



## Effects of Time, Temperature and Precursor on Solid State Synthesis of $\alpha$ -TCP

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### ABSTRACT

In this study, the correlation between impurity content of reagents used (monetite and brushite both from Merck), soaking time and firing temperature in the solid state synthesis of  $\alpha$ -tricalcium phosphate ( $\alpha$ -TCP) has been established. Mg impurity promoted formation of  $\beta$ -polymorph as a second phase in the resultant product. The extension of firing operation also led to an increase in the amount of  $\alpha$ -TCP, higher firing temperature with an Equivalent soaking time resulted in a more purely synthesized  $\alpha$ -TCP. The amount of  $\alpha$  and  $\beta$  phases at each heating program were investigated through Match software system. The highest percentage of obtained  $\alpha$ -TCP in the resultant product with the monetite precursor containing 0.43 wt.% magnesium impurity at 1350°C and 16 hours of soaking time was about 94%.

### 1. INTRODUCTION

Due to chemical and structural resemblance of calcium phosphates with that of human bone mineral, these materials have been commonly used in bone defect filling applications [1]. Having features such as osteoconductivity, bioactivity and biocompatibility, calcium phosphates are initial candidates to fix prosthesis in hard tissues. There are different types of calcium phosphates according to their diverse Ca/P molar ratio and solubility, among which  $\alpha$ -TCP with a chemical formulation of  $\text{Ca}_3(\text{PO}_4)_2$  is receiving growing attention as a raw material for injectable hydrolytic bone cement that can be completely replaced after implantation by the natural bone.  $\alpha$ -TCP is capable of setting into monolithic calcium deficient hydroxyapatite ( $\text{Ca}_{10-x}(\text{HPO})_4(\text{PO}_4)_{6-x}(\text{OH})_{2-x}$ ,  $x=0-1$ ) through a nondestructive reaction for the surrounding tissue due to hydration conditions near to body's own pH and temperature [2].

$\alpha$ ,  $\beta$  and  $\acute{\alpha}$  are the three polymorphs of TCP with monoclinic, rhombohedral, and hexagonal crystal structures respectively. Stability temperatures of phases are up to 1125 °C for  $\beta$ , between 1125-1430 °C for  $\alpha$  and above 1430°C for  $\acute{\alpha}$  [3-5]. Thermal transformation of a precursor with Ca/P $\approx$ 1.5 molar ratio, self-propagating high-temperature synthesis, combustion

synthesis and solid-state synthesis of precursors are various synthetic methods employed to synthesize  $\alpha$ -TCP. Simplicity and no need for complex equipments are the main reasons for choosing solid state reaction of a mixture of solid precursors at high temperatures as the generally realized synthetic route to maintain  $\alpha$ -TCP at room temperature as a metastable phase [4]. A major challenge to  $\alpha$ -TCP synthesis with this method is the sensitive heating program and formation of  $\beta$ -TCP as the principal phase or having a product of both  $\alpha$ -TCP and  $\beta$ -TCP [6].

The main objective of this article is to report the effect of  $\alpha$ -TCP's solid state synthesis parameters such as chemical composition of reagents used (monetite and brushite), soaking time and temperature on the number of phases present in the final product.

Quantitative analysis of phases by X-ray diffraction can be done by various technique, one of these ways is Rietveld refinement of X-ray diffraction patterns. But Rietveld refinement fails to quantify the poorly crystalline  $\beta$ -TCP that is the most common secondary phase in multiphase calcium phosphates[7]. Another way to quantitative analysis by X-ray diffraction is the Reference Intensity Ratio (RIR) methods. Some computer programs used RIR method as a method for quantitatively determining in multiphase materials. According to that method, in this work, X-ray diffraction quantitative phase analysis is obtained by "match!", which is an application software based on the RIR method commonly used in mineralogy which

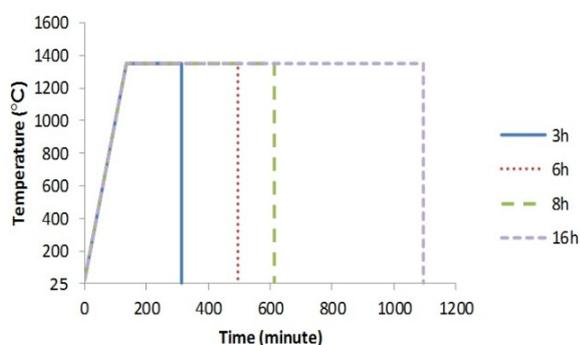
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provides a complete phase analysis, modified to use as an external rather than an internal standard[8].

## 2. MATERIALS AND METHODS

A calcium to phosphorous ratio (Ca/P) of 1.50 was achieved from a combination of Monetite (DCPA; 2144, Merck, Germany) and calcium carbonate (2076, Merck, Germany) in the first group and from Brushite (DCPD; 2046, Merck, Germany) and calcium carbonate in the second group of starting materials. In both cases stoichiometric mixtures of the starting powders were first milled in acetone for 1 hour using zirconia cup and balls. The mixtures were dried at 100°C to remove the majority of the acetone and then subsequently heated at 1350°C for 3,6,8 and 16 hours and at 1400°C for 6 hours in an electrical furnace equipped with silicon carbide elements according to heating program presented in Figure 1. Heating program is chosen based on the most common cycles used by many researchers [9-12]. Eight gr of powder was placed in a corundum crucible and heated at a rate of 10°C/min. Also compressed air was blown to ensure rapid cooling of the sintered ceramic. Samples were then quenched to room temperature and then returned to powder form using a pestle and mortar. The phase composition of the powders was determined by x-ray diffraction (powder method). In more details the powder was packed in a cavity in an aluminum sample holder. The measurements were done on a Philips PW1800 X-ray powder diffractometer (XRD) using Ni filtered Cu-K $\alpha$  generated at 40 kV and 30 mA. The specimens were scanned from 10 to 40° 2 $\theta$  (where  $\theta$  is the Bragg angle) in continuous mode.

To obtain X-ray diffraction quantitative phase analysis by “match!” the  $\alpha$ -TCP content is obtained by integrating the  $\alpha$ -TCP (331), (132), and (151) peaks from 23.8 to 24.8°. This region is immune from any other interference. A quadratic background is also assumed. The  $\beta$ -TCP content is obtained by integration from 30.5 to 31.5°. The region is prospered for  $\alpha$ -TCP (170) and (511) peak interference. The  $\beta$ -TCP peak being used for quantification, is the (0210) peak.



**Figure 1:** Heating cycles applied on starting powders at 1350°C.

The measurements of the sample elemental composition were performed with X-ray fluorescence(XRF) technique using a Philips PW1480 spectrometer equipped with an Rh-anode X-ray tube with maximum power 2.4 kW.

## 3. RESULT AND DISCUSSION

The chemical compositions of monetite and brushite used in this study are shown in table 1. The compositions are reported as oxides in weight-percentage (wt.%) and the limit of detection was 0.02 wt.%. It is better known that the relative stability of the  $\alpha$ - and  $\beta$ -polymorph is highly affected by the presence of some impurities. Magnesium is known as an element that stabilizes the  $\beta$ -phase [13, 14] and increases the  $\beta$  to  $\alpha$ -TCP phase transformation temperature to higher values [15, 16]. To confirm that further chemical impurities were not introduced into the composition from the calcium carbonate used, calcium carbonate was also analyzed by XRF. Results showed that the amount of MgO, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and SrO impurities were all below the limit of detection (< 0.02 wt.%).

**TABLE 1.** Compositions ( $\pm$  0.02%) of monetite and brushite determined by XRF. Percentage values less than 0.02% (limit

Precursor	MgO	P <sub>2</sub> O <sub>5</sub>	CaO	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SrO
monetite	0.43	55.70	43.87	-	-	-	-
brushite	0.72	55.47	43.81	-	-	-	-

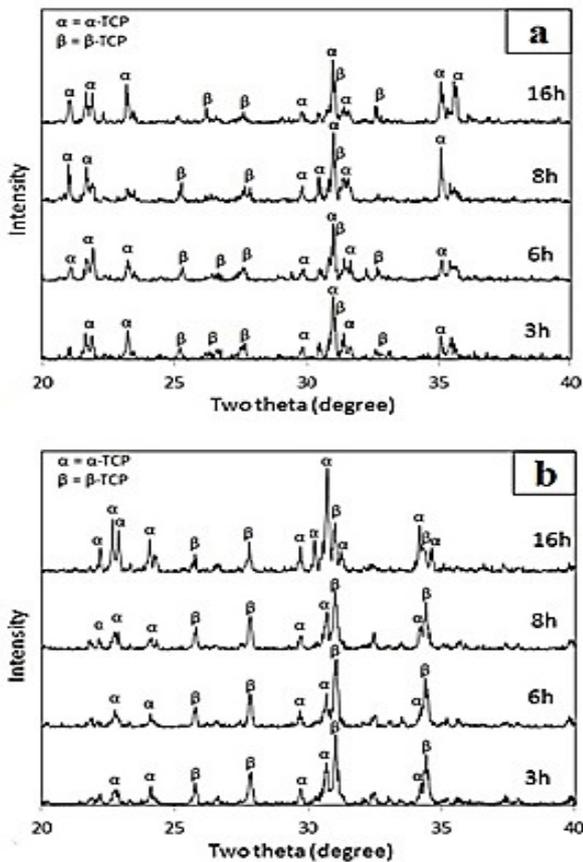
In Table 2, the data obtained for quenched samples of both groups are included and relate to the diffraction patterns of Figure 2. Powders in both groups were dwelled about 3,6,8 and 16 hours.

**TABLE 2.** match! software results of monetite-calcium carbonate and brushite-calcium carbonate powders heated at 1350°C for different periods.

Precursor	Time (hours)	$\alpha$ -TCP (%)	$\beta$ -TCP (%)
CaHPO <sub>4</sub> + CaCO <sub>3</sub>	3	81	19
	6	82	18
	8	93	7
	16	94	6
CaHPO <sub>4</sub> .2H <sub>2</sub> O + CaCO <sub>3</sub>	3	72	28
	6	65	35
	8	73	27
	16	74	26

Increasing the dwell time provides better kinetics for the reaction but in spite of quenching the heated mixtures of

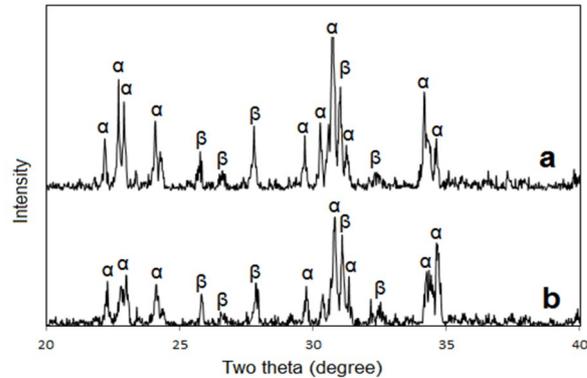
precursors from 1350°C and 1400°C,  $\beta$ -TCP is the second phase available beside  $\alpha$ -TCP in all samples. From thermodynamic considerations relevant to the synthesis of  $\alpha$ -TCP, presence of  $\beta$ -TCP can be attributed to two probabilities: a) at 1350°C equilibrium has not been reached and longer dwell time is required. b) equilibrium has been reached but because of impurities like Mg, which stabilizes  $\beta$  phase in the reaction mixture, the temperature required to obtain pure-phase  $\alpha$ -TCP has to be increased because in this case the temperature of the polymorphic transformation is beyond 1125°C [3].



**Figure 2.** XRD patterns of synthesized TCPs (a) of Monetite as precursor and of (b) Brushite as precursor heated at 1350°C for 3,6,8 and 16 hours.

According to patterns and Table 1, increasing the dwell time at 1350°C from 3 to 16 hours in both groups increases the amount of synthesized  $\alpha$ -TCP and reduces the amount of  $\beta$ -TCP simultaneously, but this change in final products amount is sharper when monetite being the precursor, since it has a lower amount of Mg impurity. It is observed that in the group of brushite as the precursor, the minimum percentage of  $\alpha$ -TCP is 72% which is obtained in 3hours and increases to 74% in 16hours which does not show a big increase. In group with monetite in 3hours of dwelling time, 81%  $\alpha$ -TCP has been achieved while increasing time from 3to 16

hours the maximum amount of synthesized  $\alpha$ -TCP reaches 94% and shows 13% increase from 3hours of dwelling time. XRD patterns of the heated samples at 1400°C for 6hours and the following Match software results are presented in Figure 3. and Table 3 respectively.



**Figure 3.** XRD patterns of synthesized TCPs (a) of Monetite as precursor and of (b) Brushite as precursor heated at 1400°C for 6 hours.

Increasing the temperature from 1350°C to 1400°C with the same soaking time (6 hours) has a greater effect on the amount of synthesized  $\alpha$ -TCP with brushite precursor and this indicates the compensating effect of temperature for the amount of Mg impurity in the starting material.

**TABLE 3.** “Match!” Software results of monetite-calcium carbonate and brushite-calcium carbonate powders heated at 1400°C for 6 hours.

Precursor	Time (hours)	$\alpha$ -TCP (%)	$\beta$ -TCP (%)
CaHPO <sub>4</sub> + CaCO <sub>3</sub>	6	88	12
CaHPO <sub>4</sub> .2H <sub>2</sub> O + CaCO <sub>3</sub>	6	84	16

In a recent study by Duncan et al. the effect of chemical impurities of different monetite sources (Acros, Alfa Aesar, Merck, Sigma Aldrich) on the amount of produced  $\alpha$ -TCP synthesized by solid state reaction at 1300°C for 16 hours has been reported. In their study only a high level of chemical purity could be obtained from monetite synthesized in-house in which the impurities were minimized [4]. In another research on the solid state reaction of calcium carbonate with ammonium hydrogen phosphate at >1300°C, in the case of using calcium carbonate with 0.49 wt.% magnesium as MgO, pure  $\alpha$ -TCP could not be obtained [17]. Cicek et al. investigated the effect of calcium carbonate purity

on the synthesis, properties and hydraulic reactivity of  $\alpha$ -TCP. Their studies with a calcium carbonate containing 0.94 wt.% magnesium impurity (as MgO) led to a mixture of  $\alpha$ -TCP and  $\beta$ -TCP when quenched from 1300°C, whereas using a purer calcium carbonate with only 0.01 wt.% Mg led to a single phase  $\alpha$ -TCP, even between 1125 and 1150°C [6]. Also it was reported in a study that it was not possible to produce a single phase  $\alpha$ -TCP when using a solid state reaction of calcium carbonate and monetite (both from Sigma Aldrich) [18].

#### 4. CONCLUSION

The present study highlights some general findings with regard to the determination of parameters affecting solid state synthesis of  $\alpha$ -TCP. It has been found that prolonged firing and increasing the firing temperature, both have a positive effect on the amount of  $\alpha$ -TCP present in the final product. Also corroborating previously reported findings by many researchers, magnesium impurity (as MgO) favored the formation of  $\beta$ -TCP. At 1350°C with 16 hours of soaking time, the maximum amount of  $\alpha$ -TCP with monetite precursor containing 0.43 wt.% MgO impurity was about 94%; whereas the obtained percentage with brushite precursor containing 0.72 wt.% MgO was about 74%.

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