

New structural features of the high-pressure synthetic sheet-disilicate Phase-X, $\text{K}_{(2-x)}\text{Mg}_2\text{Si}_2\text{O}_7\text{H}_x$

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ABSTRACT

The structure of the synthetic high-pressure sheet-disilicate Phase-X (PhX), a possible host of H₂O and K in the mantle, has been determined for a crystal synthesized at 16 GPa/1300 °C/23 h. The composition of the sample is close to K_{1.5}Mg₂Si₂O₇H_{0.5}, which is 50% PhX/50% Anhydrous-PhX and has 25% of interlayer K sites vacant. The structures of four crystals were determined by single-crystal X-ray diffraction and had very similar diffraction characteristics and structural results; the structure of one of the larger crystals is reported here. Reflection intensity statistics strongly indicate that PhX is centrosymmetric, space group *P6₃/mcm*, in contrast to other studies that have reported non-centrosymmetric space group *P6₃cm*. While it was possible to obtain good agreement indices for refinements in *P6₃cm*, there were strong correlations between atoms that are equivalent in *P6₃/mcm*, suggesting that the correct structure is centrosymmetric. Full anisotropic refinement in space group *P6₃/mcm* gave $R_1 = 0.036$, $wR_2 = 0.079$, $\text{GoF} = 1.467$. As with all previous studies of PhX, the H atom was not located. Difference-Fourier maps of the residual electron density indicated that the K atom is displaced from the *4c* site lying on the sixfold axis on to three split *12j* sites 0.2 Å away, each having ¼ occupancy, giving a total of 3 K atoms per unit cell and corresponding to 1.5 K apfu, in good agreement with the content derived from electron microprobe analysis. Diffraction patterns of all four crystals examined, reconstructed from the full-intensity data collection, consistently show the presence of a large hexagonal superstructure with dimensions $8a_{\text{sub}} \times 8a_{\text{sub}} \times c_{\text{sub}}$, having $Z = 128$, compared with $Z = 2$ for the two-layer subcell. Complex arrays of superlattice reflections occur in layers with $l = 2n$, but are absent from $l = 2n + 1$ layers.

Unpolarized infrared spectra of single crystals of PhX were obtained that are similar to those reported previously in the literature. Spectra in the OH-stretching region consist of a major absorption band at 3595 cm⁻¹ and three much weaker bands at 3690, 3560, and 3405 cm⁻¹. Bond-valence analysis of PhX indicates that O1 is very over-bonded, whereas O2 is slightly under-bonded and a possible site for protonation. We present geometrical and crystal-chemical arguments that exclude O1 as a candidate for protonation, whereas a much better case can be made for O2. In PhX structures, H must be located at a partially occupied site with a multiplicity $4 \leq m \leq 24$ in *P6₃/mcm* or $4 \leq m \leq 12$ in *P6₃cm*. Such low occupancies for H sites are the likely reason for their invisibility to diffraction. We outline a model for the incorporation of H into PhX of composition K_{1.5}Mg₂Si₂O₇H_{0.5} that suggests a mechanism for ordering based upon avoidance of H and K, coupled with K-site vacancies. Such behavior may also be the origin of the superstructure. The *P6₃/mcm* structure and the presence of an underlying superstructure may well be characteristic of ordered intermediate compositions at or near PhX₅₀/Anhydrous-PhX₅₀. Identification of a new space group and recognition of a previously unobserved superstructure point to new possibilities for PhX and its derivatives that may bear significantly upon their stability at mantle conditions.

Keywords: Phase-X, structure, X-ray diffraction, superlattice, infrared spectroscopy