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NEW POLYMORPH OF $CaHPO_4$ (MONETITE): SYNTHESIS AND CRYSTAL STRUCTURE

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A novel form of anhydrous dicalcium phosphate $CaHPO_4$ (monetite) is synthesized hydrothermally and characterized by single crystal X-ray diffraction. It crystallizes in the orthorhombic space group $Ccm2_1$ with $a = 6.242(1)$ Å, $b = 6.994(2)$ Å, $c = 7.003(3)$ Å, $V = 305.73(16)$ Å^3 and it has four independent unit formulas in the unit cell ($Z = 4$). A three-dimensional crystal structure can be described by $\{HPO_4\}_n$ infinite zigzag chains linked by Ca—O bonds. The comparison to the crystal structures of other polymorphs is given.

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The chemistry and crystal structure of calcium phosphates is an interesting field of study for a long time. These compounds have been largely studied for their important properties and applications in different domains. They are studied for biomedical applications [1], bone regeneration [2], bio-implant [3], dental and orthopaedic usage [4]. The synthesis and structural characterization of anhydrous calcium hydrogen phosphates have been well known for a long time [5]. In this work we focus on the crystal structure of new polymorph monetite.

Experimental. Synthesis of $CaHPO_4$. Colourless transparent single crystals of $CaHPO_4$ were prepared hydrothermally from a mixture of $CaCO_3$, $Fe(NO_3)\cdot 9H_2O$, and H_3PO_4 in the molar ratio Ca:Fe:P = 1:1:4 in an aqueous solution. The mixture was poured into a 20-ml Teflon-lined autoclave (filling degree 70 %) and heated under autogenous pressure at 180 °C for two weeks. Colourless and light pink single crystals were obtained. They were identified using single crystal diffraction analyses as and orthorhombic polymorph $CaHPO_4$ and $Ca_{0.5}Fe(HP_3O_{10})$ respectively. The reaction product was separated from the excess flux by successive washing with boiling water.

X-ray crystallography. X-ray diffraction data were collected at 298 K on an Enraf-Nonius CAD-4 diffractometer [6, 7] (graphite monochromator, MoK_α radiation).

The crystallographic data of the orthorhombic polymorph are: $CaHPO_4$, $FW = 136.06$, $T = 298$ K, crystal size 0.20×0.12×0.07 mm^3, colourless, prism, orthorhombic, $Ccm2_1$, $a = 6.242(1)$ Å, $b = 6.994(2)$ Å, $c = 7.003(3)$ Å, $V = 305.73(16)$ Å^3, $Z = 4$, $\rho_{calc} = 2.956$ g/cm^3, $\mu(MoK_\alpha) = 2.40$ mm^{-1}, scan mode $\omega / 2\theta$, a total of 761 reflections ($\theta_{min}/_{max} = 4.4/26.9°$), 215 reflections independent, 200 observed reflections ($I \geq 2\sigma(I)$), 35 parameters, absorption correction (ψ-scan), T_{min}, T_{max} 0.869 / 0.971, GOOF = 1.31, $R_{int} = 0.029$, $R = 0.025$, $wR(F^2) = 0.070$), max/min diff. peak 0.46/–0.68 e/Å^3, absolute structure parameter (Flack) 0.0(2).

The reflection intensities were collected at $\theta = 27°$ with two standard reflections for intensities and the orientation control. Intensity data were corrected for Lorentz and polarization effects and secondary extinction [8]. The absorption correction was obtained *via* psi-scan [9]. The structures were solved by direct methods and subsequently refined by Fourier difference techniques with full-matrix least squares based on F^2 using SHELX [8] under the WinGX software package [10]. It was found that the new compound crystallized in the orthorhombic system, space group $Ccm2_1$. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Even though the H atom occupies a general position and is only 50 % occupied, it was located in a difference Fourier map and found to be attached to a P—O vertex. Restraints were required to ensure a stable refinement of this H atom species. The refinement of the atomic coordinates led to the reliability factors $R(F) = 0.025$ and $wR(F^2) =$ $= 0.070$ considering 215 independent reflections ($I > 2\sigma(I)$). The structure graphics were drawn with diamond 2.1 supplied by Crystal Impact [11]. Further details of the crystal structure investigation can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 (0) 1223-762911; email: deposit@ccdc.cam.ac.uk (or at www.ccdc.cam.ac.uk/conts/retrieving.html) on quoting the deposit number CCDC 1049121.

Results and discussion. To the best of our knowledge, the structure of the title compound is the new polymorph monetite $CaHPO_4$. It crystallizes in the orthorhombic space group $Ccm2_1$, two others have triclinic forms; low-temperature (LT) and room-temperature (RT) polymorphs crystallize in $P1$ [12] and P-1 [13] spaces groups respectively.

The asymmetric unit of orthorhombic $CaHPO_4$ (DCPA) contains one HPO_4 group and one Ca^{2+} cation. Fig. 1 shows that these PO_4 tetrahedra are linked together by O1—H1···O3 hydrogen bonds to form $\{HPO_4\}_n$ infinite zigzag chains lying parallel to the (010) plane and running along the *c* axis. The Ca—O bonds link these chains to form a three-dimensional network structure.

The distortion indices *DI* for the coordination polyhedra around P are calculated from the empirical formulas

$$DI_d = \sum_{i=1}^{4}(|\, d_i - d_m \,|/4d_m); \quad DI_a = \sum_{i=1}^{6}(|\, a_i - a_m \,|/6a_m) \ \text{ and } \ DI_o = \sum_{i=1}^{6}(|\, o_i - o_m \,|/6o_m).$$

with *d*, *a*, and *o* signifying the P—O bond distance, the O—P—O angle, and the O—O edge respectively. The index *i* indicates individual values and the index *m* is the mean value for the tetrahedra.

The polyhedron P1 is a regular tetrahedron. The distortion index does not exceed 2 % (DI_d, DI_a, and DI_o are 0.014, 0.017 and 0.011 respectively).

The longest P1—O1 distance corresponds to P—OH bonds. With regard to the hydrogen bond system, only H1 atom is involved in weak O1—H1···O3 hydrogen bonds linking the phosphorus tetrahedra. The O1—H1 distance is 0.98(1) Å, H1···O3 is 1.98(4) Å, O1···O3 is 2.772(4) Å, and the angle O1—H1...O3 is 148(6)°.

Ca1 is coordinated to eight oxygen atoms with Ca—O ranging from 2.331(13) to 2.562(2) Å. The CaO_8 polyhedron is distorted, as shown by the Ca—O bond lengths.

The comparison of the title compound with other monetite polymorphs indicates that the most evident difference between the orthorhombic phase ($Ccm2_1$) and triclinic $CaHPO_4$ ($P1$ [12] or P-1 [13] space group) is the different atomic arrangement in the unit cell. In orthorhombic monetite, the calcium ions are coordinated by eight oxygen atoms and only one kind of hydrogen bonds exists in the structure. In each triclinic monetite (RT and LT), the Ca cations are coordinated to seven and eight oxygen atoms, and both structure types exhibit three kinds of hydrogen bonds. The PO—H distance is 0.98(1) Å in

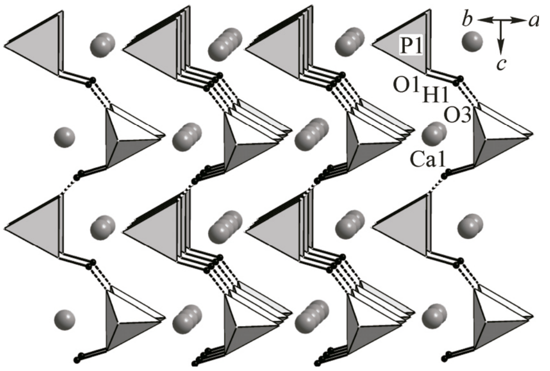

Fig. 1. Perspective view of the structure, showing the$\{HPO_4\}_n$ infinite chains running along the *c* axis, linked by the Ca—O bond, with hydrogen bonds represented as dashed lines

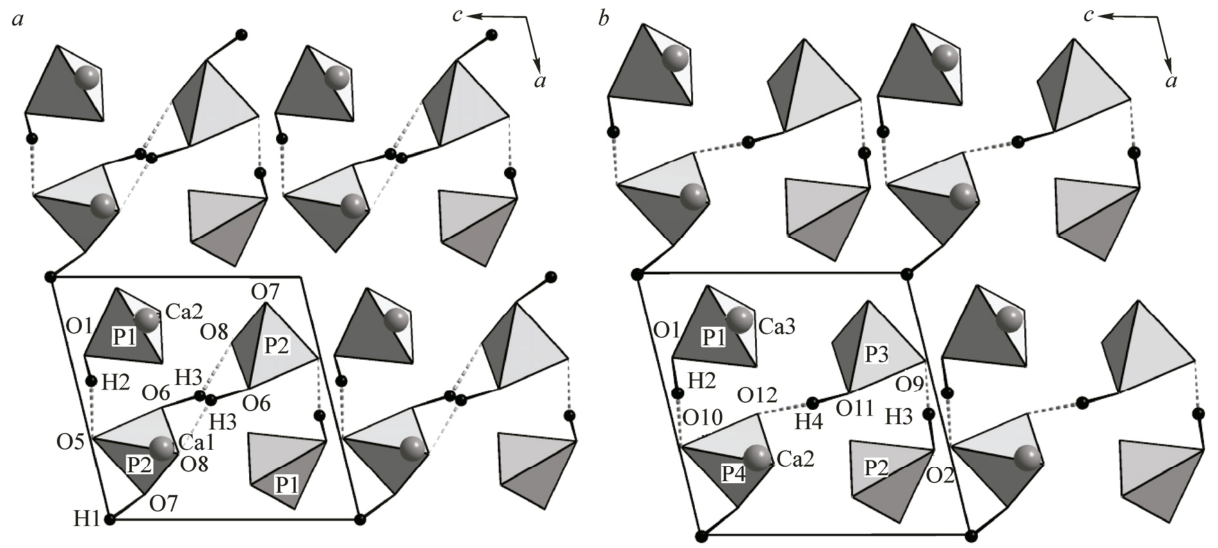

Fig. 2. Comparison of the hydrogen bonding schemes in triclinic monetite. The *P*-1 crystal structure (RT) (*a*) and the *P*1crystal structure (LT) (*b*)

the title compound and it varies from 1.039(1) to 1.227(7) Å and from 0.81(7) to 1.237(1) Å in LT and RT polymorphs respectively. The O···O distance in orthorhombic $CaHPO_4$ is 2.772(4) Å and it varies from 2.476(1) to 2.724(l) Å and from 2.474(2) to 2.815(3) Å in LT and RT polymorphs respectively [12, 13].

In the RT phase (*P*-1) [13], the H1 proton is centered on a symmetric hydrogen bond and the H3 proton is disordered over two centrosymmetrically related positions (Fig. 2, *a*). In the LT phase (*P*1) [12], monetite presents a reversible (order/disorder) phase transition in which only the hydrogen atoms are involved (Fig. 2, *b*).

Table 1

Selected structural characteristics of alkaline earth hydrogen phosphates and arsenates $M^{II}HXO_4$ (X = As *or* P)

Crystal system	Space group	Compound	*a*, Å α, deg.	*b*, Å β, deg.	*c*, Å γ, deg.	References
Triclinic	*P*1	$CaHPO_4$	6.916(2) 96.18(3)	6.619(2) 103.82 (3)	6.946 (3) 88.34 (3)	[12]
	P-1	$CaHPO_4$	6.910(1) 96.3	6.627(2) 103.8	6.998(2) 88.3	[13]
		$CaHAsO_4$	7.0591(8) 97.43(2)	6.8906(9) 103.55(2)	7.2006(16) 87.75(2)	[14]
		α-$SrHPO_4$	7.184(1) 94.7	6.790(1) 104.9	7.256(1) 88.7	[15]
		$SrHAsO_4$	14.697(3) 95.20(2)	28.230(5) 104.78(3)	14.920(3) 88.11(3)	[16]
Monoclinic	*P*2$_1$	$BaHAsO_4$	7.2370(2)	7.7133(2) 96.073(1)	21.8079(5)	[17]
Orthorhombic	*Ccm*2$_1$	$CaHPO_4$	6.242 (1)	6.994 (2)	7.003 (3)	[This work]
	Pbca	γ-$SrHPO_4$	8.131(3)	9.258(5)	18.084(7)	[18]
		$BaHAsO_4$	8.581(2)	9.896(2)	19.417(4)	[19]
	*Abm*2	α-$BaHPO_4$	4.5996(9)	22.809(5)	14.081(3)	[16]
	Pbnm	$BaHPO_4$	4.609(1)	14.195(3)	17.214(5)	[20]
	*Pn*2$_1$*a*	$BaHPO_4$	14.12(3)	17.15(3)	4.59(2)	[21]

The investigation of the crystal structure of alkaline earth hydrogen phosphates and arsenates shows that the hydrogen bonding plays an important role in the formation of anionic networks with different geometries. The alkaline earth hydrogen phosphates crystallized in three crystal systems (triclinic, monoclinic, and orthorhombic) with eight space groups (Table 1).

In summary, a new polymorph of calcium hydrogen phosphate(V) was synthesized using a hydrothermal method. It shows rich structural chemistry of the solid state. Hence, the variety and complexity of these structures and the evaluation of the factors that control and influence the crystal structures, necessarily lead to different physical properties and therefore applications in various fields.

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