Synthesis and Structure of a Calcium Polyphosphate with a Unique Criss-Cross Arrangement of Helical Phosphate Chains

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We report here the facile synthesis and structural characterization of γ-Ca$(PO_3)_2$, a novel polymorph of calcium polyphosphate. The single-step synthesis of this potential biomaterial was achieved using flux methods at 250 °C, yielding a single-phase product stable at room temperature. Single-crystal X-ray diffraction determined the structure to be of monoclinic symmetry ($a = 9.5669(2)$ Å, $b = 9.5023(2)$ Å, $c = 10.3717(3)$ Å, and $\beta = 93.474(2)°$, space group Cc), with layers of helical polyphosphate chains directed alternately along the [110] and [−110] unit cell directions to produce a unique arrangement of criss-cross polyphosphate layers separated by calcium ions. Further structural characterization by MAS-NMR and FT-IR was found to be consistent with this structure. Thermal studies indicated that γ-Ca$(PO_3)_2$ is stable up to 690 °C, whereupon it irreversibly converts to the β-Ca$(PO_3)_2$ polymorph.

Introduction

The compositional similarities between calcium phosphates and mineral components of hard tissue structures in the body, such as bone and teeth, ensure that the isolation and characterization of calcium phosphates is of particular interest to biomedical researchers. The potential for high biocompatibility and osteoconductivity afforded by calcium phosphates makes them important biomaterials for many hard tissue repair and regenerative applications, including use directly as dental and orthopedic implants, as implant coatings, or as cements.[1,2] These areas of biomaterials research have undergone an enormous expansion in recent years, fuelled by advances in treatments, demands from aging populations, and higher patient expectations. This, in turn, has led to increased interest in the synthetic and structural chemistry of calcium phosphate materials. This chemistry is complicated by the diversity of structures adopted by calcium phosphates and the stability of many of these structures to variations in composition, this often having significant influences on the resulting physical and mechanical properties. This is exemplified by hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), which most closely resembles the mineral component of natural bone but whose properties strongly depend on stoichiometry[1]. Despite displaying significant similarities with natural hard tissue, synthetic hydroxyapatite often exhibits brittleness, limited bioresorption, and modulus mismatch, which limits application as a bone substitute.

The isolation of new calcium phosphate phases is an important route to improved biomaterials, and this is best achieved through a greater understanding of their synthetic and structural chemistry. With this in mind, we have chosen to target new calcium phosphates in the relatively unexplored area of condensed phosphates. These phases contain anions of tetrahedral PO_4 units linked by shared oxygen atoms, with the simplest and most common being the pyrophosphate anion ($P_2O_7^{4-}$). Further condensation of the phosphate groups can lead to the formation of chains, rings, sheets or three-dimensional networks, which can be crystalline or amorphous in nature. It is also significant to note that condensed phosphate anions are present in many organisms and play a number of key biological roles, such as mammalian energy transfer through adenosine triphosphate (ATP) and in DNA production and thus would appear to present no biocompatibility problems. In addition, they are also known to undergo enzymatic degradation by alkaline phosphatases,[3] suggesting the potential for increased bioresorption.[4]

A number of recent studies has successfully demonstrated the potential of calcium polyphosphate as a biomaterial in a range of applications. These calcium polyphosphates, sometimes also referred to as calcium metaphosphates, have the nominal stoichiometry Ca$(PO_3)_2$ and contain long polymeric chains of PO_4 units. The excellent biocompatibility, bioresorption, and osteoconductivity properties of calcium polyphosphates, usually in a glassy form, have been demonstrated by many groups in the pursuit of bone substitute materials.[4−10]

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Other biomaterial applications suggested have included use as a drug delivery matrix,[11] composite components,[6,9] bone screws,[12] and tooth crowns.[13] Nonbiomaterials applications have also been suggested and include use as humidity sensors[14] and as alternatives to asbestos fibers.[15] Importantly, some recent studies have highlighted the significance of phase composition and microstructure on the properties of calcium polyphosphates.[6,16]

The only calcium polyphosphate for which the structure is known is β-calcium polyphosphate (or β-calcium metaphosphate, β-$Ca(PO_3)_2$),[17,18] which contains chains of corner-linked phosphate groups running in a unidirectional manner through the structure. The synthesis of this phase is commonly achieved by the staged dehydration of precursor $Ca(H_2PO_4)_2 \cdot H_2O$.[19] Early work in this area, some performed over 60 years ago, has suggested the existence of up to three other polymorphs of $Ca(PO_3)_2$,[19−23] but synthetic details are rather ambiguous, and until now, none have been structurally characterized.

To target a direct synthesis of calcium polyphosphate phases and to more fully understand the synthetic and structural chemistry of these important materials, we have chosen to explore the use of phosphoric acid flux techniques that we have previously successfully employed to synthesize other condensed phosphate phases.[24,25] This paper reports on this study and in particular on the isolation and characterization of a polymorph of $Ca(PO_3)_2$, which possesses an unusual crystal structure containing layers of perpendicularly arranged polyphosphate chains.

Experimental Procedures

The polymorph γ-$Ca(PO_3)_2$ was synthesized from an acid-flux containing phosphoric acid (H_3PO_4, 85 wt %) and calcium hydroxide ($Ca(OH)_2$) in ratios of P/Ca from 2:1 to 6:1. The reaction mixture, contained within a porcelain crucible, was heated to 250 °C for 24 h and left to cool. A range of cooling rates was investigated from quenching to cooling over 72 h and was found not to influence the product formed, only the crystallite size. It is worth noting that we always observed the presence of solid product in our flux, even at the initiation of the quenching process. The final products, of white crystalline appearance, were collected by filtration and washed three times with distilled water to remove any remaining acid and then allowed to dry for 2−3 h at 120 °C.

Single crystals suitable for single-crystal X-ray diffraction were produced under the same reaction conditions but with slow cooling from reaction temperature over a period of 72 h. Single-crystal X-ray diffraction data were recorded at 23 °C on a Bruker Smart 6000 diffractometer equipped with a CCD detector and a copper tube source. Data were processed using SaintPlus,[26] and the structures were solved and refined using SHELXTL.[27] Displacement parameters for all atoms were refined anisotropically.

Powder X-ray diffraction (PXRD) data were collected using a Siemens D-5000 diffractometer, with a Ge primary beam monochromator, providing Cu $K\alpha_1$ radiation. These data were analyzed using the Rietveld method[28] through the GSAS suite of programs[29] to confirm structure and determine the bulk purity of the samples.

Scanning electron microscopy (SEM) was performed on a JEOL JSM 6300 at an accelerating voltage of 20 kV using the software package SemAfore, with digital slow scan image recording system version 4.01 to determine the morphology of the crystals.

Thermogravimetric analysis (TG) using a Rheometric Scientific STA 1500 and differential scanning calorimetry (DSC) using a Netzsch 404 C DSC were employed to investigate and quantify the thermal stability of product phases.

The FT-IR data were collected on Shimatzu 8300 spectrometer fitted with SensIR DuraSamplIR attenuated total reflectance sampling plate.

The ^{31}P MAS NMR spectra were collected on a Varian-Chemagnetics Infinity spectrometer equipped with an 8.45 T magnet with the spectrometer operating at 145.77 MHz. A Bruker 4 mm probe was employed with the sample spinning at 10−12 kHz. A pulse delay of 20 s and pulse length of 2 ms (∼45×bc tip angle) were used. Spectra were referenced against $NH_4H_2PO_4$ as a secondary reference at −0.9 ppm; thus, all the shifts quoted here are against the accepted primary shift reference of 85% phosphoric acid solution.

Results and Discussion

Synthesis. Our use of phosphoric acid flux methods as a facile route to calcium condensed phosphates has allowed the isolation of a hitherto uncharacterized polymorph of $Ca(PO_3)_2$ in a one step synthesis at a relatively low temperature. Initial analysis of PXRD data indicated the presence of a single-phase product, which was later confirmed by Rietveld analysis. Comparison with the limited PXRD data available from previous studies of calcium polyphosphates[22,23] led to the assignment of γ-$Ca(PO_3)_2$ to this polymorph. It should also be noted that variations in reactant ratios of P/Ca from 2:1 to 6:1 produced no discernible difference in the observed product, which in all cases was γ-$Ca(PO_3)_2$.

It is clear from the literature that until now, the only synthetic route considered to these important calcium polyphosphates originated from the early studies by Hill et al.[19−21]and Morin et al.[22] In these studies, syntheses involved

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Table 1. Crystal Data and Structure Refinement Details for γ-$Ca(PO_3)_2$

empirical formula	CaO_6P_2
Fw	198.02
T	296(2) K
radiation, wavelength	Cu Kα, 1.54178 Å
cryst syst	monoclinic
space group	*Cc*
a	9.5669(2) Å
b	9.5023(2) Å
c	10.3717(3) Å
β	93.474(2)°
V	941.13(4) Å^3
Z	8
calculated density	2.795 Mg/m^3
absorption coefficient	17.75 mm^{-1}
min/max transmission	0.27/0.27
cryst size	0.10 × 0.10 × 0.10 mm
θ max	70.31°
reflns collected/unique	2836/1336
R(int)	0.037
structure solution/refinement	direct methods/full-matrix least-squares on F^2
$2\sigma(I)$ reflns/params	1317/163
R1 ($2\sigma(I)$/all data)	0.031/0.031
wR2 ($2\sigma(I)$/all data)	0.075/0.075
absolute structure param	0.045(12)
largest residual electron density	0.471/−0.617 e Å^{-3}

the multi-stage decomposition of the precursor, $Ca(H_2PO_4)_2 \cdot H_2O$. In contrast, the facile route we report here requires no precursor phases, merely the use of the simple reagents $Ca(OH)_2$ and H_3PO_4, and comparable reaction temperatures. The added advantage of our flux route is not only a direct synthesis of γ-$Ca(PO_3)_2$ but a means of utilizing slow cooling regimes during crystallization to produce single crystals of sufficient size and quality to characterize the structure. However, analysis of the PXRD data from γ-$Ca(PO_3)_2$ samples synthesized using cooling rates ranging from rapidly quenched to cooling over 72 h gave no discernible variations in Bragg peak widths. We therefore may surmise that our syntheses produced crystallites that were always larger than the peak broadening threshold (i.e., <200 nm) and that partial crystallization probably occurs in the flux prior to cooling. This is supported by our observation of some solid product in the reaction vessel at reaction temperature prior to quenching. It should also be noted that during synthesis, an optimum of 24 h at reaction temperature was observed; any increase in this was found to have an insignificant effect on crystallite size of the products, and any significant reduction in duration reduced the purity of the product.

Structure. The analysis of a suitable single crystal indicated that γ-$Ca(PO_3)_2$ crystallized in the monoclinic space group *Cc*, with the refinement details shown in Table 1 (for further details, see Supporting Information).

The structure of γ-$Ca(PO_3)_2$, represented in Figure 1, consists of layers of unidirectional helical polyphosphate chains stacked in alternating perpendicular directions along the [110] and [−110] directions, respectively, with calcium ions in 7-fold coordination interconnecting these chains. The repeat unit or chain period for these helical chains was found to contain four phosphate units and is shown in Figure 2. Helical chains are relatively rare in long chain phosphates[30] but have been found to exist in $NaPO_3$[31] and $CoK(PO_3)_3$.[32] However, to the best of our knowledge, the observation of a criss-cross arrangement of these helical tetrahedral chains is unique in polyphosphate structures. And more generally, we are unaware of reports of this arrangement existing in any other tetrahedral chain structures, including silicates.

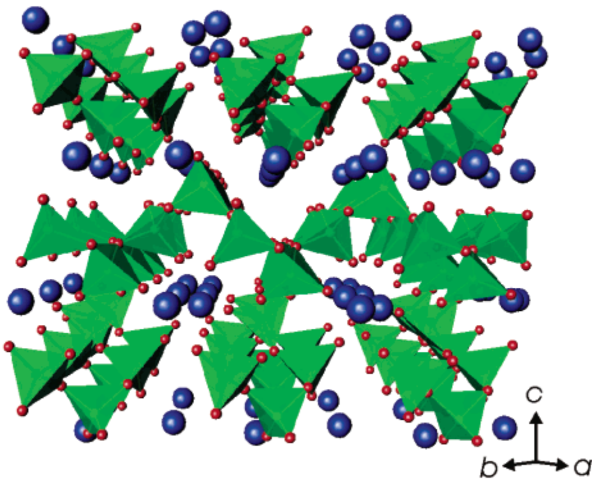

Figure 1. Crystal structure of γ-$Ca(PO_3)_2$, with calcium as blue spheres, oxygen in red, and PO_4 tetrahedra in green.

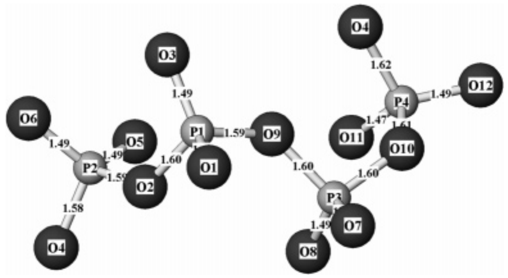

Figure 2. Polyphosphate chain structure in γ-$Ca(PO_3)_2$, showing atom labels (see Supporting Information) and bond lengths (Å) in the repeat unit.

Despite their unusual arrangement, bond lengths and angles within the polyphosphate units (see Figure 2 and Supporting Information) are closely comparable to those observed in other polyphosphate structures,[30] including β-$Ca(PO_3)_2$, the only previously characterized polymorph. The β-$Ca(PO_3)_2$ polymorph contains zigzag polyphosphate chains that are arranged in a unidirectional manner throughout the entire structure,[17,18] thus contrasting with our criss-cross arrangement of helical chains. Another difference between these two polymorph structures is that in β-$Ca(PO_3)_2$, the calcium ions are present in both 7- and 8-fold coordination, whereas in γ-$Ca(PO_3)_2$, we observed two crystallographically distinct calcium sites both of similar 7-fold coordination, in distorted capped trigonal prismatic arrangements (see Figure 3). A comparison of theoretical densities shows a small reduction in density for γ-$Ca(PO_3)_2$ over β-$Ca(PO_3)_2$ of ~2.3%.

A sample of the product from which the single crystal was taken was analyzed by PXRD to confirm the structural details of γ-$Ca(PO_3)_2$ and to provide an indication of bulk purity. This was achieved by performing a Rietveld analysis on this PXRD data using the recently obtained γ-$Ca(PO_3)_2$

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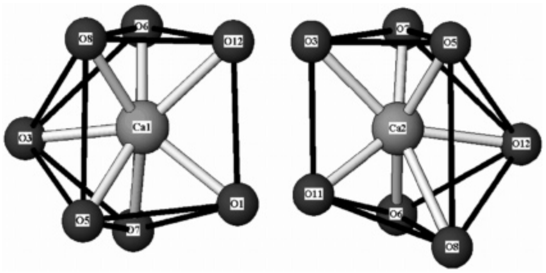

Figure 3. View of the two distorted face-capped trigonal prismatic coordination environments of calcium in γ-Ca(PO$_3$)$_2$.

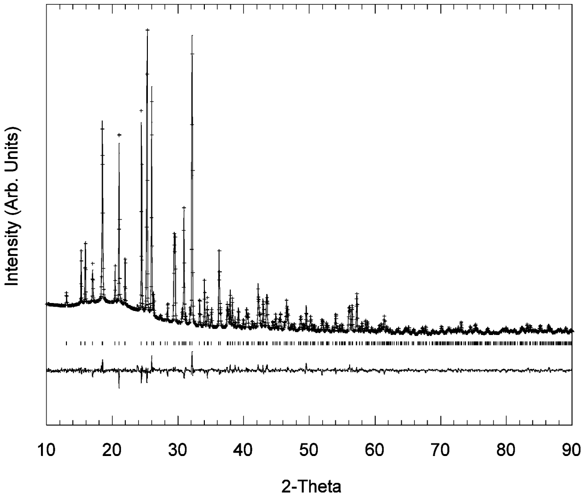

Figure 4. X-ray powder diffraction profile from the Rietveld analysis of γ-Ca(PO$_3$)$_2$, with observed data as crosses and calculated and difference as continuous lines. The tick marks indicate the reflection positions.

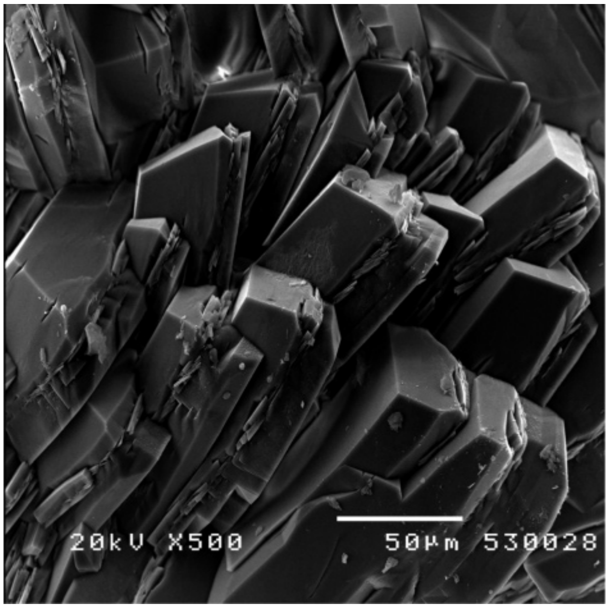

Figure 5. SEM image of γ-Ca(PO$_3$)$_2$.

structure as a starting model. Although somewhat less precise than the single crystal study, this analysis led to a good agreement between observed and calculated data (R_{wp} of 5.08%, R_{p} of 3.70%, and χ^2 of 3.304, profile shown in Figure 4), with resulting refined structural parameters confirming the γ-Ca(PO$_3$)$_2$ structure type previously obtained from the single crystal diffraction study (details in Supporting Information). In addition, the powder data clearly indicated the presence of only γ-Ca(PO$_3$)$_2$ in the sample, thus demonstrating that this synthetic route yields a single-phase product. Although not conclusive, a detailed analysis of SEM images indicating the existence of crystals of a single morphology (see Figure 5) would appear to concur with the presence of a single-phase product.

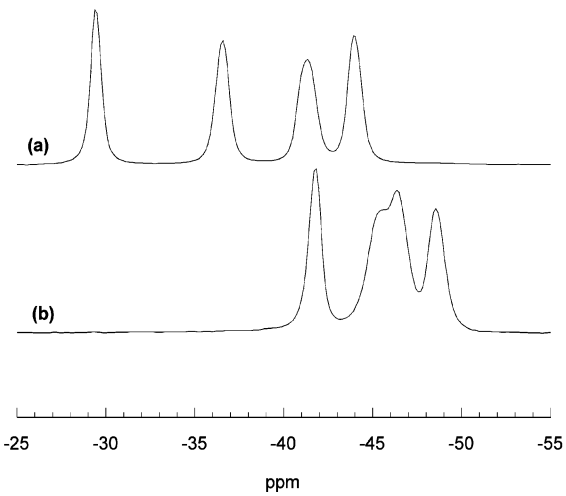

Figure 6. ^{31}P MAS NMR spectra of (a) γ-Ca(PO$_3$)$_2$ and (b) β-Ca(PO$_3$)$_2$.

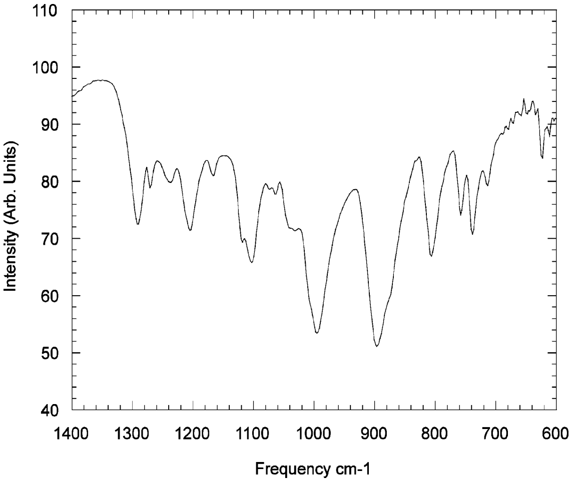

Figure 7. FTIR spectrum of γ-Ca(PO$_3$)$_2$.

A ^{31}P solid-state NMR study of γ-Ca(PO$_3$)$_2$ indicated the presence of four crystallographically distinct phosphorus environments with similar anisotropy (see Figure 6a) and was therefore in agreement with the structure obtained by diffraction. A similar NMR study was performed on a sample of β-Ca(PO$_3$)$_2$ and was found to also exhibit four distinct phosphorus sites, in line with its reported structure (Figure 6b)[17,18] but clearly distinct from those of γ-Ca(PO$_3$)$_2$. Thus, we have further proof of the single-phase synthesis of γ-Ca(PO$_3$)$_2$.

A sample of γ-Ca(PO$_3$)$_2$ was investigated by FT-IR, and the features observed were consistent with the structure we are reporting (see Figure 7) and closely match those previously reported for this polymorph.[33] The band in the region of 850−920 cm^{-1} was assigned to the antisymmetric stretching vibration of the P−O−P, which is at a low frequency due to the infinite number of PO$_4$ units. The band

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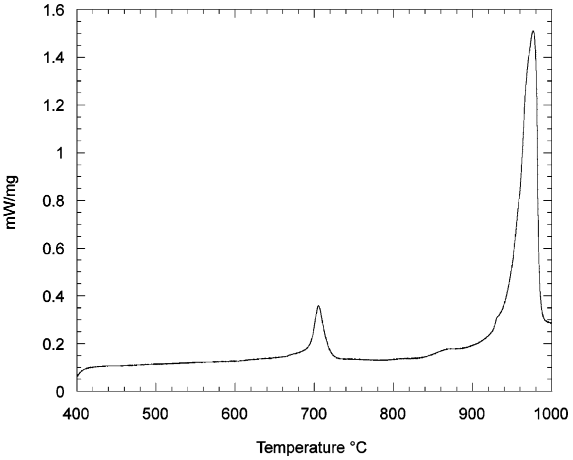

Figure 8. DSC measurement of γ-Ca(PO$_3$)$_2$.

in the region of 1160−1170 cm^{-1} was assigned to the antisymmetric stretch of the terminal PO$_3$ and the band at 1230−1250 cm^{-1} to the antisymmetric stretching vibration of the bridging PO$_2$. The symmetric stretching vibration of the bridging PO$_2$ was assigned to the band in the region of 1080−1110 cm^{-1} and the symmetric PO$_3$ stretching vibration to the region of 940−1020 cm^{-1}.

Thermal Stability and Polymorphism. The long-term room temperature and atmospheric stability of γ-Ca(PO$_3$)$_2$ was monitored over a period of 6 months, with no changes observed. To investigate the thermal stability of γ-Ca(PO$_3$)$_2$ at higher temperatures, TG and DSC were used. TG data indicated that no significant mass changes occurred when γ-Ca(PO$_3$)$_2$ was heated from room temperature to 950 °C whereupon melting to a glassy form occurred, with PXRD analysis confirming an amorphous product. The lack of any significant mass changes below 950 °C indicated an absence of stoichiometry changes, but to detect polymorphic phase transitions, DSC measurements were performed and are shown in Figure 8. These data appear to indicate a first-order phase transition occurring at 690−720 °C, associated with a transition enthalpy of 24 $\pm$ 1 kJ mol^{-1}. The structural nature of this transition was investigated using PXRD by analyzing a sample cooled from 750 °C. A detailed analysis of these data using Rietveld methods indicated that β-Ca(PO$_3$)$_2$ was the only phase present, with a good agreement (R_{wp} of 3.76%, R_p of 2.69%, and χ^2 of 2.89) to the reported structure of β-Ca(PO$_3$)$_2$[17,18] (details in Supporting Information). The presence of only the β-Ca(PO$_3$)$_2$ polymorph after this heat treatment demonstrated that an irreversible polymorphic transition from γ-Ca(PO$_3$)$_2$ to β-Ca(PO$_3$)$_2$ must account for the transition at 690−720 °C. Previous studies on this transition have been somewhat imprecise, reporting its occurrence at temperatures between of 450 and 800 °C.[20−23] Confidence in the accuracy of our observation is further supported by an initial in situ variable temperature PXRD study performed on γ-Ca(PO$_3$)$_2$ over the temperature range of 450−800 °C, which indicated that the diffraction pattern of γ-Ca(PO$_3$)$_2$ was observed until ~750 °C, whereupon we observed a change to that of β-Ca(PO$_3$)$_2$.

The existence of additional polymorphs to γ-Ca(PO$_3$)$_2$ and β-Ca(PO$_3$)$_2$ has been suggested but remains unsubstantiated. Early studies by Hill et al.[21] reported that the α-Ca(PO$_3$)$_2$ polymorph exists on the decomposition of β-Ca(PO$_3$)$_2$ at 963−968 °C, but the close proximity of this to the melting temperature at 984 °C has hindered confirmation of this report. Further analysis of our own DSC data does indicate two small features at 850−890 and 927−938 °C, which may provide evidence of polymorphic transitions, but at present, we have been unable to assign them, and studies are ongoing. The existence of a δ-Ca(PO$_3$)$_2$ polymorph, reported by McIntosh et al,[23] is also unsubstantiated, and this apparent low temperature form is also a target for our future syntheses.

Conclusions

The calcium phosphate phase, γ-Ca(PO$_3$)$_2$, has been isolated in a simple and direct synthesis. A full structural determination by single-crystal X-ray diffraction has shown this phase to possess a unique structure when compared to that of other polyphosphates due to the unusual arrangement of criss-cross helical polyphosphate chains and demonstrates that there is still potential for new and unusual structural architectures in calcium phosphate materials. In addition, this study provides a pure, well-defined calcium phosphate of novel structure with which to further probe the influence of structure on biomaterials function.

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Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles from the single-crystal X-ray diffraction study of γ-Ca(PO$_3$)$_2$, and an X-ray crystallographic file (CIF). Tables of atomic coordinates from Rietveld analysis of γ-Ca(PO$_3$)$_2$. Additional FT-IR and ^{31}P NMR data on γ-Ca(PO$_3$)$_2$. Rietveld diffraction profile of β-Ca(PO$_3$)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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