydrogen sites as the most stable structure. Adapting the structural parameters of the DFT-determined lowest-energy configuration and assuming (MgSi)-ordering, a new Rietveld refinement of the powder XRD pattern of the 3.65 Å phase was performed, which resulted in excellent refinement statistics and successful assignment of X-ray reflections that were unassigned in former structural models with orthorhombic symmetry. A configuration with ordered Mg and Si at the octahedral positions causes a small monoclinic distortion of the network of strongly tilted octahedra and thus leads to space group *P*2₁. The structural refinement yields the following unit-cell parameters: *a* = 5.1131(3), *b* = 5.1898(3), *c* = 7.3303(4) Å, β = 90.03(1)°, *V* = 194.52(2) Å³, space group: *P*2₁, *Z* = 2, ρ = 2.637 g/cm³. The structure of the 3.65 Å phase can be considered as a modified A-site defective perovskite with a unique network of corner-sharing alternating Mg(OH)₆ and Si(OH)₆ octahedra and is probably related to the structure of stottite group minerals. Low-*T* IR spectroscopy confirms the presence of 6 different H-positions in the proposed structure. Measured IR-spectra and computed spectra compare favorably, which further supports the computed structure as the correct model for the 3.65 Å phase.

Keywords: 3.65 Å phase, DHMS, DFT-calculations, low-*T* IR, crystal structure