Structure Determination of $CaH_2P_2O_7$ From *In Situ* Powder Diffraction Data

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Abstract

The formation of the phase $CaH_2P_2O_7$ by a dehydration reaction of $Ca_2P_4O_{12} \cdot 4H_2O$ at above 473 K has been observed by *in situ* high temperature diffraction measurements with synchrotron radiation. The structure was solved *ab initio* using synchrotron data from the *in situ* experiment. Additional Rietveld analysis of a room temperature powder pattern, collected on a conventional X-ray diffractometer, confirmed the obtained model and allowed the determination of the H atom position. It is the first known structure of a divalent metal cation dihydrogendiphosphate. $CaH_2P_2O_7$ crystallizes in the monoclinic space group C2/c with the cell parameters: a = 7.3276(1) Å, b = 8.1282(1) Å, c = 9.7632(1) Å and β = 101.2392(7)° and consists of isolated distorted CaO_6 octahedra connected via corner-sharing diphosphate groups. The anion groups $[H_2P_2O_7]^{2-}$ are interconnected by strong hydrogen bonds and form infinite layers parallel to the *c* direction.

Introduction

Investigations into calcium phosphates which are important components for fertilizer and animal nutrients lead also to the synthesis of $CaH_2P_2O_7$. The chemical preparation and powder patterns of it have been reported by several groups since the late 1940s [1, 2, 3, 4] but neither crystallographic data nor a structure have been determined up to now. The compound was either prepared by flux methods [3, 4], mixing of monophosphoric acid heated up to about 483 K and $Ca(H_2PO_4)_2 \cdot H_2O$, or by thermal dehydration-condensation reactions [1, 2] of $Ca(H_2PO_4)_2 \cdot H_2O$ or its dehydrated form under steam at 543-553 K.

In a more recent study by G.S. Mandel et. al. [5] calcium dihydrogendiphosphate was used as precursor for the preparation of biologically relevant crystals which are involved in the arthritic calcium pyrophosphate dihydrate deposition disease.

In contrast to monovalent-cations crystallographic and structural information about $M^{II}H_2P_2O_7$ are very limited and only a few lattice determinations for compounds with M=Mg, Zn, Ba and Sr have been reported [6, 7, 8].

Experimental

The formation of the calcium acidic diphosphate has been investigated *in situ* with synchrotron radiation at the powder diffraction beamline BM 16 of the ESRF. A wavelength of 0.63346(6) Å, calibrated using the NIST Si standard, selected from the double Si-monochromator, and a nine-crystal analyser stage as detector were employed for the measurements. The sample $Ca_2P_4O_{12} \cdot 4H_2O$ (calcium cyclophosphate tetrahydrate) [9] filled in a 1.0 mm quartz capillary, with one end not sealed but fitted with a ceramic tube to the goniometer head, was heated from RT to 1073K with a hot air blower by 1K/min and monitored by 10 min scans with a 2θ range between

0-20°. After formation of the new $CaH_2P_2O_7$ phase at 523 K a longer data collection (1.5 h) was carried out over a 2θ range of 0 to 50°. The in continuous mode measured data were later converted to equal step size of 0.005° (2θ). Patterns from the *in situ* investigation are displayed in Fig. 1.

Samples of $CaH_2P_2O_7$ for room temperature X-ray measurements have been prepared by dehydration reactions of $Ca(H_2PO_4)_2·H_2O$ (commercial compound) or $Ca_2P_4O_{12}·4H_2O$ in sealed glass capillaries with 2 mm in diameter at temperatures of 473-523 K for at least 12 hrs.

The reaction products were investigated by X-ray powder diffraction on a transmission diffractometer STOE STADI P with an incident beam curved germanium monochromator selecting $CuK\alpha_1$ radiation and a 6° linear position sensitive detector (PSD). One sample was filled in a 0.3 mm glass capillary and rotated during the data collection. More details are given in Table 1.
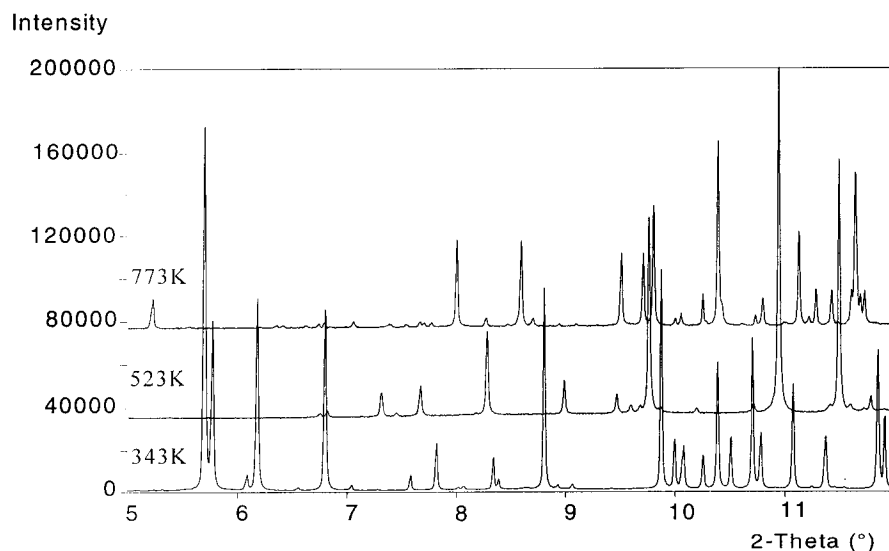

Fig. 1 Powder patterns from the *in situ* synchrotron measurements:
α-$Ca_2[P_4O_{12}]$ • $4H_2O$ (343 K), $CaH_2P_2O_7$ (523 K), β-$(Ca_2[PO_3]_4)_x$ (773 K).

Results

The *in situ* studies of the dehydration of $Ca_2P_4O_{12}·4H_2O$ (calcium cyclophosphate tetrahydrate) in quartz capillaries showed that the formation of the phase $CaH_2P_2O_7$ starts at about 463-473K under the hydrolytic influence of the self-generated water steam atmosphere. Further heating leads to a dehydration-condensation of the calcium dihydrogendiphosphate and the known phase β-$Ca_2(PO_3)_4$ (calcium polyphosphate) [10] is formed at about 673K. Three patterns from the *in situ* measurements are displayed in Fig. 1. In contrast to that the dehydration of $Ca_2P_4O_{12}·4H_2O$ by heating in dry air proceeds as a topotactic reaction via four intermediate phases to β-$Ca_2(PO_3)_4$ [11]. A crystallographic evaluation (indexing, lattice refinement) of a longer scan taken at 523 K after the formation of $CaH_2P_2O_7$ was carried out with the software package VISUAL X^{POW} © [12]. A monoclinic cell with two possible space groups C2/c and Cc was determined. The measured pattern with a 2θ range between 2 and 40° was decomposed with the program PROFIL [13] using the Le Bail Algorithm [14] and the 289 extracted reflections were used for a structure solution with the Direct Methods of SHELXS-97 [15]. Only for the space group C2/c a solution with atom positions

for Ca, P and one O was found. The remaining three oxygens were located from a Fourier difference map using SHELXL-97 [15]. The subsequent Rietveld refinement with PROFIL confirmed the obtained structure model converging with $R_{WP} = 11.8\%$ and $R_I = 7.1\%$ (background subtracted).

Table 1 Rietveld results for $CaH_2P_2O_7$, STOE STADI P data with $CuK\alpha_1$, 0.3mm capillary*

2θ-range (°), counting step (°)	15 - 115, 0.5
space group, Z	C2/c, 4
lattice constants	
a (Å)	7.3276(1)
b (Å)	8.1282(1)
c (Å)	9.7632(1)
β (°)	101.2392(7)
FWHM (°2θ) at 32°(2θ)	0.097
No. of contributing reflections	385
No. of refined parameters	32
No. of structural parameters	22
Profile R-factors (%)	
(background excluded)	$R_{wp} = 9.0$ $R_{exp} = 6.1$
(background included)	$R_{wp} = 4.6$ $R_{exp} = 3.5$
Intensity R-factor (%)	$R_I = 6.5$

* absorption correction $\mu*R = 0.69$ applied

For the Rietveld refinement of the structure $CaH_2P_2O_7$ at room temperature a data set with a 2θ range between 15 and 115° collected on the transmission diffractometer STOE STADI P was selected. The refinement with individual isotropic displacement parameters for each atom converged at reasonable R-values with $R_{WP} = 9.1\%$ and $R_I = 6.8\%$. The improved F("obs") values of 376 reflections were employed for another Fourier difference calculation and the position of the H atom bonded to O(2) could be located. The following Rietveld refinement led to an improvement of R_I to 6.5%. The position of the hydrogen could be refined without any restraints but the displacement factor had been fixed at about 1.2 times of the B-value of the O(2) atom. A summary about the Rietveld refinement with the STOE STADI P data is given in Table 1. The final refined atomic positions and displacement parameters including the H atom are given in Table 2, a Rietveld plot is displayed in Fig. 2. The Rietveld refinements revealed small amounts of an impurity phase which is according to the ICDD database (PDF 15-0230) $Ca_3H_2P_4O_{14}$ (3, 16).

Table 2 Final positional and displacement parameters and number of atoms per unit cell (N)

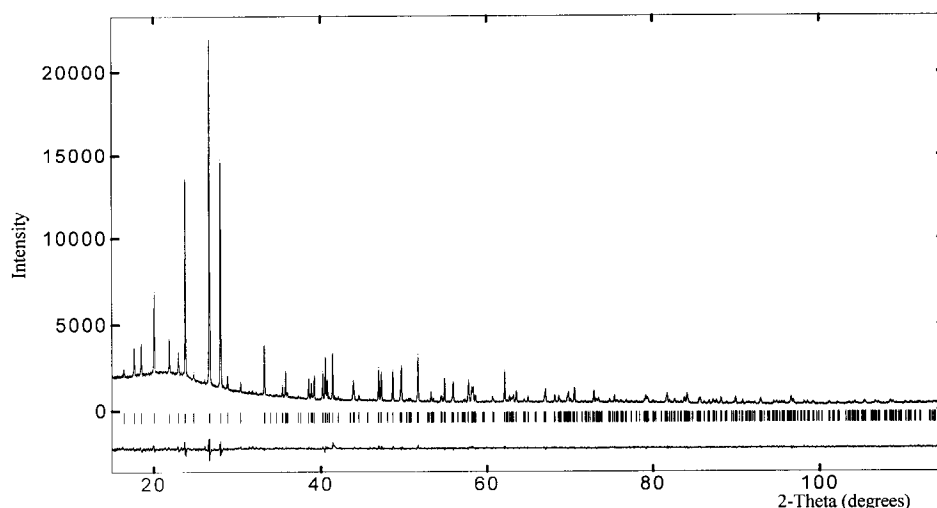| Atom	x	y	z	B_{iso} (Å^2)	N
Ca	0	0	0	0.36(6)	4
P	0.1643(4)	0.3836(3)	0.1899(3)	0.75(6)	8
O(1)	-0.2444(7)	0.0177(8)	0.1221(5)	0.9(1)	8
O(2)	0.3062(8)	0.3261(6)	0.3248(6)	0.8(2)	8
O(3)	0.0900(8)	0.2385(7)	0.1027(5)	1.0(1)	8
O(4)	0	0.4750(9)	1/4	0.8(2)	4
H	0.284(9)	0.226(9)	0.355(8)	1	8

Fig. 2 Rietveld plot: experimental, calculated and difference XRD profiles, tick marks for peak positions.

Description of the structure

Table 3 Selected bond lengths (Å), interatomic distances (Å), and angles (°)

Ca-O(1)	2 x 2.341(6)		
Ca-O(1)	2 x 2.448(5)		
Ca-O(1)	2 x 2.223(5)		
Ca-Ca (< 5 Å)	2 x 4.882(0)		
P-O(1)	1.498(7)	O(1)-P-O(2)	107.8(3)
P-O(2)	1.581(6)	O(1)-P-O(3)	117.8(4)
P-O(3)	1.494(6)	O(1)-P-O(4)	104.7(3)
P-O(4)	2 x 1.619(4)	O(2)-P-O(3)	110.4(3)
P-P (< 3 Å)	2.877(4)	O(2)-P-O(4)	104.4(2)
		O(3)-P-O(4)	110.8(2)
		P-O(4)-P	125.4(5)
O(2)-H	0.89(7)	P-O(2)-H	115(4)
H···O(1)	1.74(7)	O(2)-H···O(1)	167(7)
O(2)··O(1)	2.618(8)		

The structure of $CaH_2P_2O_7$ consists of isolated distorted CaO_6 octahedra which are connected via corner-sharing diphosphate groups. Calcium is placed on an inversion centre and has bonds to six different diphosphate groups. The Ca-O bond lengths are in the range between 2.22 and 2.45 Å as given in Table 3.

The P-O bonds in a PO_4 tetrahedron (Table 3) are characterized by two shorter bonds at about 1.50 Å, one intermediate bond at 1.581 Å, which corresponds to the P-O(2)H connection, and the long P-O(4) distance with 1.619 Å, where O(4) is the bridging oxygen of the diphosphate group. The bridging O(4) atom lies on a twofold axis which is also the internal symmetry of the $[H_2P_2O_7]^{2-}$ group. The P-P

distance with 2.877 Å and the P-O-P angle with 125.4° are relatively small compared to other diphosphate compounds [17].

Due to the acidic phosphate ions there is also a strong hydrogen bonding between neighbouring diphosphate groups. The closest distances between O(2) and O(1) from different diphosphate entities are at 2.618 Å. The corresponding H···O(1) bonds and the angles P-O(2)-H and O(2)-H···O(1) are also given in Table 3 and comparable to other dihydrogendiphosphates [17]. Due to these hydrogen bonds the acidic diphosphates are arranged in an infinite anionic network as displayed in Fig. 3. In this case the structure consists of corrugated bidimensional layers parallel to the c direction and connected by the calcium atoms. The hydrogen bonds are within these layers and the orientation of them is quasi-parallel to the b direction and the twofold axes.
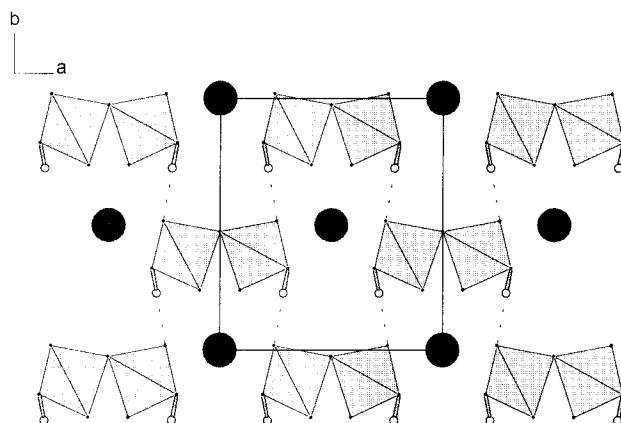

Fig. 3 Projection along the c direction, polyhedral representation of the anionic network with dashed lines for H bonds and the Ca atoms as dark grey spheres.

Conclusion

The compound $CaH_2P_2O_7$ has been prepared by a dehydration reaction of $Ca_2P_4O_{12} \cdot 4H_2O$ and the hydrolytic influence of the self-generated water steam atmosphere. The formation of this new phase has been investigated by $in \ situ$ synchrotron experiments and the structure has been solved $ab \ initio$ from the $in \ situ$ data. Furthermore, it was also possible to locate the hydrogen position using conventional laboratory data measured at room temperature. It is the first known structure of a divalent metal cation dihydrogendiphosphate.

Acknowledgements

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