

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

MARK D. WELCH,<sup>1,\*</sup> JÜRGEN KONZETT,<sup>2</sup> LUCA BINDI,<sup>3</sup> SIMON C. KOHN,<sup>4</sup> AND DANIEL J. FROST<sup>5</sup>

<sup>1</sup>Department of Mineralogy, The Natural History Museum, Cromwell Road, London SW7 5BD, U.K.

<sup>2</sup>Institute of Mineralogy and Petrology, University of Innsbruck, Innrain 52, A-6020 Innsbruck, Austria

<sup>3</sup>Dipartimento di Scienze della Terra, Università di Firenze, Via La Pira 4, I-50121 Firenze, Italy

<sup>4</sup>School of Earth Sciences, University of Bristol, Queens Road, Bristol BS8 1RJ, U.K.

<sup>5</sup>Bavarian Research Institute of Experimental Geochemistry and Geophysics, University of Bayreuth, D-95440 Bayreuth, Germany

### ABSTRACT

The structure of the synthetic high-pressure sheet-disilicate Phase-X (PhX), a possible host of H<sub>2</sub>O 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<sub>1.5</sub>Mg<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>H<sub>0.5</sub>, 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 *P6<sub>3</sub>/mcm*, in contrast to other studies that have reported non-centrosymmetric space group *P6<sub>3</sub>cm*. While it was possible to obtain good agreement indices for refinements in *P6<sub>3</sub>cm*, there were strong correlations between atoms that are equivalent in *P6<sub>3</sub>/mcm*, suggesting that the correct structure is centrosymmetric. Full anisotropic refinement in space group *P6<sub>3</sub>/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  $\frac{1}{4}$  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<sup>-1</sup> and three much weaker bands at 3690, 3560, and 3405 cm<sup>-1</sup>. 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 *P6<sub>3</sub>/mcm* or  $4 \leq m \leq 12$  in *P6<sub>3</sub>cm*. 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<sub>1.5</sub>Mg<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>H<sub>0.5</sub> 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 *P6<sub>3</sub>/mcm* structure and the presence of an underlying superstructure may well be characteristic of ordered intermediate compositions at or near PhX<sub>50</sub>/Anhydrous-PhX<sub>50</sub>. 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