

An investigation of the chemical synthesis and high-temperature sintering behaviour of calcium hydroxyapatite (HA) and tricalcium phosphate (TCP) bioceramics

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The experimental conditions for the synthesis of sub-micrometre, spherical particles of calcium hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] (HA) and tricalcium phosphate [$\text{Ca}_3(\text{PO}_4)_2$] (TCP) are investigated through chemical coprecipitation from the aqueous solutions of calcium nitrate and di-ammonium hydrogen phosphate salts. The precipitation process employed was also found to be suitable for the production of sub-micrometre HA/TCP composite powders *in situ*. The synthesized pure HA and TCP powders were found to be stable even at 1300 °C in air for prolonged heating times. Bioceramic sample characterization was achieved by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and density and surface area measurements. Crystallographic analyses of HA powders were performed by the Rietveld method on the powder XRD data.

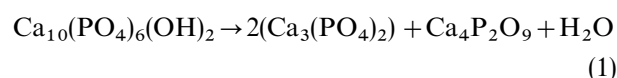
1. Introduction

Ceramics are historically the oldest of the synthetic materials and their medical use can be traced back to the Egyptians. In Egyptian sarcophagi, both filled and artificial teeth have been found in the mouths of mummies. According to a dentistry book from the late 1700s, dental implantation and transplantation were already popular in the eighteenth century [1]. In 1892, Dreesman published a report on the use of plaster of Paris to fill bone defects [2]. Almost 30 years later, Albee and Morrison were the first to report on the use of tricalcium phosphate (TCP) to fill bone gaps [3]. However, it was not until the 1960s that research into the application of ceramics as bone replacements increased, with osteoceramic (a composite ceramic of TCP and MgAl_2O_4) being one of the first to be proposed, and used successfully in experiments on dogs [4, 5].

Calcium hydroxyapatite (HA) and tricalcium phosphate (TCP) are the most commonly used calcium phosphate ceramics for bone replacement due to their biocompatibility [3–12]. Variations in atomic Ca/P ratios between 2 and 1.5 among the calcium phosphate ceramics, i.e., $\text{Ca}_4\text{P}_2\text{O}_9$, HA and TCP (β -Whitlockite), are known to lead to differences in degradability [13]. It is probably because of this difference in biodegradation behaviour that biodegradable TCP ceramics give rise to extensive bone remodelling around the implant [11].

It has been shown by Asada *et al* [14] that by-products have been found in HA ceramic powders

obtained by precipitation from $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{HPO}_4$ solutions and sintered above 800 °C, such as α - and β -TCP. Jarcho *et al.* [15] have previously shown in polycrystalline HA ceramics obtained by precipitation from $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{HPO}_4$ solutions, that at higher sintering temperatures such as 1250 °C (for 1 h) HA samples would decompose according to:



and documented this with an electron micrograph depicting the formation of a second phase at the HA grain boundaries in sintered samples.

Jarcho *et al.* [16], in a later study, claimed that the synthesis of “pure” β -tricalcium phosphate (Whitlockite) powders would only be possible in the presence of SO_4^{2-} anions in precipitation solutions containing Ca-nitrate and di-ammonium hydrogen phosphate salts. They reported that all samples which had not been doped (by about 1% of solution) with dilute $(\text{NH}_4)_2\text{SO}_4$ produced composite ceramics containing TCP and HA phases, simultaneously.

Decomposition of the ceramics or fluctuation of the Ca/P ratio is expected to result in such formation of unwanted by-products. The objective of this study was to synthesize “pure” HA and TCP sub-micrometre particulated bioceramic powders using aqueous synthesis solutions containing dissolved Ca-nitrate and di-ammonium hydrogen phosphate salts, and to

investigate their high-temperature (800–1300 °C) calcination/sintering behaviour and stability in air atmosphere.

2. Materials and methods

2.1. Ca-hydroxyapatite ceramic powder synthesis*

HA powders were prepared by an aqueous precipitation technique using 0.156 M $(\text{NH}_4)_2\text{HPO}_4$ (reagent grade, Merck) and 0.4 M $\text{Ca}(\text{NO}_3)_2$ stock solutions. $\text{Ca}(\text{NO}_3)_2$ solutions were prepared by dissolving stoichiometric amounts of CaO (99.9%, BDH Chemicals) in the presence of HNO_3 (reagent grade, Merck). The required amounts of both stock solutions to give the desired Ca/P atomic ratio of 1.667 in the aqueous mixture were measured, and the pH of both solutions was adjusted to about 10 by the addition of a dilute NH_4OH solution of proper strength. Following pH adjustment, 0.096 M $(\text{NH}_4)_2\text{HPO}_4$ solution was fed from a burette, in a dropwise manner (2–5 ml/min), into a stirred solution of 0.16 M $\text{Ca}(\text{NO}_3)_2$ heated to 60 °C on a hot plate. After mixing, the solution was aged and vigorously stirred at its boiling point for about 2 h in a sealed container. The HA precipitates were recovered from the solution by centrifugal filtration and washed three times with distilled water, followed by drying at 100 °C overnight.

2.2. Tricalcium phosphate ceramic powder synthesis

Stoichiometric proportions of $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{HPO}_4$ stock solutions were measured and the diammonium hydrogen phosphate aliquot was slowly added to the Ca-nitrate solution maintained at 60 °C. The pH of the reaction solution was maintained constant at 7 by the continuous addition of a dilute NH_4OH solution. Following a 2 h ageing, the solution was cooled to room temperature and the TCP precipitates were recovered by centrifugal filtration from the mother liquor.

2.3. Phase and microstructure analysis

The phase purities and crystal structures of the dried and lightly calcined (400–600 °C) HA and TCP powders were investigated by powder X-ray diffraction using a Rigaku D-Max/B diffractometer. Details of the XRD runs are given in Table I. The powder XRD data collected (with counting time increased to 10 s) on the synthesized HA powders were analysed using the Rietveld method [17,22–24] to obtain information on the HA unit cell contents.

The morphological features of the bioceramic samples were studied through gold-coated fracture surfaces of sintered pellets on a scanning electron microscope (SEM: JEOL-JSM 6400) at an accelerating voltage of 15 kV. Particle size was assessed from the SEM micrographs. The powders were first lightly ground in an agate mortar and then uniaxially pressed at 25 to 390 MPa into green pellets (1 cm diameter and 3 mm

TABLE I Experimental conditions for X-ray diffractometer runs

Radiation	Fe $K_{\alpha 1}$, 40 kV, 20 mA (incident beam monochromator)
Divergence slit:	0.5°
Receiving slit:	0.1 mm
Scattering slit:	0.5°
Profile breadth:	0.1° 2 θ
Specimen form:	Side loaded powder, packed for 2 θ s
Temperature:	24 ± 2 °C
Range of 2 θ from:	10° 2 θ to 100° 2 θ
Step width:	0.02° 2 θ
Counting time:	2 s at each step
External 2 θ standard:	Si (Lattice parameter = 0.54315 nm)
2 θ error correction:	Linear interpolation from nearest 2 θ s of std.
Intensity meas. technique:	Automated computer software (Rigaku D-Max/B) Profile fitting via Pearson VII (Peakfit 3.0, Jandel Scientific)
Cell refinement method:	Least-squares (Appleman & Evans, 1973).

thick) in a steel die, without causing a lamination problem in the green compacts. The sintering runs were performed at 1050 ° to 1300 °C (10 h) in air atmosphere. The fired pellets were cooled naturally to the ambient temperature in the furnace.

Semi-quantitative analyses of the chemical composition of HA and TCP samples were conducted by EDXS (energy dispersive X-ray spectroscopy, Tracor Series-2) on a JEOL JSM-6400 SEM. Data acquisition was performed at 15 kV for 200 s on the gold-coated fracture surfaces of the pellets used for morphological analyses. A given particle was analysed at the particular magnification at which it filled the monitor screen. Ca/P mole ratios of the samples were determined as the average of six consecutive runs on each sample. EDXS results are believed to be accurate to ± 3%.

3. Results and discussion

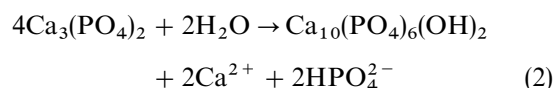
3.1. Calcium hydroxyapatite synthesis

Calcium hydroxyapatite precursor powders recovered from the mother liquor using the procedure outlined above were observed to display an agglomerate of extremely fine individual particles of spherical character, following drying at 100 °C. This was in agreement with previous observations of Asada *et al.* [14] and Jarcho *et al.* [15]. Powders calcined at higher temperatures (500–1000 °C) were found to contain 0.6 to 0.7 μm spherical and relatively monodispersed particles. The HA powders had BET specific surface areas in the range 45–65 m²/g, the variation being dependent on the extent of agglomeration present in particular powder samples. XRD runs indicated that HA precipitates calcined at 500 °C in air for 6 h possessed a hexagonal crystal structure with lattice parameters (least-squares refined with the PC subroutine Appleman and Evans [18]); $a = 0.9417$ nm and $c = 0.6880$ nm. The powder XRD patterns of our HA samples agreed closely with the JCPDS (Joint Committee on Powder Diffraction Standards [19]) # 9-432 file for calcium hydroxyapatite. The XRD data of the HA precipitates were analysed in 1 °C 2 θ intervals

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(over the range 10 to 100° 2θ) for more accurate detection of weak reflections and possible peak overlaps using a commercial spectroscopic profile fitting program (Peakfit 3.0, Jandel Scientific, Corte Madera, CA, USA) having built-in pseudo-Voigt and Pearson VII distribution functions. In contrast to some previous studies [12, 14, 16, 20] utilizing relatively similar starting materials and precipitation procedures in the synthesis of HA powders, our samples were found to be free of unwanted by-products or phases such as CaO, α- or β-TCP, Ca₂P₂O₇, CaHPO₄ and Ca₄P₂O₉, even after calcining at temperatures as high as 1300 °C in air for 6–10 h.

The process yields (percentage of HA recovered in the form of solid precipitates, after calcination at 600 °C, from aqueous solutions) during these HA synthesis experiments remained constant at around 75%, being fairly independent of the bath temperatures (in the range 25–85 °C) and ageing times (0.5–4 h) studied. The boiling step, following completion of the addition of di-ammonium phosphate solution into the calcium nitrate solution, was found to be quite effective in decreasing the pH of the solution from 8.5 to 5–5.5, which is probably accompanied by an advance of the re-precipitation reaction [11] for the elimination of remnants of the more stable TCP phase



and thus making it possible to obtain pure HA phase by the end of the precipitation processes. The recovered HA precipitates after centrifugation were found to be mixed with around 10% TCP phase, especially at the lower bath temperatures (25–45 °C) maintained during the process. Increase of bath temperatures to about 60 °C eliminated the containment problem.

It was also observed that the delicate washing steps (with distilled water) following decantation of the mother liquor were crucial, to the point that the retainment of Ca²⁺ and HPO₄²⁻ ions in an amorphous layer surrounding the particles would in turn help reaction (2) to take place in the reverse direction at calcination temperatures above 800 °C and, thereby, might explain the consequent observation of unwanted phases in synthetic HA powders at high temperatures [12, 14–16, 20].

3.2. Tricalcium phosphate synthesis

Ca₃(PO₄)₂ was shown to be synthesized more readily by the procedure described above than HA powders, owing to the fact that it did not require an additional boiling step. The precipitates recovered from the solutions were already crystalline and sub-micrometre, as was the case with HA precipitates, and the refined [18] lattice parameters of the hexagonal (of rhombohedral symmetry) TCP phase were measured to be *a* = 1.0434 nm and *c* = 3.7409 nm, following light calcination at 500 °C in air. These parameters were found to be in close agreement with the JCPDS PDF # 9-169 for β-Whitlockite [19].

3.3. HA/TCP composite powder synthesis

The production of composite, sub-micrometre powders, with a predetermined crystalline HA/TCP ratio in the recovered precipitates, was also shown to be possible, at least for the 40% TCP and 60% HA composition, with the starting materials and general procedures of this study. Work is in progress towards a more precise and systematic determination of the experimental conditions of *in situ*, composite bioceramic powder synthesis.

The composite powders of 40% TCP–60% HA composition were synthesized from solutions containing calcium nitrate and di-ammonium hydrogen phosphate at a Ca/P ratio of 1.60. The solutions were aged for 2 h at 60 °C and then boiled for 1 h, following completion of the addition of phosphate solution to the nitrate solution. The pH of the reaction solutions was kept constant at about 6 by the addition of diluted HNO₃ or NH₄OH. The precipitates recovered by centrifugation were later calcined at 500 °C, basically to “dry out” the samples.

3.4. Sintering studies

The pure HA, TCP, and composite (40% TCP–60% HA) powders synthesized were first homogenized in an agate mortar and then uniaxially pressed at a pressure range of 180–390 MPa into small pellets. The green pellets prepared at the maximum pressure of 390 MPa (of all compositions) were sintered to above 99% of the theoretical density at 1200 °C in air in about 10 h. The sintered samples did not show any signs of structural decomposition or degradation. The experimental densities of the sintered pellets were measured using Archimedes’ liquid-displacement method in xylene as the liquid medium. Although work is still in progress towards full determination of the sintering behaviour of such high surface area and high reactivity bioceramic powders, it is quite evident now that with these powders it would not be necessary to go to temperatures as high as 1400 °C [21] to reach full densities, thus avoiding the problems of dehydration and structural decomposition especially for the HA powders. Fig. 1 shows the XRD traces of HA, TCP, and 40% TCP–60% HA samples sintered at 1200 °C. Since the traces depicted in this figure were taken from the direct, as-is surfaces of the sintered pellets, the peaks were seen to have somewhat broken tops. The specific crystal reflections for each phase in the 2θ region of interest are labelled as particular planes in each figure. The EDXS analyses performed on these samples confirmed the expected Ca/P ratios of 1.67 (HA), 1.50 (TCP), and 1.60 (40% TCP–60% HA composite), within the accuracy limits of this method.

The sintering behaviour of the synthesized sub-micrometre, spherical HA powders changes, as expected, with variations in the initial, green state packing pressure applied. Fig. 2 shows SEM micrographs of the fracture surfaces of HA pellets pressed uniaxially at a pressure of 180 MPa as a function of sintering temperature. The pellets of 1 cm diameter and 3 mm

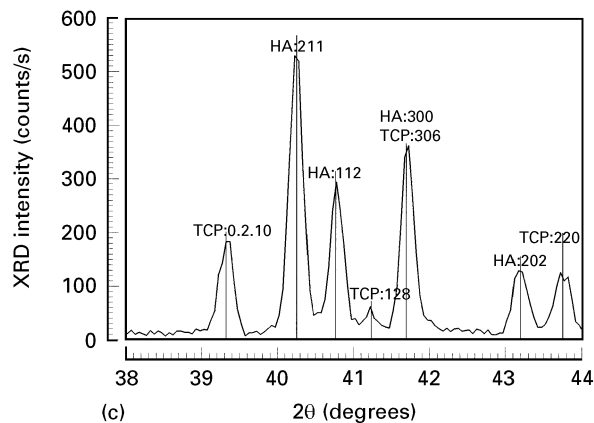
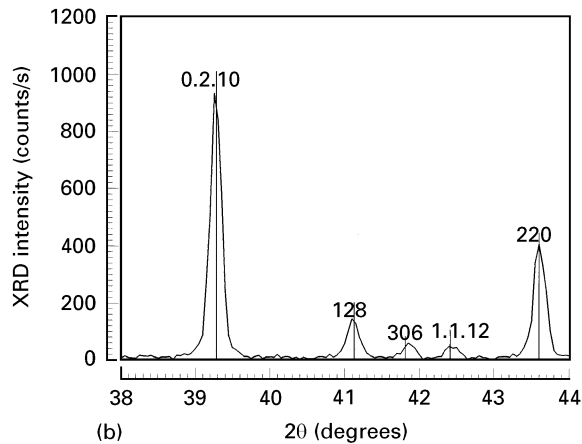
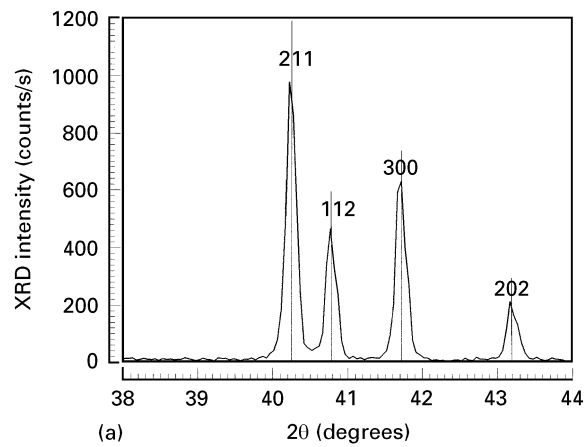


Figure 1 Powder XRD traces of samples sintered at 1200 °C in air for 10 h after being uniaxially pressed at 390 MPa. (a) calcium hydroxyapatite, (b) tricalcium phosphate, (c) 40% TCP-60% HA composite powder.

thickness were pressed in the presence of 1.5 ml of 2 wt % stearic acid–ethanol solution per gram of powder as a binder. It is apparent from Fig. 2 that the extent of densification abruptly increases with increase in sintering temperature from 1200 °C to 1300 °C (at a constant sintering time of 12 h). Therefore, it could be stated that while the HA pellets pressed at 180 MPa could only reach a percentage theoretical density of about 97% (Fig. 2c) at 1300 °C after 12 h, the pellets prepared from the same powders at 390 MPa displayed a density of 99.2% at 1200 °C in a reduced time of 10 h. The HA pellets sintered at 1300 °C exhibited the crystal structure of pure calcium hydroxyapatite with no signs of decomposition of the

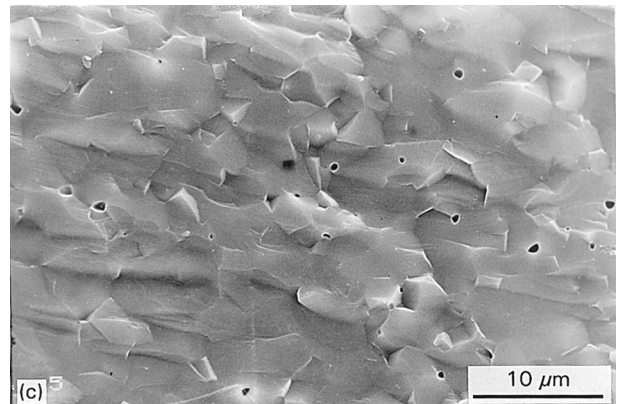
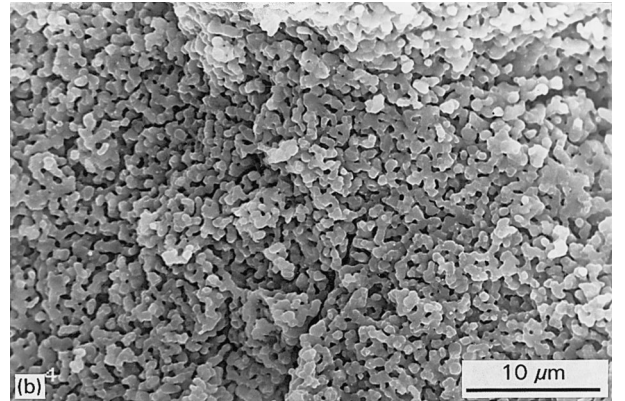
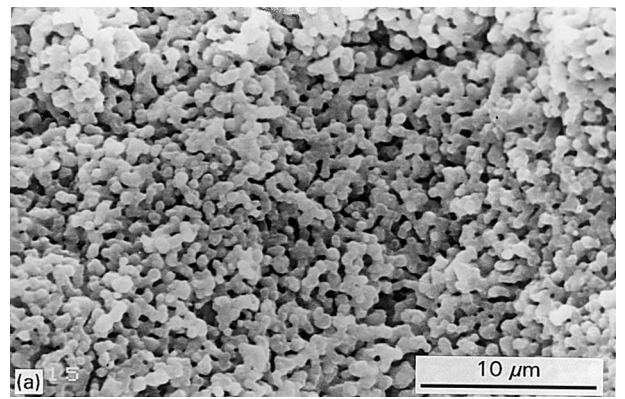


Figure 2 SEM micrographs of HA powders sintered at various temperatures in air for 12 h after being uniaxially pressed at 180 MPa: (a) 1050 °C; (b) 1200 °C; (c) 1300 °C.

apatitic structure (such as a possible decrease in the intensities of 004 reflections in the case of dehydroxylation problems), according to the powder XRD results.

3.5. Rietveld refinements for crystallographic analyses

The Rietveld method [22–24] for the detection and analysis of small structural variations and distortions, which may not readily be tangible from the bare inspection of the powder XRD traces, is a widely accepted tool in the field of inorganic materials and ceramics research. The Rietveld method was applied to the powder XRD data of the HA powder samples of this study sintered at 1200 °C for 12 h in air. The initial crystal structure model used in the Rietveld refinements of these samples was adopted from the single

TABLE II Positional (unit cell) parameters of the HA powders (1200 °C)

Atom	x	y	z	Site occupancy
O(1)	0.3351(9)	0.4890(9)	0.2500	1.006(29)
O(2)	0.5875(8)	0.4606(9)	0.2500	1.009(42)
O(3)	0.3304(9)	0.2468(11)	0.0687(13)	1.017(79)
P	0.3982(6)	0.3696(6)	0.2500	1.002(4)
Ca(1)	0.3333(2)	0.6667(1)	0.0060(10)	0.6905(12)
Ca(2)	0.2473(6)	0.9914(8)	0.2500	0.9982(23)
O(H)	0	0	0.1767(5)	0.5067(121)
H	0	0	0.0673(5)	0.5032(129)

Estimated standard deviations (e.s.d) for the parameters varied are given in parentheses following the digits for which they are applicable.

crystal structural studies of Young [25, 26] on calcium hydroxyapatite.

The Rietveld refinements were performed using PC software [17] on a 486DX2-66 machine. The background, mixing, half-width, cell, preferred orientation and peak asymmetry, atomic position, site occupancy parameters and the anisotropic temperature factors were refined in each cycle, and the structure factors were calculated. The number of parameters refined in the cycles was 64, and the program-generated final structural model converged successfully within 12 cycles. The weighted R-factor was observed to be 6.9% and the final positional parameters are given in Table II. The parameters found in this study of the HA crystal structure were observed to be in close agreement with those reported for a “single crystal” of natural calcium hydroxyapatite by Young *et al.* [25]. Examination of the site occupancy factors for synthetic HA revealed that the sum of the values of calcium atoms (Ca(1) and Ca(2)) found at two crystallographically different sites equals 1.6887. The ratio of this number to that of the occupancy factor of P (1.002) would give the mean Ca/P ratio in this sample as 1.685 ± 0.0102 . This means that the HA samples sintered at 1200 °C do not have any calcium deficiency and they display a Ca/P ratio very close to the stoichiometric phase. The low value, 6.9%, for the weighted R-factor of the Rietveld refinements also shows that the HA samples do not have any significant structural variations or distortions present even after sintering in air at 1200 °C for about 12 h. The hexagonal unit cell parameters of the above sample were found to be $a = 0.94147(9)$ nm and $c = 0.68777(7)$ nm by Rietveld analysis, and these values coincide strongly with the “single crystal” parameters reported by Young *et al.* [25].

One of the typical plots [27] obtained in Rietveld refinements of the powder data on the 1200 °C HA sample is reproduced in Fig. 3, divided into three 2θ intervals to facilitate easier assessment. This plot depicts the extent of disagreement between the structural model fitted and the raw powder XRD data. The dots in Fig. 3 represent the raw data, the solid lines following the dots denote the final structural model, and the tiny vertical lines at the bottom indicate the peak positions. The final Rietveld plot displays reasonable

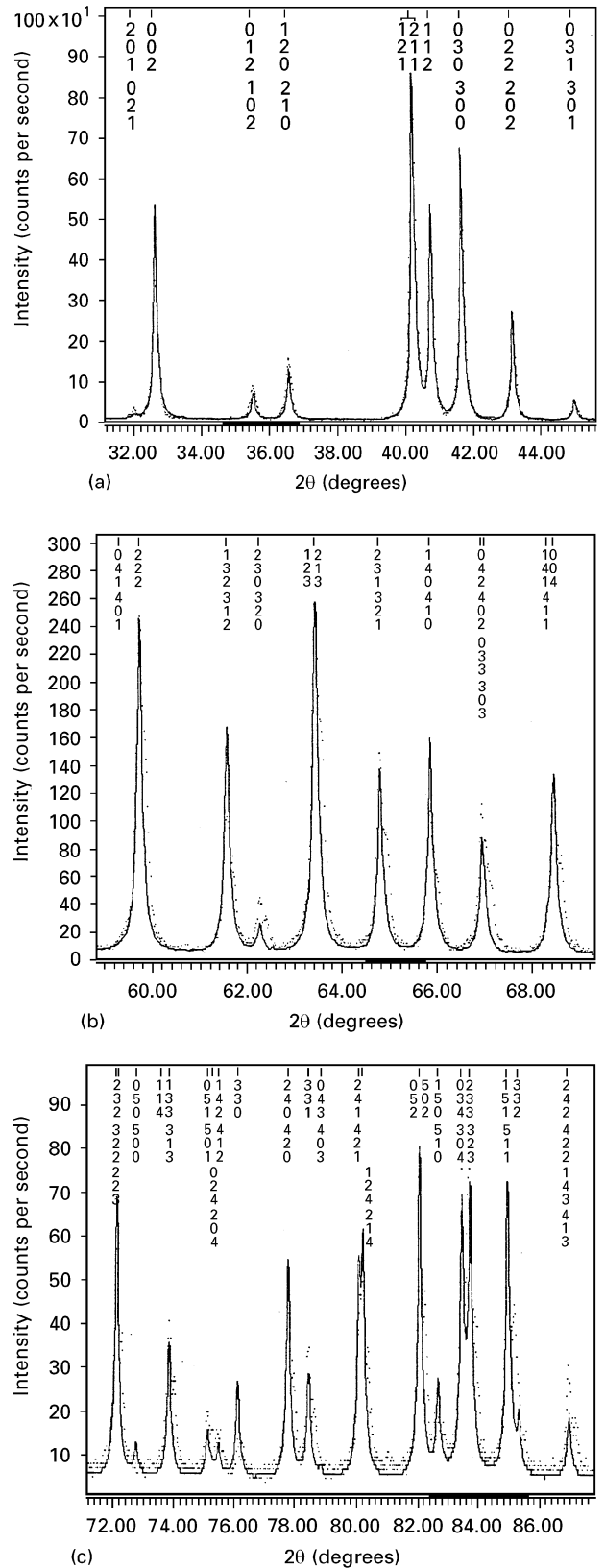


Figure 3 Rietveld plots of an HA sample sintered at 1200 °C in air for 12 h.

agreement between the structural model and the raw data.

The crystallite size of the HA powder samples sintered at 1200 °C in air was determined to be 102 ± 2 nm by using the peak half-widths from the XRD data according to the Warren–Averbach method [28, 29]. In calculating the crystallite size of

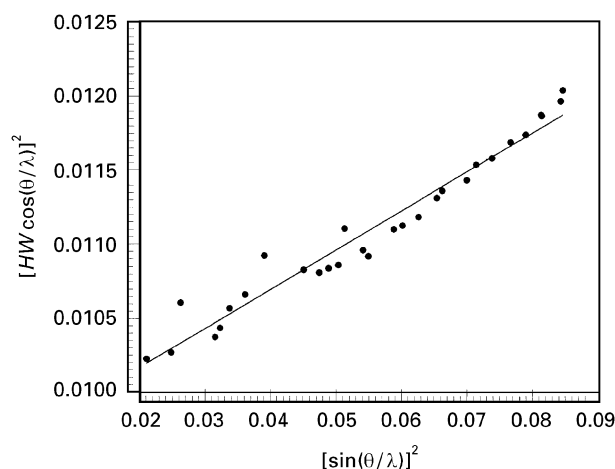


Figure 4 The Warren–Averbach plot of an HA sample sintered at 1200 °C in air for 12 h for the determination of crystallite size.

the samples, diffraction angles corresponding to the peak positions and the full width at half maximum values were used. The numerical values of the terms defining the x- and y-axes of Fig. 4 were calculated, and a linear regression was performed on the generated data points. The intercept of the regression line was found to be at 0.009 635 9 which corresponded to the square root of the reciprocal of the crystallite size.

4. Conclusions

Sub-micrometre, spherical, and chemically homogeneous powders of calcium hydroxyapatite (HA), tricalcium phosphate (TCP), and composite powders containing tailorable amounts of both of the above two phases were synthesized by chemical precipitation from aqueous solutions of nitrate and phosphate salts. The sintering and densification behaviours of the powders were monitored. It was seen through crystallographic analyses based on the atomic positions in the unit cells of HA powders that the synthesized powders remained pure and uniform in chemical composition, even after sintering at 1300 °C for prolonged times. The attainment of percentage theoretical densities in excess of 99% was easily achieved in cold samples, uniaxially pressed for about 10 h at a relatively low temperature of 1200 °C in air, with no signs of structural decomposition. It was also shown that the degree of porosity in the pressed samples could be controlled by careful monitoring of the heating schemes.

Acknowledgements

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