

# Behaviour of the variscite-1O polytype of $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ under non-ambient conditions

Xuejing He<sup>1</sup>, Hiroyuki Kagi<sup>1</sup>, Kazuki Komatsu<sup>1</sup>, Gerald Giester<sup>2</sup>, Shengxuan Huang<sup>3</sup>, Hiroki Kobayashi<sup>1</sup>, Sofija Miloš<sup>2</sup>, Herta S. Effenberger<sup>2</sup>, Satoshi Nakano<sup>4</sup>, Xiang Wu<sup>5</sup>, and Ronald Miletich<sup>2</sup>

<sup>1</sup> Geochemical Research Center, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo, Tokyo 113-0033, Japan, <sup>2</sup> Department of Mineralogy and Crystallography, University of Vienna, A-1090 Wien, Austria, <sup>3</sup> Key Laboratory of Planetary Science and Frontier Technology, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, 100029, P.R. China, <sup>4</sup> Key Laboratory National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan, <sup>5</sup> State key laboratory of geological processes and mineral resources, China University of Geosciences, Wuhan 430074, China

xuejinghe@g.ecc.u-tokyo.ac.jp; ronald.miletich@univie.ac.at

Aluminum phosphate hydrates ( $\text{AlPO}_4 \cdot x\text{H}_2\text{O}$ ) are known to exhibit a rich variety of individual phases. Stability and formation are significantly influenced by factors such as water content, environmental pH, temperature, and pressure conditions. This group of materials has gained considerable interests as functional materials, such as phase change materials (PCM), ceramic coatings, and corrosion-resistant materials. A comprehensive understanding of their crystal structure response to pressure and temperature is crucial with respect to the relevance of technical application.

Variscite-1O ( $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ , *Pbca*,  $Z = 8$ ), a member of the  $\text{MTO}_4 \cdot 2\text{H}_2\text{O}$  variscite group compounds ( $M^{3+} = \text{Al, Fe, Sc, Ga, In; } T^{5+} = \text{P, As}$ )<sup>[1]</sup>, is composed of vertex-sharing  $[\text{AlO}_4(\text{H}_2\text{O})_2]$  octahedra and  $[\text{PO}_4]$  tetrahedra<sup>[2]</sup>. The two structural water molecules give rise to four distinct hydroxyl groups (OW1-H11, OW1-H12, OW2-H21, and OW2-H22), three of which form hydrogen bonds with adjacent oxygen atoms (OW1-H12 $\cdots$ O1, OW2-H21 $\cdots$ O2, and OW2-H22 $\cdots$ O4), thus building up a hydrogen bond network in the voids between the polyhedra<sup>[2]</sup>.

In this work, we investigated the equation of state, crystal structure, and vibrational properties of the variscite-1O polytype under high pressure conditions up to  $\sim 20$  GPa and temperature variations from 100 to 500 K, using powder X-ray diffraction (PXRD), single-crystal X-ray diffraction (SCXRD), first-principles calculations, and Raman spectroscopy.

PXRD data showed that the variscite-1O structure remains stable up to the highest investigated pressure of 15.6 GPa. Under ambient conditions, OW1-H12 is the only non-hydrogen-bonding hydroxyl group, with a relatively large donor-acceptor distance of  $d(\text{OW1}\cdots\text{O3}) = 3.47988(6)$  Å. SCXRD data collected up to 6.6 GPa revealed a linear decrease in  $d(\text{OW1}\cdots\text{O3})$ , indicating pressure-induced OW1-H12 $\cdots$ O3 hydrogen bond strengthening. First-principles calculations were performed in a wider pressure scale up to  $\sim 20$  GPa. The results demonstrated nonlinear correlations and predicted the formation of the OW1-H12 $\cdots$ O3 hydrogen bond at pressures between 13 and 21 GPa, corresponding to  $d(\text{OW1}\cdots\text{O3})$  approaching  $\sim 2.7$  Å. Raman spectra collected up to 21.3 GPa exhibited a continuous redshift of the OW1-H12 hydroxyl stretching mode, further confirming the pressure-induced hydrogen bond strengthening and formation.

SCXRD experiments under temperature variations revealed thermal dehydration of variscite-1O starting at 450 K and found completed at 500 K. The removal of the two water molecules led to a transformation of the  $[\text{AlO}_4(\text{H}_2\text{O})_2]$  octahedron into an  $[\text{AlO}_4]$  tetrahedron, resulting in a phase transition from variscite-1O to a berlinite-type  $\text{AlPO}_4$  phase. This dehydration process was also tracked by temperature-varying Raman spectroscopy, which indicated completion at 503 K.

[1] Kolitsch, U., Matthias, W., Kovrugin V.M. & Krivovichev S.V. (2020). *Mineral. Mag.* **84**, 568-583.

[2] Kniep, R., Mootz D. & Vegas A. (1977). *Acta Cryst.* **B33**, 263-265.