

## Intermediate Phases Formed during Synthesis of $\beta$ -Tricalcium Phosphate via Wet Precipitation and Hydrothermal Methods

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### ABSTRACT

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Beta-tricalcium phosphate ( $\beta$ -TCP) was synthesized using an aqueous wet precipitation method as well as a hydrothermal method. The processing parameters adopted in both methods were maintained to be as similar as possible. The precursor materials reacted in both methods were 0.3 mole of phosphoric acid,  $H_3PO_4$ , and 0.45 mole of calcium hydroxide,  $Ca(OH)_2$ . The available processing parameters for the precipitation method are much more varied whilst the parameters for the hydrothermal method are much more limited. Hence, the parameters chosen were based on the availability of the parameters to accommodate both methods, viz. the use of the same precursor materials in a stoichiometric ratio of 1.5, a reaction temperature of 70°C, a reaction time of 2 hours, a stirring speed of either 200 or 100 rpm, and a stirring duration of 2 hours. The intermediate phases formed upon precipitation were compared. It was confirmed by x-ray diffraction that the powder formed from the precipitation method was monetite and hydroxyapatite, whilst the initial the powder formed from the hydrothermal method consisted of brushite and hydroxyapatite. Thermal analysis was performed on both powders to ascertain the best heat-treatment temperature. Both powders were subsequently subjected to a heat-treatment temperature of 900°C and both were confirmed by x-ray diffraction to be single-phase  $\beta$ -tricalcium phosphate. Scanning electron microscopy was performed on both heat-treated powders and the microstructures observed were found to be distinctly different. The precipitated powder consisted of nano-sized powders that were heavily agglomerated, whilst the hydrothermal powder consisted of a flattened microstructure due to the pressure imposed upon reaction.

#### Keywords:

brushite, monetite, hydrothermal, precipitation,  $\beta$ -Tricalcium

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## 1. Introduction

Biomaterials are a new group of functional materials that have emerged and exhibited a prolific growth to fulfill the demands in medicine and dentistry. Over the past few decades, new biomaterials

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for bone replacement, total hip prosthesis and dental implants have been synthesized and commercialized for various needs. Currently, a number of these materials can be found easily in the market [1]. 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 orthopedic biomaterials is expected to increase each year due to the need for better solutions for injuries, diseases and ageing population all over the world.

Synthetic bone graft materials such as ceramics, polymers and metals were introduced as an alternative to the traditional natural bone substitutes. Among these materials, calcium phosphate ceramics, such as hydroxyapatite (HA), carbonated hydroxyapatite (cHA) and  $\beta$ -tricalcium phosphate ( $\beta$ -TCP), are the most suitable materials with excellent biological properties [2,3]. There are not so many research works to date that have been carried out on the synthesis of  $\beta$ -TCP. Generally,  $\beta$ -TCP was prepared either by a solid-state reaction, a wet chemical reaction or a hydrothermal method. The solid-state reaction had been reported [3,4] whilst the wet chemical reaction was carried out by a number of researchers [5,6]. These synthesized  $\beta$ -TCP powders were not stable in terms of thermal properties whereby they were converted to  $\alpha$ -TCP at temperatures above 1125°C.

HA can be synthesized by using the system of  $\text{Ca(OH)}_2$  and  $\text{H}_3\text{PO}_4$  with a Ca/P ratio of 1.67 [6,7]. The present research work, which was modified from these studies, used a wet chemical reaction, such as the precipitation method and the hydrothermal method, to prepare  $\beta$ -TCP. Instead of using a Ca/P ratio of 1.67, a Ca/P ratio of 1.5 was used.

In the wet precipitation and hydrothermal methods, there are a number of reaction parameters, such as the composition of the precursor materials, stirring speed, stirring duration, calcination temperature and calcination soaking duration that affect the resultant synthesized powders. In this comparative work, the processing parameters in both methods were fixed as follows, viz. the precursor materials used, a stirring speed of either 200 rpm or 100 rpm, a stirring duration of 2 hours, a calcination temperature of 900°C, and calcination duration of 2 hours. X-ray diffraction was performed on the as-synthesized powders from the two methods before and after calcination at 900°C. The morphologies of the heat-treated powders were also observed using scanning electron microscopy.

## 2. Methodology

The starting or precursor materials that were used to produce  $\beta$ -TCP powders in this work included calcium hydroxide,  $\text{Ca(OH)}_2$  (96% purity, FLUKA, 21181), and phosphoric acid,  $\text{H}_3\text{PO}_4$  (15M, MERCK, 100573, Germany). Distilled water was used as a solvent.

In order to synthesize  $\beta$ -TCP, two solutions were prepared, namely phosphoric acid solution (solution A1) and calcium hydroxide solution (solution A2). A 0.3 mole phosphoric acid solution (solution A1) was prepared by extracting 20 ml of 15M  $\text{H}_3\text{PO}_4$  using a 20-ml pipette and hand pump, and placed in a 100-ml volumetric flask. Distilled water was then added to top up to the mark on the flask. After dilution, the concentration of solution A1 was 3M.

In order to prepare 0.45 mole  $\text{Ca(OH)}_2$  solution (labelled as solution A2), 33.3 grams of  $\text{Ca(OH)}_2$  was mixed with 300 ml distilled water in a 500-ml beaker (equal to 0.45 mole  $\text{Ca(OH)}_2$ ). Then, the mixture was stirred on a hot plate for 30 minutes to obtain a homogeneous solution A2.

100 ml phosphoric acid (solution A1) was dropped slowly into 300 ml calcium hydroxide solution (solution A2). The mole ratio of  $\text{Ca(OH)}_2$  to  $\text{H}_3\text{PO}_4$  was 1.5, which was based on the  $\beta$ -TCP stoichiometric composition. The reaction was performed in a water bath (Elma, Transsonic T660 model) to control the temperature of the reactants. The temperature during the reaction was fixed at 70°C. During the reaction, the suspension was stirred at a fixed stirring speed of 200 rpm for a

duration of 2 hours. The pH of the mixture before and after reaction was monitored by a pH meter (Eutech LH7). After the reaction had completed, the precipitate was filtered and washed twice with 50 ml distilled water. Subsequently, the wet powder was dried in an oven (Binder) at 100°C for 24 hours before being ground into a fine powder (as-prepared powder) using an agate pestle and mortar.

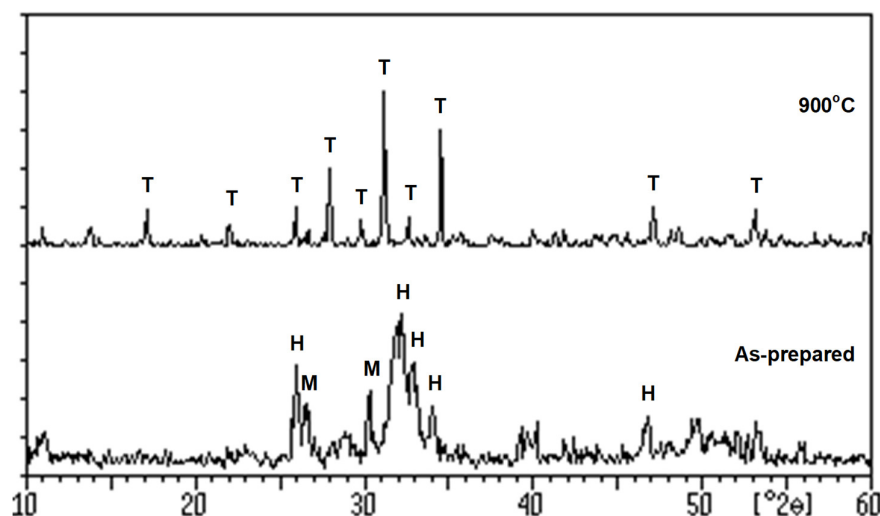
Similar to the wet precipitation method, 0.3 mole of  $H_3PO_4$  (solution A1) was mixed with 0.45 mole  $Ca(OH)_2$  (solution A2) in a high pressure Berghof reactor (model HR-700). The reactor was properly sealed and heated to a reaction temperature of 70°C. The reaction duration was set for 2 hours, based on the minimum time to obtain  $\beta$ -TCP in the wet precipitation method. The reactor only has 3 stirring speeds, and as such, the highest stirring speed of 100 rpm was chosen to match closely that of the other method. As a point of note, a stirring speed of 100 rpm in the precipitation method did not produce single-phase  $\beta$ -TCP upon calcination to 900°C. Apart from that, the same procedures were adopted on the as-precipitated powder, i.e. drying and grinding.

The dried and ground as-prepared powders from both methods were calcined at a temperature of 900°C for a soaking duration of 2 hours. The as-prepared and calcined powders were then characterized using x-ray powder diffraction (XRD) [Siemens D5000] for phase identification. The as-synthesized powders were also characterized by thermal analysis to identify the chemical reactions taking place (Netzsch Luxx, STA 409). The morphologies after calcination were then observed using scanning electron microscopy (SEM) [Leo Supre 35VP] to ascertain any changes in morphology.

### 3. Results and Discussion

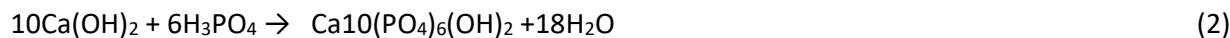
#### 3.1 X-Ray Diffraction

The x-ray powder diffraction analyses, for the as-prepared powder and the powder calcined at 900°C, from the wet precipitation method are as shown in Figure 1. It is observed that the phases formed after reaction are hydroxyapatite ( $Ca_{10}(PO_4)_6(OH)_2$ ) and monetite ( $CaHPO_4$ ). Upon calcination to 900°C, the phases transform completely to single phase  $\beta$ -TCP.



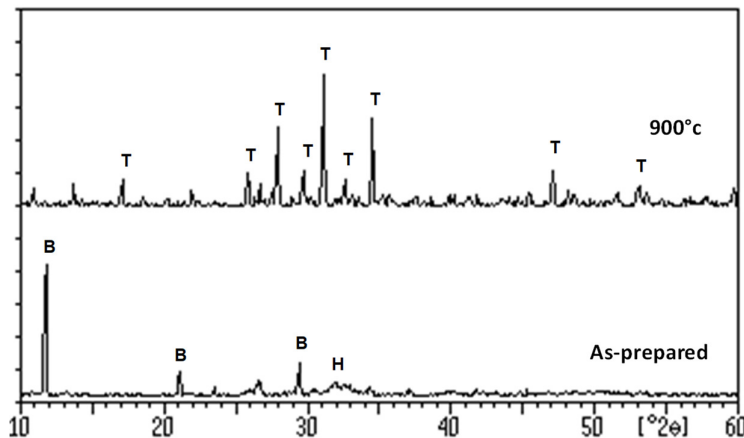
**Fig. 1.** X-ray diffractograms of (a) as-prepared, and (b) after calcination at 900°C, for powders prepared by the wet precipitation method. Legend: M- monetite, H- hydroxyapatite, and T -  $\beta$ -tricalcium phosphate

The possible reactions to produce monetite and hydroxyapatite from the precursors  $\text{Ca}(\text{OH})_2$  and  $\text{H}_3\text{PO}_4$  are given by Equations 1 and 2.



Upon calcination, both monetite and HA will react to form  $\beta$ -TCP. By comparison, the x-ray powder diffraction analyses, for the as-prepared powder and the powder calcined at  $900^\circ\text{C}$ , from the hydrothermal method, are as shown in Figure 2. It is observed that the phases formed after reaction are hydroxyapatite and brushite ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ). Upon calcination to  $900^\circ\text{C}$ , the phases transform completely to single phase  $\beta$ -TCP.

By comparison, the x-ray powder diffraction analyses, for the as-prepared powder and the powder calcined at  $900^\circ\text{C}$ , from the hydrothermal method, are as shown in Figure 2. It is observed that the phases formed after reaction are hydroxyapatite and brushite ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ). Upon calcination to  $900^\circ\text{C}$ , the phases transform completely to single phase  $\beta$ -TCP.

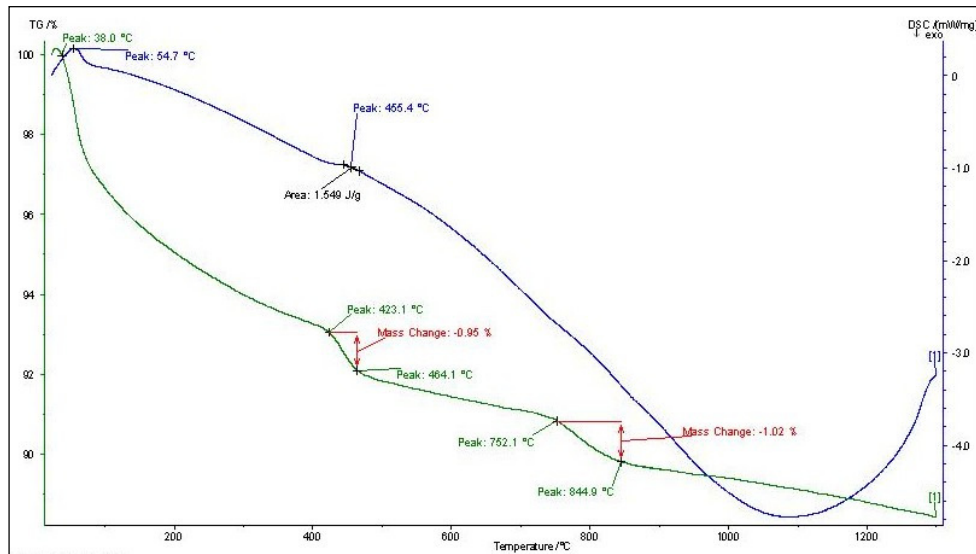


**Fig. 2.** X-ray diffractograms of (a) as-prepared, and (b) after calcination at  $900^\circ\text{C}$ , for powders prepared by the hydrothermal method. Legend: B is brushite, H is hydroxyapatite and T is  $\beta$ -tricalcium phosphate.

From the above results, it can be seen that the intermediate phases in the powder prepared via a wet precipitation method differ from the phases observed in the powder prepared by the hydrothermal method, viz. hydroxyapatite and monetite in the former, and hydroxyapatite and brushite in the latter.

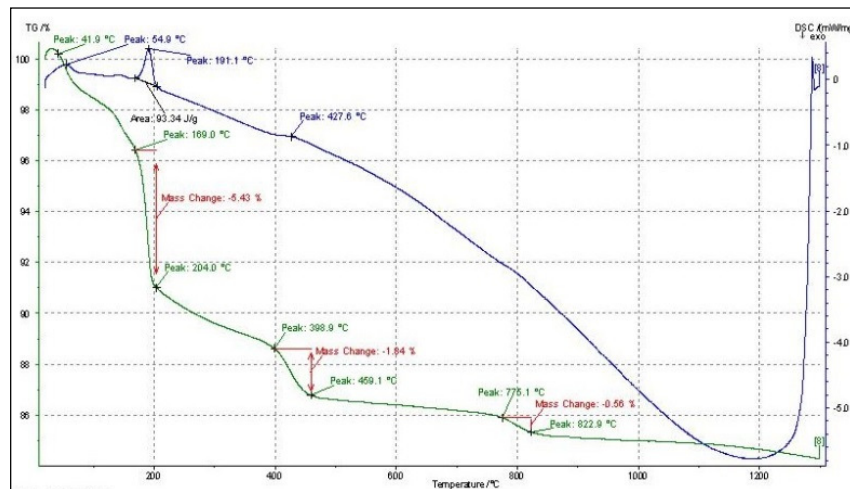
### 3.2 Thermal Analyses

Thermal analyses were conducted on the as-prepared powders from the two methods. The result for the powder prepared by the wet precipitation method is shown in Figure 3. It can be seen that the first weight loss at around  $90^\circ\text{C}$  is associated with the loss of adsorbed water, the second weight loss at around  $450^\circ\text{C}$  due to the decomposition of monetite to dicalcium phosphate  $\text{Ca}_2\text{P}_2\text{O}_7$ , and finally the subsequent reaction with hydroxyapatite to form  $\beta$ -tricalcium phosphate at around  $800^\circ\text{C}$  [8].



**Fig. 3.** Thermal analyses of the as-prepared powder via the wet precipitation method

The thermal analysis result for the powder prepared by the hydrothermal method is shown in Figure 4. It can be seen that the weight losses are associated with the loss of adsorbed water, decomposition of brushite to monetite, decomposition of monetite to dicalcium phosphate, and subsequent reaction with hydroxyapatite to form  $\beta$ -tricalcium phosphate [9, 10].



**Fig. 4.** Thermal analysis of as-prepared powder via the hydrothermal method

The reactions that took place during the hydrothermal synthesis  $\beta$ -tricalcium phosphate can be represented by the equations below. Initially, the precursors react in the hydrothermal chamber to produce brushite instead of monetite (Equation 3)



Upon calcination, brushite dehydrates at 190°C to form monetite (Equation 4)

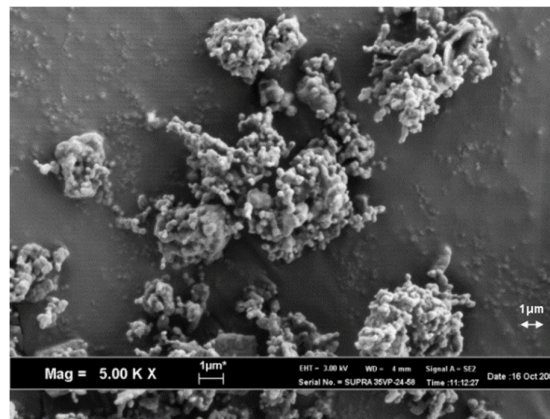


Then, as in the case of the wet precipitated powder, monetite transforms into dicalcium phosphate as the temperature increases (Equation 5). Subsequently, dicalcium phosphate and hydroxyapatite react to form  $\beta$ -TCP (Equations 6 and 7).

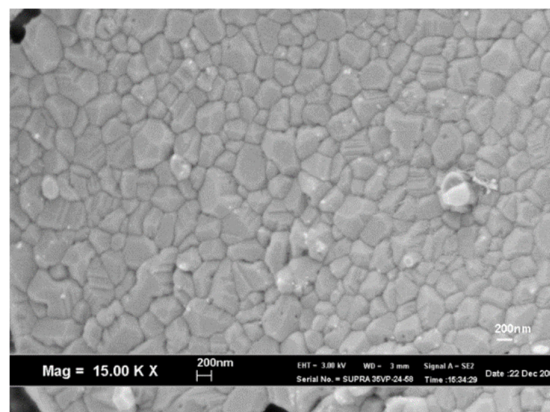


### 3.3 Morphological Observations

The calcined powders from both methods were examined under a scanning electron microscope. Figures 5 and 6 show the microstructural observations of both powders which are apparently very much different from one another. For the calcined wet precipitated powder, the particles which are in nano-size range appear to be tightly agglomerated (Figure 5). On the other hand, the calcined hydrothermally produced powder appears to be flattened due to the imposition of pressure during synthesis within the hydrothermal pressure vessel (Figure 6). It is apparent that the grain size can be observed much more clearly, and can be deduced to be within the nano range size as well.



**Fig. 5.** SEM micrograph of the calcined powder prepared by a wet precipitation method



**Fig. 6.** SEM micrograph of the calcined powder prepared by the hydrothermal method

#### 4. Conclusion

This work has successfully ascertained that the intermediate phases formed via a wet precipitation method are monetite and hydroxyapatite, whilst that formed via a hydrothermal method are brushite and hydroxyapatite. Apart from that, this work has also confirmed the nanocrystalline nature of the powders produced using both methods. Brushite, hydroxyapatite and  $\beta$ -TCP have found numerous applications in dentistry and orthopaedics, as well as in pharmaceutical applications [11-15].

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