Parameters affecting the synthesis of β-tricalcium phosphate powder using a wet precipitation method

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ABSTRACT

In this work, precursor materials that are normally used to directly synthesise hydroxyapatite (HA) were adopted to obtain tricalcium phosphate (TCP). Calcium hydroxide, ($Ca(OH)_2$), and phosphoric acid, (H_3PO_4), with a Ca/P ratio of 1.5, were mixed as the precursor materials. The mixture was stirred at various stirring speeds ranging from 0 to 400 rpm, over a range of stirring durations of 1 to 4 hours. Upon completion of the reaction, the as-prepared powders were calcined at different temperatures ranging from 500ºC-1300ºC for a soaking duration that was varied between 1-4 hours. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were used for thermal analyses to ascertain the calcination temperatures, whilst x-ray diffraction (XRD) was utilised to determine the phases formed before and after calcination. Field emission scanning electron microscopy (FESEM) was used to monitor the morphological changes at different calcination temperatures. Based on the XRD results, the phases formed were dependent on the processing parameters employed. This work has successfully ascertained that the most optimum parameters to synthesise single-phase β-TCP are a stirring speed of 200 rpm, a calcination temperature of 900ºC, a calcination soaking duration of 2 hours and a mixing duration of 1 hour. Microstructural observation conducted on the β-TCP powders obtained at calcination temperatures of 900ºC to 1300ºC showed an aggregated structure of particles with massive grain growth as the temperature was raised up to 1300ºC.

Keywords: Hydroxyapatite; monetite; tricalcium phosphate; calcination.

INTRODUCTION

Biomaterials are a new group of functional materials that have emerged and exhibited a prolific growth to fulfil the demands in the fields of medicine and dentistry. Over the past few decades, new biomaterials for bone replacement, total hip prosthesis and dental implants have been synthesised and commercialised for various needs. Currently, thousands of these materials can be found easily in the market. The world market for orthopaedic biomaterials is worth over US$25 billion in 2006 and has a growth rate of more than 5% a year. The market for orthopaedic biomaterials is expected to increase each year due to the need for better solutions for injuries, diseases and the ageing

population all over the world. The orthopaedic biomaterials market consists primarily of bone graft substitutes, bone growth factors, degradable tissue fixation and tissue technologies for cartilage regeneration. Generally, orthopaedic prostheses should offer a functional life of at least 20 years to match the life span of most patients. This presents a considerable problem for most orthopaedic biomaterials [1]. In Malaysia, research works on orthopaedic biomaterials, especially on bone graft and degradable materials, are still in the infancy stage. Up to now, Malaysia has spent more than RM20 million each year to purchase synthetic bone grafts from foreign countries such as Switzerland, Germany and the United States. Therefore, the Malaysian government intends to produce bone grafts of its own with the supporting research from Universiti Sains Malaysia (USM), the Malaysian Institute for Nuclear Technology Research (MINT), Universiti Kebangsaan Malaysia (UKM) and International Islamic University Malaysia (IIUM) (Material Medical Malaysian website, 2006). Synthetic bone graft materials such as ceramics, polymers and metals are introduced as alternatives to the traditional bone substitutes. Among these materials, calcium phosphate ceramics such as hydroxyapatite (HA) and β-tricalcium phosphate (β-TCP) are the most suitable materials with excellent biological properties [2]. To date, there is still a limited number of research on the synthesis of β-TCP. Generally, β-TCP is prepared using a solid-state reaction or a wet chemical reaction. The solid-state reaction was reported by several researchers [3-5], whilst the wet chemical reaction was carried out in a handful of studies [6-9]. However, these synthesised β-TCP powders were not stable in terms of its thermal properties whereby they were converted to α-TCP at temperatures above $1125^{\circ}C$ [5]. In terms of starting materials, the present research modified the study used by Cheang and Khor [10] and other researchers [11-13] to synthesise β-TCP. According to Afshar and his co-workers [11, 12], HA can be synthesised using the system of $Ca(OH)_2$ and H_3PO_4 with a Ca/P ratio of 1.67. This reaction was expected to be developed as an industrial-scale method to produce HA with the correct stoichiometric composition according to the Eq. (1):

$$10Ca(OH)_2 + 6H_3PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O \qquad (1)$$
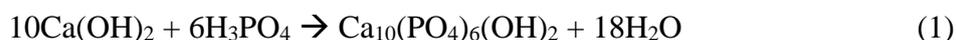
In the present research work, a wet chemical reaction such as the precipitation method was carried out to prepare β-TCP. Instead of using a Ca/P ratio of 1.67, a modification was attempted whereby $Ca(OH)_2$ and H_3PO_4 were used as the starting materials with a Ca/P ratio of 1.5. The mechanism of phase transformation in this synthesis method was fully explored. In a wet precipitation method, there are a number of process parameters such as the composition of starting materials, stirring speed, stirring duration, calcination temperature and calcination soaking duration. Therefore, the objectives of this research is to synthesise single-phase β-TCP powders using a wet precipitation method and starting materials that have not been attempted before by optimising the reaction parameters (stirring speed, stirring duration) and calcination conditions (calcination temperature, soaking time) to form a single phase β-TCP. The mechanism of the phase transformation upon calcination as well as the morphology and thermal stability of the β-TCP powder so-produced will be studied as well.

MATERIALS AND METHODS

Wet Precipitation Method

The starting materials used to produce β-TCP powders in this work include calcium hydroxide, $Ca(OH)_2$ (96% purity, FLUKA, 21181, UK) and phosphoric acid H_3PO_4 (15M, MERCK, 100573, Germany). Two solutions were prepared to synthesise β-TCP,

namely a 0.30 mole phosphoric acid solution and a 0.45 mole calcium hydroxide solution. 100 ml of 0.45 mole phosphoric acid was pipetted slowly into 300 ml of 0.30 mole calcium hydroxide solution. The mole ratio of $Ca(OH)_2$ to H_3PO_4 was 1.5 based on the β-TCP stoichiometric composition. The reaction was performed in a water bath (εlma, Transsonic T660 model, UK) set at 70ºC to control the temperature of the reactants. During the reaction, the suspension was unstirred as well as stirred at different stirring speeds of 100 rpm, 200 rpm, 300 rpm and 400 rpm (labelled as S0, S100, S200, S300 and S400, respectively) for 2 hours, and this stirring duration was later varied to 1 hour, 3 hours and 4 hours by using a stirring machine (KILA, RW20DZM model, Germany). The pH of the mixture before and after the reaction was also monitored using a pH meter (Eutech brand, LH7 model, UK). After the reaction had completed, the mixture was filtered and washed twice with 50 ml distilled water.

Drying and Calcination of As-Prepared Powders
Subsequently, the wet powder was dried in an oven (Binder, UK) at 100ºC for 24 hours before being ground into a fine powder (thereafter referred to as-prepared powder) using an agate pestle and mortar. About 0.2 gram of the powder was sampled for thermal analysis (Netzsch, STA 409 PC Luxx) to determine the most suitable calcination temperature to be used. Based on these results, the as-prepared powders were calcined at 500ºC, 700ºC, 900ºC, 1000ºC, 1100ºC, 1200ºC and 1300ºC for a soaking duration of 2 hours, which was later varied to 1, 3 and 4 hours. The powders were characterised using XRD for phase identification. The powders that were calcined over 900ºC-1300ºC were observed using the FESEM to elucidate any morphological changes.

X-ray Diffraction of Uncalcined and Calcined Powders
The as-prepared powders produced from the wet precipitation method using, firstly, different mixing speeds were analysed using X-ray diffraction before calcination. Then, these powders produced from five different mixing speeds of 0, 100, 200, 300 and 400 rpm were also analysed using XRD after calcination. From these observations, it became apparent that the S200 and S300 powders were most suited for detailed investigation at different calcination temperatures of 500ºC, 700ºC, 900ºC, 1000ºC, 1100ºC, 1200ºC and 1300ºC. Consequently, the lowest temperature to calcine the as-prepared powder and the optimum mixing speed during the wet precipitation method were ascertained. Using the established parameters of 200 mixing speed and 900ºC calcination temperature, the minimum duration of mixing was subsequently established.

Effect of Different Calcination Soaking and Mixing Durations
Once the optimum mixing speed and calcination temperature had been ascertained, the S200 powder was calcined at different soaking durations before the phases obtained were analysed using XRD. Similarly, the S200 powders mixed for various mixing duration of 1, 2, 3 and 4 hours were calcined for 1 hour at 900ºC before analysed using XRD.

RESULTS AND DISCUSSION

Thermal Analysis Using DSC/TG
All five as-prepared powders produced at different stirring speeds, S0, S100, S200, S300, and S400 were analysed using DSC/TG. From Figure 1, a small endotherm (and weight loss) was observed for all at 100ºC (due to adsorbed water), a second endotherm (and weight losses) at about 450ºC for S0-S300 except for S400, and a third weight loss (with

no noticeable endotherm) at 600-900°C for all five powders. The second endothermic peak at 450°C is attributed to the decomposition of monetite into dicalcium phosphate [DCP, $Ca_2P_2O_7$] as reported in [14]. The presence of monetite and DCP is confirmed by XRD. The areas under these endothermic peaks decrease with increasing stirring speeds. Similarly, the weight losses on the TG curves corresponding to these peaks also decrease with increasing stirring speeds, indicating that the amount of compound decomposed also decreases (Table 1). The weight loss between 600°C to 900°C can be observed clearly in the five samples, indicating the decomposition of HA into β-TCP. Since these endothermic peaks and/or weight losses were observed around 600°C-900°C, the XRD patterns of the as-prepared powders, calcined at 900°C, were also determined so as to unravel the reactions that took place. The possible reactions postulated in Table 1 are based on the work by [14-16]. However, this will be confirmed through XRD.
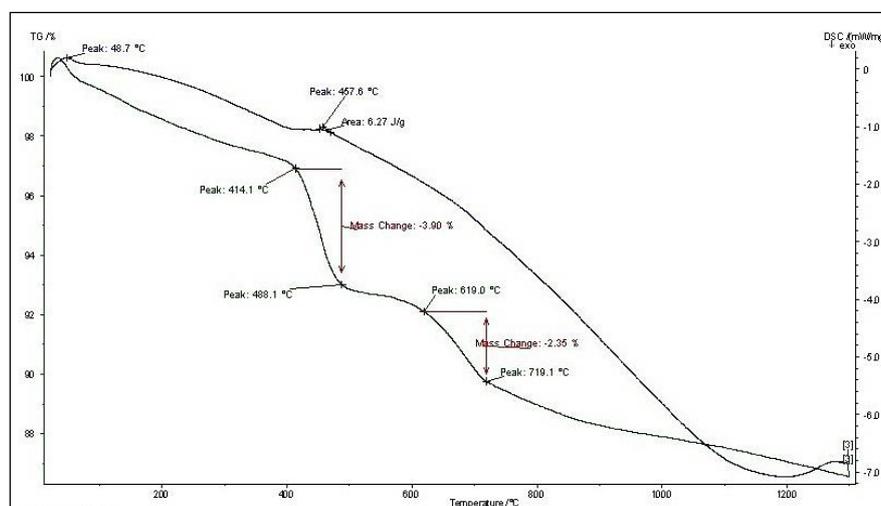

Figure 1. DSC/TG Curves for As-Prepared Powder S100

Table 1. DSC/TG Results for As-Prepared S0, S100, S200, S300 and S400 Powders

	1st TG Peak	Weight loss	2nd TG Peak	Weight loss	3rd TG Peak	Weight loss
S0	50.8	0.7	456	5.7	-	1.9
S100	48.7	0.6	458	3.9	-	2.4
S200	58.0	2.1	455	0.9	-	1.0
S300	53.3	1.3	449	1.1	-	1.0
S400	42.1	0.8	No peak discernible	Not obvious	-	0.6
Note:	endo-thermic	loss of adsorbed water	endo-thermic peak not discernible	decomposition of monetite to DCP	TG peak not discernible	decompose of HA to β-TCP

Phases Formed as a Consequence of Variable Stirring Speeds
The as-prepared powders mixed at various speeds were analysed using XRD and the results are shown in Table 2. At mixing speeds of 0 and 100 rpm, the as-prepared powders consist of monetite ($CaHPO_4$) and calcium hydroxide, ($Ca(OH)_2$). As the mixing speed

was increased to 200 and 300 rpm, the phases formed are monetite and hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$). At the highest mixing speed, the phase detected by XRD is HA of poor crystallinity as exhibited by the diffused broad peaks. Based on the premise that at temperatures above 900°C, no further weight loss or reactions were observed on the DSC/TG curves, a temperature of 900°C was chosen to calcine the various powders produced at different mixing speeds of 0-400 rpm. Table 2 shows that powders S0, S100 and S400 exhibit a mixture of phases after calcination, whilst only those of S200 and S300 exhibit single-phase β-TCP.

Table 2. Phases of As-Prepared and Calcined (900°C) Powders as Determined Using XRD.

Mixing Speed Code	As-prepared powders	Powders calcined at 900 °C
S0	Monetite + $Ca(OH)_2$	β-TCP + HA
S100	Monetite + $Ca(OH)_2$	β-TCP + HA
S200	Monetite + HA	β-TCP
S300	Monetite + HA	β-TCP
S400	HA with low degree of crystallinity	β-TCP + HA + CaO

From these observations, it can be concluded that $Ca(OH)_2$ had not reacted completely with H_3PO_4 at the stirring speeds of 0 and 100 rpm and had still remained in the as-prepared powder (Table 2). Consequently, the reaction between $Ca(OH)_2$ and H_3PO_4 at low stirring speed does not follow stoichiometric reaction. However, when the speed of stirring was increased to 200 rpm and 300 rpm, the XRD patterns of the as-prepared S200 and S300 powders no longer show the presence of $Ca(OH)_2$. Hence, it can be concluded that $Ca(OH)_2$ had reacted completely with H_3PO_4 at these two higher stirring speeds to produce a mixture phase of monetite and HA in the as-prepared powders (Table 2). Eqs. (2) and (3) describe the formation of monetite and HA from the reaction between the precursor or starting materials $Ca(OH)_2$ and H_3PO_4. The direct precipitates from Eq (2) and Eq. (3) are monetite and HA. In other words, this work confirms the conclusion of previous studies [9, 17] which stated that β-TCP cannot be precipitated directly from an aqueous solution.

$$Ca(OH)_2 + H_3PO_4 \rightarrow CaHPO_4 + 2H_2O \qquad (2)$$
$$10Ca(OH)_2 + 6H_3PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O \qquad (3)$$

It is also enumerated in Table 2 that the phases that are formed when these powders (S200 and S300) were calcined at 900°C for 2 hours produce β-TCP (ICDD 9-169) with a Ca/P ratio =1.5. A similar finding based on a solid-state reaction was reported by Yoshida [5] where he found that if a mixture of $CaHPO_4$ and HA with a Ca/P ratio of 1.5 was calcined at 1100°C for 24 hours, a single-phase β-TCP could be obtained. Indirectly, this work has successfully proven that a single phase β-TCP can be produced at a much lower calcination temperature of 900°C (compared to 1100°C) and a much shorter soaking duration of 2 hours (as compared to 24 hours). The XRD analysis of the as-prepared S400 powder shows a single-phase HA with a low degree of crystallinity formed (Table 2) which is in accordance to Eq. (3). The partial decomposition of HA into β-TCP at 900°C with the remnants of HA and CaO according to Eq. (4) was reported in literatures [15, 16].

$$Ca_{10}(PO_4)_6(OH)_2 \xrightarrow{\Delta} 3\beta\text{-}Ca_3(PO_4)_2 + CaO + H_2O \qquad (4)$$
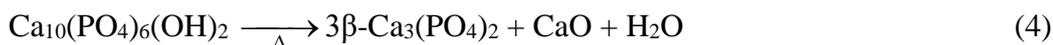
In summary, the stirring speed plays an important role in the synthesis of β-TCP. Since β-TCP cannot be precipitated directly from an aqueous solution, i.e. the direct product of the reaction between $Ca(OH)_2$ and H_3PO_4 depends on the mobility and the diffusion of Ca^{2+}, PO_4^{3-}, H^+ and OH^- ions which are influenced by the stirring speed. Table 2 summarises the phase(s) in the as-prepared powders at different stirring speeds and the corresponding powders calcined at 900°C. Thus, it can be summarised that stirring speeds of 200 and 300 rpm as well as a calcination temperature of 900°C for 2 hours soaking duration are successful in producing a single-phase β-TCP.
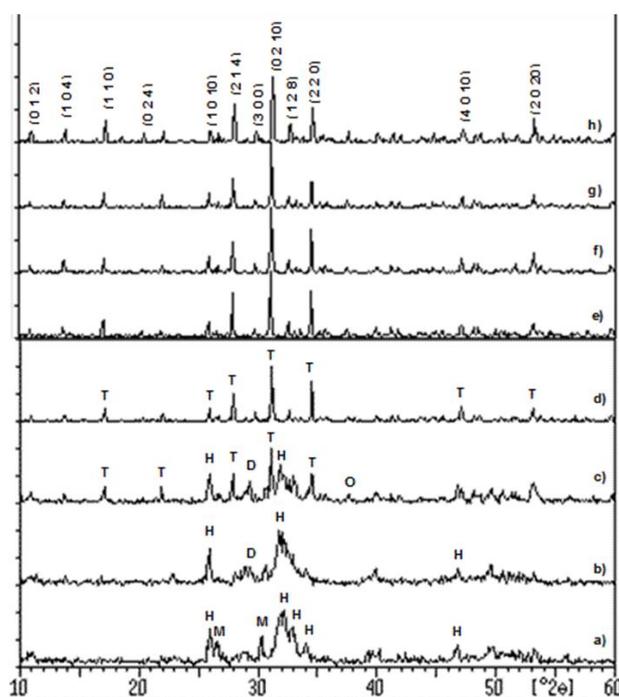

Figure 2. XRD patterns of S200 powders before and after calcination at different temperatures for 2 hours soaking (a) as-prepared powder, (b) 500°C, (c) 700°C, (d) 900°C, (e) 1000°C, (f) 1100°C, (g) 1200°C, and (h) 1300°C. [H – HA; M – Monetite; D – β-DCP; T- β-TCP; O – CaO].

Phases Formed as a Function of Calcination Temperatures
From the preceding observations using DSC/TG and XRD, the as-prepared powder produced at 200 rpm (S200) was deemed to be the best powder for further calcination studies. Hence, S200 powders before and after calcination at various temperatures of 500°C, 700°C, 900°C, 1000°C, 1100°C, 1200°C and 1300°C were subsequently analysed using XRD and the results are shown in Figure 2. Powders calcined at 500°C and 700°C still display remnants from the precursor phase (HA) as well as intermediate phases (DCP, HA, CaO). From these results, it can be observed that a single-phase β-TCP can successfully be produced at a calcination temperature of as low as 900°C. This is much lower than the 1100°C reported earlier [5]. This phase remains thermally stable even up to 1300°C which is much higher than those reported in previous works, viz. 1120°C-1170°C [18, 19] and 1100°C [5] before the transformation to α-TCP takes place.

Effect of Different Soaking Durations During Calcination
In order to study the effect of soaking durations, the as-prepared S200 powder was chosen to be calcined at 900°C for different soaking durations of 1 hour, 2 hours, 3 hours and 4 hours. The XRD patterns in Figure 3 shows the effect of soaking duration on the synthesis of β-TCP. The diffraction peaks of the calcined powders at 1 hour, 2 hours, 3 hours and 4 hours matched with the reference patterns of β-TCP (ICDD 9-169). The crystallite sizes along the (0 2 10) direction of these powders were calculated using the Scherrer equation, whilst the grain sizes were observed using SEM. These sizes were found not to differ much at different soaking durations. Nevertheless, it was found in a separate experiment that calcination temperature has a much significant influence on the crystallite sizes and grain sizes. At a soaking duration of 1 hour, a single-phase β-TCP can be obtained with the smallest crystallite size of 38.5 nm and the smallest grain size range of 0.1 - 0.2 μm. Henceforth, the optimum soaking duration is maintained at 1 hour compared to 24 hours as reported by Yoshida [5].

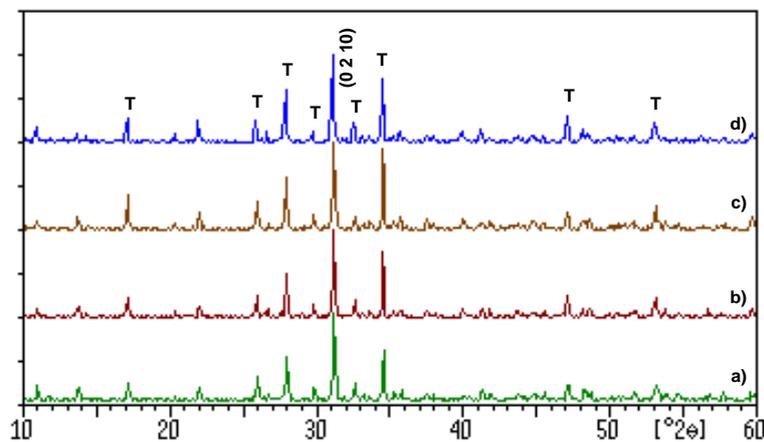Figure 3. XRD patterns of S200 powder calcined at 900°C for different soaking durations [All peaks are assigned to β-TCP] a) 1 hour, b) 2 hours, c) 3 hours and d) 4 hours.

Effect of Different Mixing Durations
The as-prepared powders produced from mixing the reactants at 200 rpm for different mixing durations of 1, 2, 3 and 4 hours were calcined at 900°C for 1 hour. The uncalcined powders were analysed using XRD and it was revealed that all the as-prepared powders, except for that mixed for 1 hour, produced monetite and HA which transformed to single-phase β-TCP upon calcination. However, the powder mixed for 1 hour showed incomplete reaction, and the calcined phase consisted of β-TCP, HA and CaO. Hence, a minimum of 2 hours mixing duration was adopted as the most optimum parameter.

Morphological Analysis Using FESEM
The morphologies of powders calcined at five different temperatures between 900°C to 1300°C were observed using the FESEM but only the micrographs for powders calcined at 900°C and 1000°C are shown in Figure 4. The powder calcined at 900°C shows an aggregated structure with an estimated grain size of 0.2μm, whilst that at 1000°C still exhibit aggregation but the grain size shows a grains growth of approximately 5 folds due to mass diffusion and the merging of grains to achieve stability. The grain size subsequently showed exaggerated grain growth as the temperature increases to 1300°C.

Nonetheless, as shown in Figure 2, the crystalline phase of the powder remains as single-phase β-TCP even when calcined up to 1300°C [20-22].
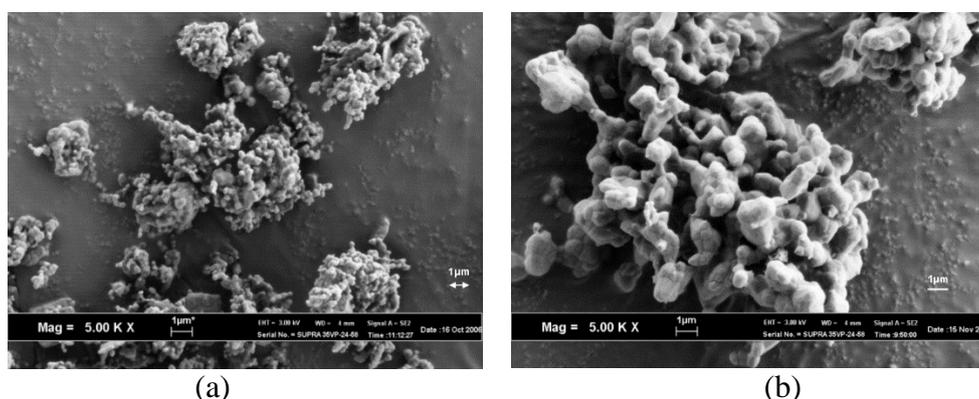

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<tr><td>(a)</td><td>(b)</td></tr>
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Figure 4. Morphology by FESEM of S200 powders calcined for 1 hour at (a) 900 °C and (b) 1000 °C

CONCLUSIONS

This study has succeeded in synthesising a single-phase β-TCP using the wet precipitation method, and as a consequence, the most optimum processing parameters have been successfully ascertained. Firstly, this includes the precursor or starting materials used, i.e. calcium hydroxide, $Ca(OH)_2$, and phosphoric acid, H_3PO_4, which were previously reported to be mainly used in the direct synthesis of hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$. Secondly, the processing parameters have been optimised to ascertain a stirring speed of 200 rpm, a calcination temperature of 900 °C, a calcination soaking duration of 1 hour and a stirring duration of 2 hours. The calcination temperature is much lower than that previously reported, and so is the calcination soaking duration. It has also been established that even though there is significant grain growth upon calcination from 900 °C to 1300 °C, the phase remains thermally stable up to 1300 °C which is much higher than the transformation temperature to α-TCP thus reported so far. These promising features so-obtained in this work is attributed not only to the precursor materials being used but also the processing protocols thus adopted. Possible recommendation is to carry out similar studies using different raw materials in order to further understand the significant influences of the processing parameters.

ACKNOWLEDGEMENTS

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