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A New Method for the Solid-State Synthesis of Tetracalcium Phosphate, a Dental Cement: X-Ray Powder Diffraction and IR Studies

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Abstract

Tetracalcium phosphate, $Ca_4P_2O_9$, (TetCP) a major compound of a cement in dentistry was prepared through different solid-state reactions at 1300 and 1350°C. Modified methods were used for the reported reactions and a new method of synthesis was suggested which was given by the following equation:

$$4\,CaCO_3 + 2\,NH_4H_2PO_4 \rightarrow Ca_4P_2O_9 + 4\,CO_2 + 2\,NH_3 + 3\,H_2O$$

The refined monoclinic parameters of TetCP were found to be $a = 7{\cdot}017\ (4)$, $b = 12{\cdot}021\ (8)$, $c = 9{\cdot}483\ (6)$ Å and $\beta = 88{\cdot}21°\ (8)$, which are in good agreement with the reported data. The space group is $P2_1/m$. The IR spectra of TetCP was analysed with respect to space group $P2_1/m$ and the band assignments were done for the first time in this work. © 1997 Elsevier Science Limited.

1 Introduction

Advances in biomaterials are occurring at an accelerated rate and attention is being directed to research and development of calcium phosphate biomaterials which can be used instead of metals, plastics and other ceramics conventionally available.[1,2]

Calcium phosphates are a class of materials which fulfill a wide range of uses and functions. Bones and teeth contain a high percentage of mineralized calcium phosphate. Therefore the most promising applications of calcium phosphates were made in dentistry. Dental application of calcium phosphate biomaterials can be summarized as below:[3]

1. Immediate tooth root replacement to prevent resorption of alveolar ridge
2. Restoration of alveolar ridge for better fit of dentures
3. Fillers for the repair of periodontal defects or bone loss
4. Coatings for metal implants to improve bone-implant adhesion and stabilize the implant

Research is still going on for further applications. These are:

1. Repair of cleft palate
2. Repair of maxillofacial defects
3. Pulp-capping materials

The most important properties of calcium phosphate biomaterials are their bioresorption and bioactivity. These phenomena are essentially dynamic and strongly depend on biological parameters.[4] Either resorbable (β TCP) or nonresorbable (HAp sintered at high temperature) types of calcium phosphate biomaterials can be used in dentistry depending on the field of application.[3,4]

Cement forms of calcium phosphate biomaterials can also be used in endodontics as a root canal sealer/filler material.

The idea of having a calcium phosphate implant material that sets like a cement is a very attractive one, because such material would have the high biocompatibility of calcium phosphate implants and handling characteristics of a cement.[5] In 1982 Le Geros *et al.* presented preliminary studies on the possibility of developing apatitic calcium phosphate cements.[6] Calcium phosphate cements were prepared by the reaction of dilute H_3PO_4 solutions with apatitic calcium phosphates. Brown and Chow patented a process of preparing a calcium phosphate cement by reacting TetCP with acidic

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calcium phosphate,[7–9] e.g. $CaHPO_4.2H_2O$ given by the following equation:

$$CaHPO_4 + Ca_4P_2O_9 \rightarrow Ca_5(PO_4)_3OH.$$

They react to form HAp which is biocompatible and comparable in density to hard tooth structures as observed by several researchers.[10–12] It is known that calcium phosphate ceramics, especially calcium hydroxyapatite and tricalcium phosphate (TCP), form bonds with living bones and many experimental investigations have been carried out in order to use those ceramics as hard tissue implant materials.[13] On the other hand it is well known that these ceramics after sintering in the range of 1100 to 1300°C contain impurities such as CaO and other kinds of calcium phosphates.[14]

Tetracalcium phosphate, TetCP (Hilgenstockite) is the most basic calcium phosphate known. It is a constituent of Thomas slag which is obtained in iron production and of other basic calcium phosphate systems at high temperatures. Its structure has been described as triclinic, monoclinic and orthorhombic. The space groups of the monoclinic and orthorhombic forms are reported as $P2_1$, $P2_1/m$ or $P2_122$ respectively.[15,16] On the other hand JCPDS data (Card No. 25-1137) gives the monoclinic type of $P2_1$ space group but the unit cell parameters are interchanged with $a = 7{\cdot}010$, $b = 11{\cdot}980$, $c = 9{\cdot}469$ Å and β, $= 90{\cdot}8°$ with $z = 4$. It has been reported that TetCP and hydroxyapatite (HAp) have similarities in their X-ray diffraction patterns and the two salts are structurally related.[15–18] This makes difficult the detection of TetCP in the presence of HAp. This difficulty is compounded by the fact that the indexes of refraction of TetCP and HAp are close to each other and the IR spectrum has no strong peaks that distinguish it in the presence of HAp. Kay *et al.* have carried out structure refinement studies for tetracalcium phosphate with X-ray and neutron diffraction studies.[17]

The common reaction for the preparation of calcium phosphates is to mix a suspension of $Ca(OH)_2$ and phosphoric acid to obtain an insoluble product which should be filtered, dried and milled but due to the difficulty of removal of contaminants, the wet process has rarely been used, and solid-state reactions are preferred. Solid-state reactions using lime and phosphoric acid derivatives proved that there are no byproducts or impurities. The commercially important basic calcium phosphate, known generally as tricalcium phosphate, is actually HAp and can be obtained through precipitation reactions till neutral pH. The α-form of TCP can be obtained by heating the product above 1000°C and the β form is obtained below this temperature. On the other hand synthesis of TetCP is done only by solid-state methods. The following reactions were suggested.[15,19]

$$2\,CaHPO_4 + 2\,CaCO_3 \rightarrow Ca_4P_2O_9 + 2\,CO_2 + H_2O \quad (1)$$

$$CaO + Ca_3(PO_4)_2 \rightarrow Ca_4P_2O_9 \quad (2)$$

$$2\,CaO + 2\,Ca_5(PO_4)_3OH \rightarrow 3\,Ca_4P_2O_9 + H_2O \quad (3)$$

$$\alpha\text{-}Ca_2P_2O_7 + 2\,CaO \rightarrow Ca_4P_2O_9 \quad (4)$$

The aims of the work described in this paper were as follows:

I. Preparation of TetCP through modified and new solid-state reactions and identification of the intermediate products such as HAp and TCP, by X-ray and IR techniques. In this research the following modifications have been done in the preparation methods given above.

(a) $CaCO_3$ and $Ca(OH)_2$ were used instead of CaO in some reactions.
(b) Temperatures between 1000 and 1400°C have been investigated and all the intermediate and final products have been studied by X-ray powder diffraction and IR methods.
(c) A new solid-state reaction has been proposed to prepare TetCP as given by the following equation:

$$4\,CaCO_3 + 2\,(NH_4)_2HPO_4 \rightarrow Ca_4P_2O_9 + 4\,CO_2 + 4\,NH_3 + 3\,H_2O \quad (5)$$

Instead of $(NH_4)_2HPO_4$, $NH_4H_2PO_4$ was also employed in these reactions. The reactions with ammonium phosphate were reported by Sarver[20] but he also used $Ca_3(PO_4)_2$ together with $CaCO_3$ and $(NH_4)_2HPO_4$. However the X-ray data of the prepared TetCP which were given in JCPDS File No. 11-232 fit the powder data of HAp. In this case the formation of HAp could be explained by the reaction given below:

$$Ca_3(PO_4)_2 + 2\,CaCO_3 + (NH_4)_2HPO_4 \rightarrow Ca_5(PO_4)_3OH + 2\,NH_3 + 2\,CO_2 + H_2O \quad (6)$$

II. The examination of the reaction products and the intermediate byproducts by X-ray and IR analysis and elucidation of the relations between HAP and TetCP through IR measurements.

2 Experimental

2.1 Chemical substances

The following chemicals are used in the synthesis of the products: $CaCO_3$, CaO, $Ca(OH)_2$,

$Ca_3(PO_4)_2.3H_2O$, $Ca_5(PO_4)_3OH$, $CaHPO_4$, $(NH_4)_2HPO_4$, $NH_4H_2PO_4$, α-$Ca_2P_2O_7$ (from Merck, Riedel, and Aldridge), KBr (Spectroscopic Grade).

2.2 Instrumentation

X-ray powder diffraction patterns were taken by using a Philips Diffractometer with PW 1050 /25 goniometer (FeK_α radiation, 30–40 kV, 10–20 mA, λ = 1·93728 Å). A Nicolet 510 FT-IR spectrometer was used in the 4000–350 cm^{-1} region. For measuring solid IR spectra, pellets with 2:100 mg product to KBr ratio were employed. All the reactions were carried out in air with the use of a tubular (Carbolite model STF 1500) furnace. Heatings were done in the range of 1000–1400°C.

2.3 Procedures

2.3.1 Solid-state reactions

In the following procedures the reactants were weighed separately and ground together in an agate mortar, then the mixtures were weighed again and transferred to platinum crucibles or silica boats for heating. The reactions were performed at several temperatures in the range of 1000–1400°C for 6 h. They were taken out of the hot furnace and transferred into a desiccator for quick cooling then weighed. The following seven reactions were tried.

$$CaCO_3 + Ca_3(PO_4)_2.3H_2O \rightarrow Ca_4P_2O_9 + CO_2 + 3H_2O$$

$$Ca(OH)_2 + Ca_3(PO_4)_2.3H_2O \rightarrow Ca_4P_2O_9 + 4H_2O$$

$$2CaHPO_4 + 2CaCO_3 \rightarrow Ca_4P_2O_9 + H_2O + 2CO_2$$

$$2Ca_5(PO_4)_3OH + 2CaCO_3 \rightarrow 3Ca_4P_2O_9 + 2CO_2 + H_2O$$

$$\alpha\text{-}Ca_2P_2O_7 + 2Ca(OH)_2 \rightarrow Ca_4P_2O_9 + H_2O$$

$$2(NH_4)_2HPO_4 + 4CaCO_3 \rightarrow Ca_4P_2O_9 + 4CO_2 + 4NH_3 + 3H_2O$$

$$2NH_4H_2PO_4 + 4CaCO_3 \rightarrow Ca_4P_2O_9 + 4CO_2 + 2NH_3 + 3H_2O$$

2.3.2 Chemical analysis of $Ca_4P_2O_9$

Determination of Ca was done by gravimetric analysis. It was precipitated as calcium oxalate then ignited in a platinum crucible to CaO. The supernatant from a calcium analysis was acidified with dilute HCl, phosphorus was precipitated as magnesium ammonium phosphate and ignited to $Mg_2P_2O_7$.[21]

3 Results and Discussion

3.1 Solid-state reaction of $CaCO_3$ + $Ca_3(PO_4)_2.3H_2O \rightarrow Ca_4P_2O_9 + CO_2 + 3H_2O$

The reactions were carried out under the conditions given below and the products observed by X-ray diffraction are reported in Table 1.

The expected reaction which should give pure $Ca_4P_2O_9$ was not observed in these experiments, but due to similarities in the X-ray diffraction patterns of apatite and TetCP it was decided to examine the products obtained at each temperature by IR spectroscopy.

3.1.1 Results of the reaction at 1000°C (sample Z2)

The IR spectrum of sample Z2 is given in Fig. 1 and the assigned frequencies to the IR bands are tabulated in Table 2.

3.1.2 Reactions at 1100, 1200 and 1300°C

X-ray powder pattern and IR spectra (Fig. 1) of the samples were all the same as the product obtained at 1000°C.

3.1.3 Reaction at 1400°C (sample Y1)

In the X-ray data of the product obtained at this temperature, apart from CaO and HAp d-spacings, extra lines due to TetCP also appeared. In the IR spectrum (Fig. 1, Y1) the splitting of the ϑ_3 and ϑ_4 vibrations, and shifts to higher frequencies (such as 1117 cm^{-1}) compared with the others, showed the lowering of symmetry from the space group $P6_3/m$ to $P2_1/m$ which are due to hexagonal HAp and monoclinic TetCP respectively. The observed frequencies are given in Table 3. ϑ_1, ϑ_2, ϑ_3, ϑ_4 are the vibrational modes that belong to HAp[22-24] and TetCP.[25-26]

3.2 Solid-state reactions of $Ca(OH)_2$ + $Ca_3(PO_4)_2.3H_2O \rightarrow Ca_4P_2O_9 + 4H_2O$

The reactions were performed at 1000, 1100, 1200, 1300 and 1400°C under the same conditions given

Table 1. Results of the solid-state reactions of $CaCO_3$ + $Ca_3(PO_4)_2.3H_2O$

Sample no.	*Temp. (°C)*	*Time (h)*	*Products*
Z2	1000	6	$Ca_5(PO_4)_3OH + CaO + CaCO_3$
Z3	1100	6	$Ca_5(PO_4)_3OH + CaO + CaCO_3$
Z8	1200	6	$Ca_5(PO_4)_3OH + CaO + CaCO_3$
Z9	1300	6	$Ca_5(PO_4)_3OH + CaO + CaCO_3$
Y1	1400	6	$Ca_4P_2O_9 + Ca_5(PO_4)_3OH + CaO$

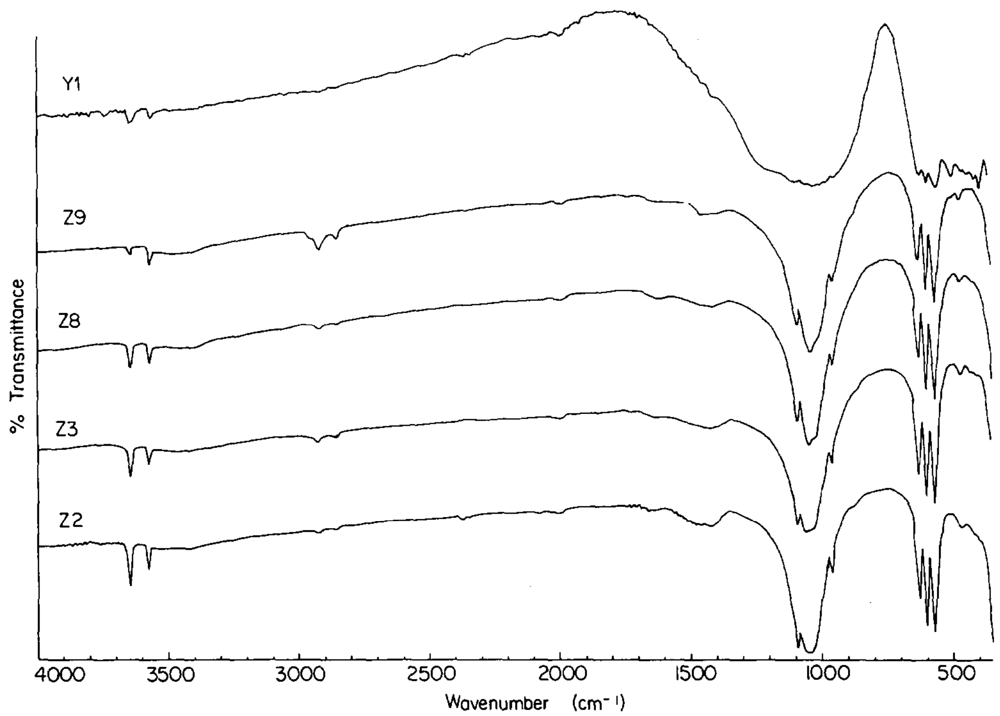


Fig. 1. IR spectra of the products of $Ca_3(PO_4)_2.3H_2O$ + $CaCO_3$ reactions at different temperatures (Z2, Z3, Z8, Z9, Y1).

before. Reaction at 1000, 1100, 1200 and 1300°C gave a mixed product as mentioned in the previous experiment but for the product obtained at 1400°C, a TetCP pattern was observed in the X-ray powder diffraction data which agreed quite well with the JCPDS data No. 25-1137. In the IR spectrum, the OH stretching mode of HAp disappeared. The peak at 3641 cm^{-1} which is due to $Ca(OH)_2$ is still present but weaker. The IR spectrum of this product was quite different from the previous ones and agreed with the reported IR data of TetCP[26] (Fig. 2).

Table 2. IR frequencies and assignments for sample Z2

Frequencies (cm^{-1})	*Assignments*
3648	OH^- stretching vibration (from $Ca(OH)_2$)
3571	OH^- stretching vibration (from HAp)
1470-1420	CO_3^{2-}
1089-1053 (ϑ_3)	PO_4 bands in HAp
962 (ϑ_1)	PO_4 bands in HAp
878	CO_3^{2-}
639	Vibrational mode of OH^-
603, 569 (ϑ_4)	PO_4 bands in HAp
477, 437 (ϑ_2)	PO_4 bands in HAp

Table 3. IR frequencies and assignments for sample Y1

Frequencies (cm^{-1})	*Assignments*
3648, 3571	OH stretching
1117, 1080, 1030 1010, 1000	ϑ_3
980, 960	ϑ_1
620, 615, 590, 560	ϑ_4
490, 455, 415	ϑ_2

3.3 Solid-state reactions of $2CaHPO_4 + 2CaCO_3 \rightarrow Ca_4P_2O_9 + H_2O + 2CO_2$

The reactions were performed at 1000, 1100, 1200, 1300 and 1350°C.

3.3.1 Reactions at 1000, 1100 and 1200°C (samples Z15, Z16 and Z17)

At these temperatures a mixed phase was obtained again ($CaCO_3$, CaO, HAp and β-TCP). In the IR data, bands due to OH stretching in $Ca(OH)_2$ and HAp, vibrational modes of phosphates (ϑ_1, ϑ_2, ϑ_3, ϑ_4), and carbonate peaks around 1400 cm^{-1} were observed.

3.3.2 Reactions at 1300 and 1350°C (samples Z18 and Z19)

TetCP appeared in the X-ray pattern but there were still some weak HAp and β-TCP and CaO peaks. In the IR data of the products, the splitting in the ϑ_4 region showed the formation of TetCP.

3.4 Solid-state reactions of $2Ca_5(PO_4)_3OH + 2CaCO_3 \rightarrow 3Ca_4P_2O_9 + 2CO_2 + H_2O$

3.4.1 Reactions at 1000, 1100 and 1200°C (samples Z20, Z21, Z22)

In the X-ray powder diffraction data a mixed phase was observed. The IR data were exactly the same as for the products obtained at these temperatures in the previous sets.

3.4.2 Reaction at 1300 and 1350°C (samples Z23 and Z24)

In both reactions only $Ca_4P_2O_9$ was obtained. The X-ray powder data agreed very well with the JCPDS pattern No. 25-1137. Sample Z23 has better crystallinity than the sample prepared at 1350°C. It was indexed in the monoclinic system with the unit cell parameters of a = 7·017(4), b = 12·021(8), c = 9·483(6)Å and β = 88·21°(8). In Table 4 the refined X-ray powder diffraction data for TetCP are given together with the reported data. Figure 3 (Z23 and Z24) shows the IR spectrum of the TetCP product which agreed with the results of the previous sets.

3.5 Solid-state reactions of α-$Ca_2P_2O_7$ + 2 $Ca(OH)_2 \rightarrow Ca_4P_2O_9 + H_2O$

3.5.1 Reactions at 1000, 1100 and 1200°C (Z28, Z27 and Z26)

In the X-ray and IR data of the products, HAp and β-TCP, α-TCP peaks were observed.

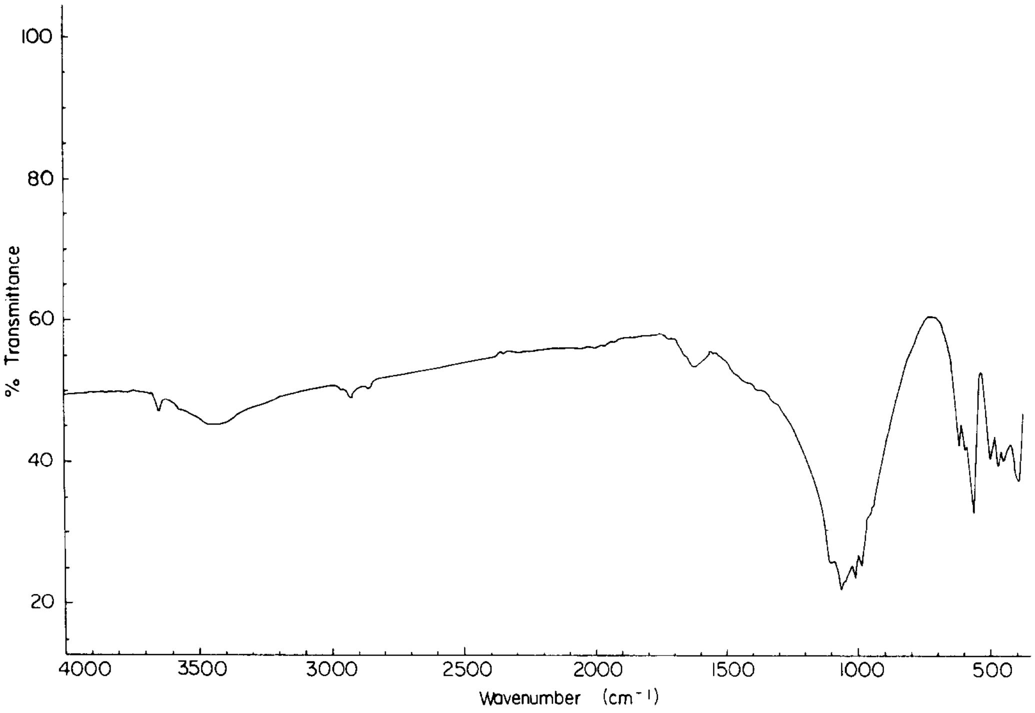


Fig. 2. IR spectra of the product of $Ca_3(PO_4)_2.3H_2O$ + $Ca(OH)_2$ reaction at 1400°C (Z14).

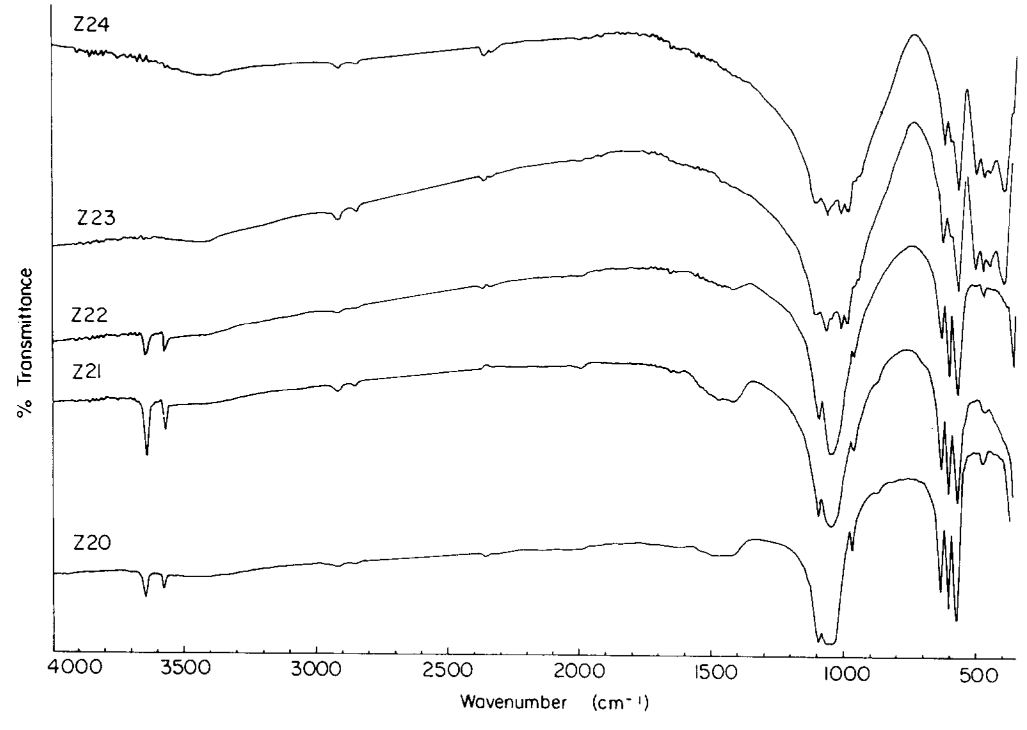


Fig. 3. IR spectra of the products of $CaCO_3$ + $Ca_5(PO_4)_3OH$ reactions at different temperatures (Z20, Z21, Z22, Z23, Z24).

3.5.2 Reactions at 1300 and 1350°C (Z25 and Z29)

α-TCP and TetCP were observed in the X-ray powder pattern of the product. These two compounds have the same space group ($P2_1/m$) with the same factor group C_{2h}. So in the IR spectrum, the 18 modes reported for C_{2h} system as discussed in Section 3.8 would be also observed for α-TCP. Therefore we could confirm the formation of α-TCP only from the X-ray powder pattern.

Table 4. X-ray powder data of $Ca_4P_2O_9$ (Sample Z23), monoclinic, a = 7·017 (4), b = 12·021 (8), c = 9·483 (6) and β = 88·21°(8), space group $P2_1/m$, radiation FeK_α

I/I_0	d_{obs}	d_{calc}	*hkl*	*JCPDS data*
16	6·055	6·055	110	6·06
17	5·968	6·012	020	5·99
5	5·714	5·685	–101	5·69
5	5·074	5·066	111(021)	—
11	4·735	4·738	002	4·74
13	4·556	4·563	120	4·56
11	4·404	4·408	012	4·405
11	4·118	4·131	–121	4·122
14	4·091	4·092	121	4·092
11	3·947	3·959	–102	3·959
12	3·881	3·892	102	3·897
10	3·755	3·760	–112	3·754
11	3·711	3·721	022	3·711
11	3·692	3·691	031	3·684
12	3·508	3·504	200	3·511
11	3·482	3·479	130	3·473
6	3·360	3·364	210	3·366
6	3·306	3·306	–122	3·302
8	3·276	3·276	–131	3·268
13	3·190	3·188	–211	3·190
12	3·160	3·158	211(003)	3·160
19	3·065	3·060	032	3·053
24	3·002	3·006	040	2·995
8	2·903	2·900	–103	2·895
14	2·873	2·871	221	2·872
15	2·815	2·817	–132	2·811
13	2·785	2·782	132(113)	2·789
12	2·782	2·782	113	2·784
16	2·766	2·766	–212	2·763
12	2·721	2·721	212	2·724
—	—	—	–141	2·649
—	—	—	141	2·642
7	2·637	2·638	230	—
7	2·608	2·612	–123	2·607
6	2·586	2·583	123	2·583
5	2·566	2·569	–222	2·567
5	2·547	2·551	–231	2·545
—	—	—	222	2·534
6	2·480	2·481	033	2·476
—	—	—	–142	2·387
5	2·377	2·379	142	—
4	2·349	2·349	–133	—
—	—	—	004	2·367
—	—	—	014	2·322
7	2·319	2·319	–232	2·314
6	2·292	2·293	232	2·292
—	—	—	150	2·268
4	2·255	2·257	–104	—
4	2·236	2·238	–311	2·237
—	—	—	–151	2·207
8	2·206	2·204	151(024)	2·204
—	—	—	043	2·173
6	2·169	2·168	233	—
—	—	—	052	2·137
5	2·129	2·130	–321	2·130
5	2·111	2·113	–124	2·109
—	—	—	124	2·092
5	2·085	2·087	–143	2·082
5	2·078	2·079	–312	2·077
5	2·2065	2·065	–242	2·061
5	2·055	2·055	–152	2·050

3.6 Solid-state reactions of $2(NH_4)_2HPO_4 + 4CaCO_3 \rightarrow Ca_4P_2O_9 + 4CO_2 + 4NH_3 + 3H_2O$

3.6.1 Reaction at 1000, 1100 and 1200°C (sample nos 1X 8X, 9X)

β-TCP and weak HAp lines were present in the X-ray pattern of the products.

3.6.2 Reaction at 1300 and 1350°C (samples 10X, 11X)

TetCP was the main product; CaO was also present in the X-ray pattern but its intensity was quite low. The following reaction mechanisms can be considered at these temperatures.

$$2(NH_4)_2HPO_4 + 4CaCO_3 \rightarrow CaO + \beta\text{-}Ca_3(PO_4)_2 + 4NH_3 + 3H_2O + 4CO_2 \qquad \text{1X}$$

$$3\beta\text{-}Ca_3(PO_4)_2 + 3Ca(OH)_2 \rightarrow 2Ca_5(PO_4)_3OH + 2CaO + 2H_2O \qquad \text{8X, 9X}$$

$$2Ca_5(PO_4)_3OH + 2CaO \rightarrow 3Ca_4P_2O_9 + H_2O \qquad \text{10X, 11X}$$

The second reaction is possible since CaO absorbs water in air and turns into $Ca(OH)_2$. The IR spectrum of TetCP agreed very well with the one reported by Ciesla *et al.*[26]

3.7 Solid-state reactions of $2NH_4H_2PO_4 + 4CaCO_3 \rightarrow Ca_4P_2O_9 + 4CO_2 + 2NH_3 + 3H_2O$

The reactions performed at 1000, 1100, 1200°C (samples 3X, 4X, 5X) gave the same results as the previous sets, except for the product obtained at 1200°C. In this case TetCP formation occurred at a lower temperature than in the previous sets. Reactions at 1300 and 1350°C (6X, 7X) gave a very pure TetCP. The IR spectrum of the TetCP obtained at 1350°C is given in Fig. 4. The vibrational frequencies for TetCP are tabulated in Table 5. Analysis of TetCP (7X) with respect to Ca and P content is given in Tables 6 and 7.

3.8 Interpretation of IR spectra

The crystal structure data for trigonal TCP, hexagonal HAp and monoclinic TetCP are tabulated in Table 8.

The factor group of TetCP is C_{2h} which is different from the two calcium phosphate structures reported above. Therefore the factor group analysis should be performed on TetCP since there

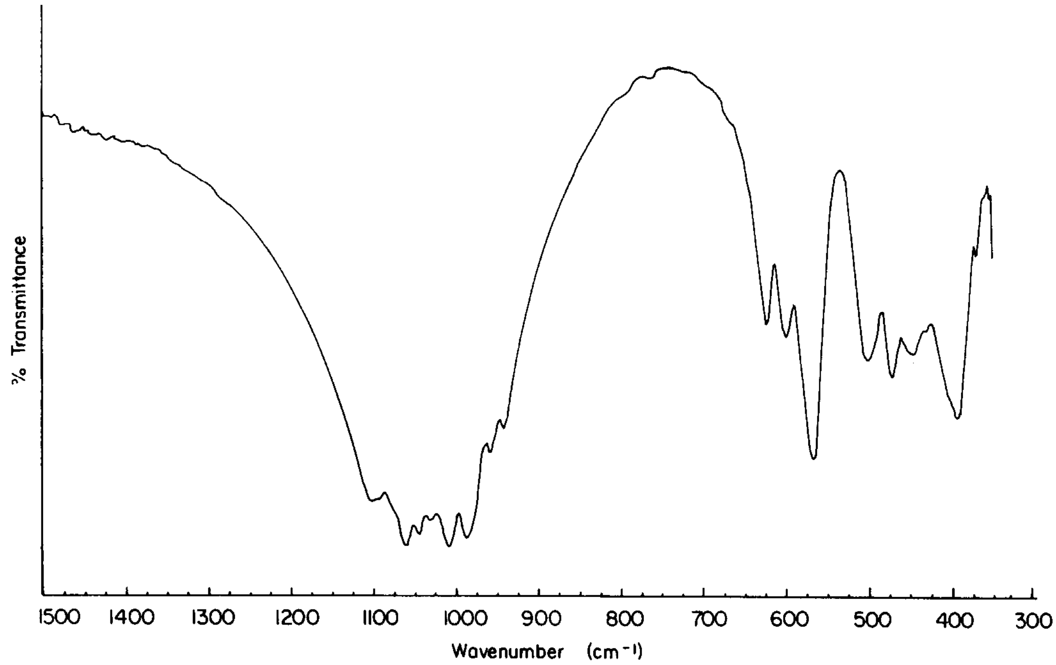


Fig. 4. IR spectra of the product of 2 $NH_4H_2PO_4$ + 4 $CaCO_3$ reaction at 1350°C (7X).

are very many common lines in the X-ray powder patterns of the three phosphates. To differentiate them from each other by means of X-ray powder diffraction was difficult.

The distribution of modes for C_{2h} factor group of T_d symmetry is given in Table 9.

From those $A_u + B_u$ are IR and $A_g + B_g$ are Raman active, then, as seen from Table 10, 18 internal modes are expected ($9\ A_u + 9\ B_u$). The above analysis gives the division of internal modes into symmetry classes but does not relate these 36 modes to the modes ϑ_1, ϑ_2, ϑ_3, ϑ_4 of the free PO_4^{3-} ion. It is not possible to carry out a direct correlation because the factor group, C_{2h}, is not a subgroup of the molecular point group, T_d; however in accordance with the rules laid down by Halford,[27] the site group C_1 of the PO_4^{3-} ion is a subgroup of both C_{2h} and T_d. Incidentally, the requirement that the site group be a subgroup of the molecular point group eliminates the possibility of the PO_4^{3-} ions occupying the C_i sites of the group C_{2h}^5 since C_i is not a subgroup of T_d. However inspection suggests that each component of an internal mode of the free ion gives rise to four components, one of each symmetry class, in the unit cell.[28] This would be given by the following correlation diagram in Table 10.

Figure 4 shows the splitting of ϑ_1, ϑ_2, ϑ_3 and ϑ_4 into 18 bands for TetCP.[29,30]

4 Conclusion

In this work the synthesis of TetCP has been performed through different solid-state synthesis methods but the reactions were carried out beginning

Table 5. Vibrational frequencies for TetCP (sample 7X)

ϑ_1	ϑ_2	ϑ_3	ϑ_4
960	417	1095	621
945	400	1064	601
	365	1044	570
	350	1030	500
		1012	473
		987	446

Table 6. Calcium content of the product 7X, (g)

Weight of initial product	*Experimental weight as CaO*	*Experimental weight as Ca*	*Theoretical weight as Ca*
0·2008	0·1217	0·0869	0·0878
0·2001	0·1128	0·0806	0·0876

Table 7. Phosphorus content of the product 7X, (g)

Weight of initial product	*Experimental weight as $Mg_2P_2O_7$*	*Experimental weight as P*	*Theoretical weight as P*
0·2006	0·1089	0·0339	0·0303
0·1999	0·1099	0·0338	0·0306

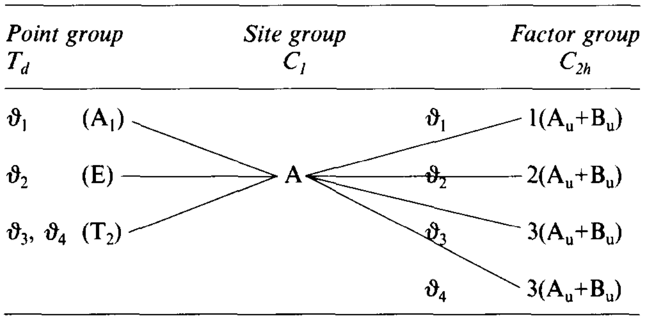
Table 8. Crystal structure data for trigonal TCP, hexagonal HAp and monoclinic TetCP

Crystal structure	*Product*	*Space group*	*Point group*	*Factor group*
Trigonal	$Ca_3(PO_4)_2$	R3c (D_{3h})	3m	D_{3d}
Hexagonal	$Ca_5(PO_4)_3OH$	$P6_3/m$ (C_{6h})	6/m	C_{6h}
Monoclinic	$Ca_4P_2O_9$	$P2_1/m$ (C_{2h})	2/m	C_{2h}

Table 9. Distribution of modes for C_{2h} factor group of T_d symmetry

Symmetry classes	A_g	A_u	B_g	B_u	*Total*
Total	18	18	18	18	72
Acoustic	0	1	0	2	3
Translational	6	5	6	4	21
Rotational	3	3	3	3	12
Internal	9	9	9	9	36

Table 10. Factor group analysis of T_d symmetry



with lower temperatures. It was observed that the reaction mechanism passes through HAp in the synthesis of TetCP. In all the reactions the intermediate phases were usually HAp or TCP (α or β) but the final product at higher temperatures was always TetCP as it was clearly seen in the IR data of several sets. The solid-state reaction performed at 1300 and 1350°C, with $CaCO_3$ + $NH_4H_2PO_4$ which was not reported in the literature, gave the best crystallized product of TetCP. It was also obtained at lower temperatures (1200–1350°C) than reported before (1400°C). TetCP was indexed in the monoclinic system with the refined unit cell parameters of a = 7·017 (4), b = 12·021 (8), c = 9·483 (6) and β = 88·21° (8) and the space group is $P2_1/m$. Its chemical analysis was in agreement with the theoretical values. On the other hand the factor group analysis of IR spectra with respect to space group $P2_1/m$ and band assignments were done for the first time in this work. This could probably be the best method for distinguishing TetCP from the other calcium phosphates.

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