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Aqueous precipitation method for the formation of Mg-stabilized β-tricalcium phosphate: An X-ray diffraction study

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Abstract

The preparation of magnesium (Mg)-stabilized β-tricalcium phosphate [β-TCP, β-$Ca_3(PO_4)_2$] was carried out by an aqueous precipitation method and the characterization was performed by powder X-ray diffraction. The transformation of calcium-deficient apatite (def-apatite) into β-TCP occurred in the range of 600–700 °C in the case of Mg substitution, whereas in the absence of Mg the transformation took place at higher temperatures (700–800 °C). The thermal stability of Mg-stabilized β-TCP powders was observed until 1400 °C resulting in higher density values when compared to that of pure β-TCP, which indicated thermal stability only till 1100 °C and comparably lower density values. Addition of Mg to the precursors Ca/P molar ratio = 1.5 resulted in the formation of small amounts of hydroxyapatite [HAP, $Ca_{10}(PO_4)_6(OH)_2$]. The calculated values for lattice parameters confirm the stabilization role played by Mg.

Keywords: Def-apatite; Magensium; β-TCP; XRD

1. Introduction

Hydroxyapatite [HAP, $Ca_{10}(PO_4)_6(OH)_2$] and β-tricalcium phosphate [β-TCP, β-$Ca_3(PO_4)_2$] are the most commonly used materials in the biomedical applications due to their close chemical similarity to the inorganic component of bone and teeth mineral [1,2]. Due to its resorbable features and excellent osseoconductive properties, β-TCP has found wide use as a bone cement and implant material [3]. In recent years, substitution of magnesium (Mg) in the apatite structure has received much attention due to its impending role on bone metabolism, reducing cardiovascular disease, promoting catalytic reaction and controlling biological functions [4,5]. It has been found that in biological apatites, Mg in trace levels is substituted for calcium sites in β-TCP that is commonly termed as whitlockite (β-TCMP) [6]. Recent studies have indicated that whitlockite occurs under physiological or pathological conditions at extra- (or) intra-tissular sites, mainly in tissues of non-epithelial region [7]. Whitlockite is also considered as a major constituent of human dental calculus [8] and it also found to occur in carious lesions [9]. Hence, the preparation of whitlockite is essential for application in both bone and tooth replacement and augmentation programs.

Some previous studies have reported on the formation of Mg-stabilized β-tricalcium phosphate (whitlockite) [10]. The procedure generally adopted is the synthesis through solid-state reaction that involves magnesium oxide (MgO) as sintering additive to stabilize the β-TCP phase above 1000 °C. However, the solid-state reaction limits are inhomogeneity, non-uniformity in the particle size distribution of the final powder and also a major chance of added impurities in the final product, such as unreacted MgO. In the present study a new route was attempted to prepare β-TCMP via aqueous precipitation method, which has not been reported elsewhere in the literature. The significance of the aqueous precipitation method relies on the homogeneous mixture of the final product with uniform particle size, making this method more reliable for the fabrication of powders, granules, dense or porous bodies and for coatings of metallic or polymeric implants used in biomedical applications.

The preparation of β-TCP through aqueous precipitation usually involves the synthesis of calcium deficient apatite (def-apatite) by adjusting the initial Ca/P molar ratio of the precursors to 1.5 and subsequent calcination in the range of

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700–800 °C to form β-TCP, with the loss of water as represented in the Eq. (1).

$$Ca_9(HPO_4)(PO_4)_5(OH) \rightarrow 3Ca_3(PO_4)_2 + H_2O \qquad (1)$$

This methodology was adapted to form Mg stabilized β-TCP by introducing a precursor of Mg into the reaction system. Some authors have reported on the Mg-substituted hydroxyapatite via aqueous precipitation method and have described that Mg stabililized the β-TCP phase above 800 °C along with the formation of HAP phase [11,12]. In the present study, the authors are concerned with the synthesis of pure β-TCMP with no extra phases.

2. Experimental

2.1. Powder preparation

Reagent grade calcium nitrate tetrahydrate [$(Ca(NO_3)_2 \cdot 4H_2O$], magnesium nitrate hexahydrate [$Mg(NO_3)_2 \cdot 6H_2O$] and diammonium hydrogen phosphate $(NH_4)_2HPO_4$ were used as starting chemicals (Vaz Pereira, Portugal) precursors, respectively for calcium, magnesium and phosphorous. For the preparation of def-apatites, predetermined Ca/P molar ratios (concentrations of the precursors are depicted in Table 1) were set by the slow addition of $(NH_4)_2HPO_4$ solution to the continuously stirred (1000 rpm) solution of $Ca(NO_3)_2 \cdot 4H_2O$. A predetermined concentration of $Mg(NO_3)_2 \cdot 6H_2O$ was added slowly to the above solution containing calcium and phosphorous ions. The pH of the mixed solution/suspension was increased to 7.4 and maintained at this value by adding the required amounts of 8 M ammonium hydroxide (NH_4OH) solution. After the completion of addition, the reaction was performed at 90 °C for 2 h under constant stirring conditions (1000 rpm). The precipitated suspension was poured out from the reactor and precipitates were separated through vacuum filtration technique and were dried at 80 °C overnight. The dried cakes were ground to fine powders, sieved through a mesh size of 200 μm and used for characterization studies.

2.2. Characterization

The as prepared powders were calcined at different temperatures ranging from 600 to 1400 °C in a Thermolab furnace (Pt30%Rh/Pt6%Rh-thermocouple) with a heating rate of 5°/min to achieve a predetermined temperature range and a dwelling time for 2 h and again cooled to room temperature at the rate of 5°/min. Phase identification of the powders before and after calcination was determined by X-ray diffraction (using a high resolution Rigaku Geigerflex D/Mac, C Series diffractometer). Copper Kα radiation (λ = 1.5406 nm) produced at 30 kV and 25 mA scanned the diffraction angles (2θ) between 20° and 50° with a step size of 0.02° 2θ/s. Crystallographic identification of the phases of synthesized apatites was accomplished by comparing the experimental XRD patterns to standards complied by the Joint Committee on Powder Diffraction Standards (JCPDS), which were card # 09-0169 for β-TCP and # 09-0432 for HAP. Lattice constants for β-TCP phase composition were determined by least square refinements from the well-determined positions of the most intense reflections, which are processed by MDI Jade 6.1 soft ware. The reflections of the plane (1 0 1 0), (2 1 4), (3 0 0), (0 2 1 0), (2 2 0) and (4 0 1 0) were used for calculation. The volume $V$of the rhombohedral unit cell was determined for each β-TCP formulation from the relation $V = 0.8660 \times a^2 \times c$. Quantitative determination of the phase compositions of biphasic mixtures were made using X'Pert High Score 1.0 f, PANalytical B.V using International Center for Diffraction Data (2004) database. Densities of the powders were determined by helium gas multi-pycnometry with an Accupyc Quantachrome apparatus (Florida, USA).

Table 1
Molar concentrations of the precursors Ca, P and Mg used in the synthesis

Sample code	Molar concentrations of the precursors			Ca/P ratio	(Ca + Mg)/P ratio
	Ca	P	Mg		
tcp-1	0.900	0.600	0.000	1.50	1.50
tcp-2	0.882	0.600	0.018	1.47	1.50
tcp-3	0.864	0.600	0.036	1.44	1.50
tcp-4	0.900	0.600	0.018	1.50	1.53
tcp-5	0.900	0.600	0.036	1.50	1.56

3. Results and discussion

The XRD patterns of the as prepared powders are presented in Fig. 1. All the powders have indicated the formation of apatite phase with varying peak width and absolute intensity of the diffraction patterns. The substitution of Mg did not appear to affect the diffraction patterns of the as prepared powders. It should be noted that the X-ray diffraction pattern of an as-precipitated apatite powder can resemble that of HAP even though the Ca/P ratio is greater or less than the stoichiometric molar ratio of 1.67 for HAP [13]. For this reason it is essential to carry out X-ray diffraction analysis on samples that have been heat treated at temperatures higher than 600 °C in order to

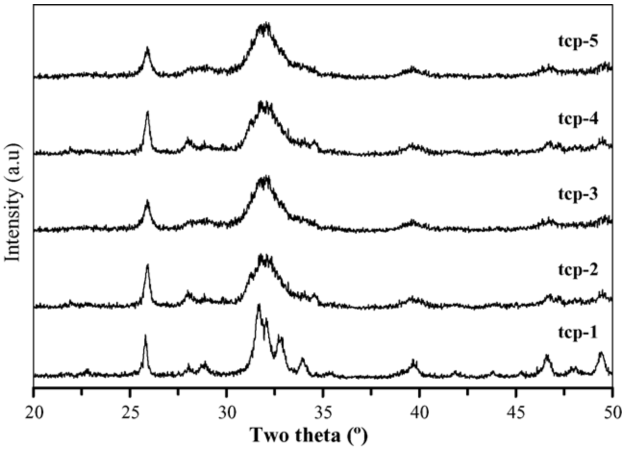

Fig. 1. Powder X-ray diffraction pattern for the as prepared powders.

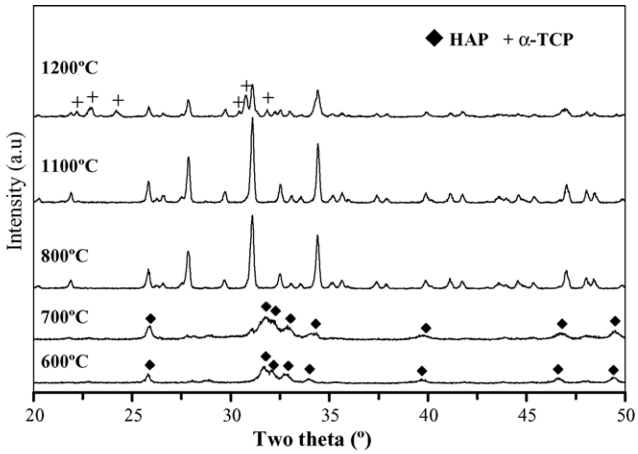

Fig. 2. Powder X-ray diffraction patterns for the tcp-1 calcined at different temperatures (unmarked peaks refer to β-TCP).

assess the effect of chemical changes on the phase composition and formation of pure β-tricalcium phosphate with Mg incorporation in its structure. The XRD patterns for the powders tcp-1, tcp-2 and tcp-3 calcined at different temperatures are displayed in Figs. 2–4, respectively. It is well seen that the evolution of tcp-1 (with a Ca/P molar ratio of 1.5 and no added Mg) patterns, corresponds to the transformation of def-apatite to β-TCP in the range of 700–800 °C. This fact is in good agreement with the findings of Gibson et al. [14], who have reported the occurrence of a similar transformation at this temperature range for a powder prepared via aqueous precipitation method. In case of tcp-2 and tcp-3 that contain added Mg during the reaction, the X-ray patterns at 600 °C have indicated the formation of poorly crystalline apatite phase with no signs for the presence of β-TCP. Calcination at 700 °C resulted in the formation of pure β-TCP for both the samples tcp-2 and tcp-3. However, in these powders the precursors (Ca + Mg)/P molar ratio during the course of synthesis was adjusted to 1.5 to ensure the incorporation of Mg into β-TCP. As discussed above, the transformation of def-apatite without Mg addition occurred in the range of 700–800 °C, hence it is reasonable to explain the role of Mg in enhancing the transformation to β-TCP below 700 °C. The role of Mg in stabilizing the β-TCP phase can be represented by the following equation

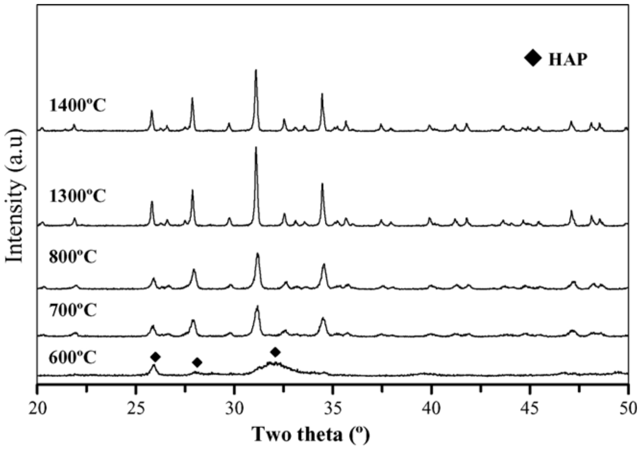

Fig. 3. Powder X-ray diffraction patterns for the tcp-2 calcined at different temperatures (unmarked peaks refer to β-TCP).

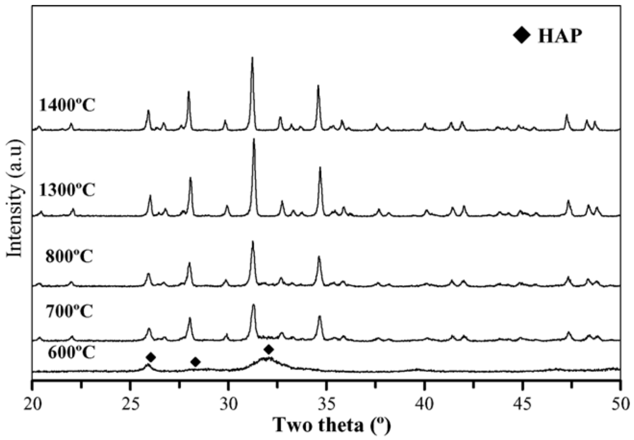

Fig. 4. Powder X-ray diffraction patterns for the tcp-3 calcined at different temperatures (unmarked peaks refer to β-TCP).

$$\mathrm{Ca_9Mg_{\mathit{x}}(HPO_4)(PO_4)_5(OH)} \rightarrow 3(\mathrm{Ca}_{3-(x/3)}\mathrm{Mg}_{x/3})(\mathrm{PO_4})_2 + \mathrm{H_2O} \qquad (2)$$

Further heating above 700 °C has indicated the maintenance of thermal stability till 1400 °C for tcp-2 and tcp-3, which is solely due to the role played by added Mg. This was not the case for tcp-1 that has been transformed into α-tricalcium phosphate (α-TCP) at 1200 °C (Fig. 2), according to some previous reports [15,16]. Although β-TCP has reached acceptance in biomedical applications, its poor mechanical properties like brittleness and insufficient densification upon sintering below

Table 2
Calculated lattice constant values, diffraction parameters for (0 2 1 0) intensity plane and the measured density values for different powders

Sample code	Lattice constants (Å)			Diffraction values for (0 2 1 0) plane		Density (g/cm^3)
	a-axis (±0.0004)	*c*-axis (±0.0004)	Volume (±0.04)	2*θ*	*d*-spacing (Å)	
JCPDS # 09-169	10.429	37.38	3520.91	31.026	2.8800	–
tcp-1	10.4492	37.3709	3533.70	31.02	2.8805	2.842
tcp-2	10.4187	37.2615	3502.72	31.10	2.8734	2.996
tcp-3	10.4101	37.1268	3484.29	31.22	2.8626	3.016

For tcp-1: parameters were measured at 1100 °C; For tcp-2 and tcp-3: parameters were measured at 1400 °C.

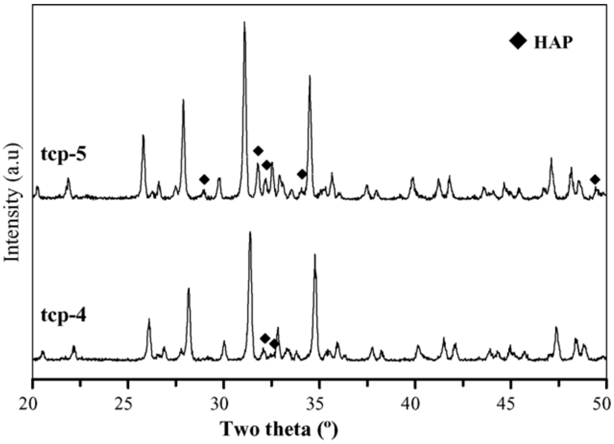

Fig. 5. X-ray diffraction pattern for the powders tcp-4 and tcp-5 calcined at 1400 °C (unmarked peaks refer to β-TCP).

the β- to α-transformation temperature have limited its applications in non-load-bearing applications. It was shown that the phase transformation of β-TCP to α-TCP is closely related with the expansion of sample volume and declining in shrinkage rate [17]. Some research reports considered that the phase transformation from β- to α-TCP prevents TCP from further densification [18]. Additionally, the expansion of TCP during sintering process causes micro-cracks in phase-transformed TCP that reduce the mechanical strength of TCP ceramics and make β-phase-containing TCP ceramics unsuitable for surgical implant applications that require improved mechanical strength [19]. The dual purpose of our present study is to prepare a thermally stable and homogeneous powder able to achieve a high-density level on sintering. The measured density values (Table 2) for the powders tcp-1, tcp-2 and tcp-3 follow the order: tcp-1 < tcp-2 < tcp-3. The powder tcp-3 that possesses higher concentration of added Mg has recorded a relatively density value higher with respect to tcp-2 that possesses low concentration of added Mg.

On the other hand, the X-ray diffraction patterns for the powders tcp-4 and tcp-5 (Fig. 5) calcined at 1400 °C have indicated the formation of trace HAP phase. The powder tcp-5 with the higher concentration of added Mg has indicated 12% HAP in the composition, whereas 7% of HAP was recorded for the sample tcp-4 that contains a lower concentration of added Mg. This shows that the incorporated Mg has stabilized the β-TCP phase and replaced some Ca sites upon calcination at high temperatures. Since, the precursor [Ca + Mg/P] ratios for the powders tcp-4 and tcp-5 have exceeded the stoichiometric molar ratio of 1.5 required to form pure β-TCP, it is reasonable to assume that the Mg^{2+} ions are preferentially incorporated into the whitlockite lattice and the excess of Ca^{2+} ions tend to form HAP. It is worthwhile to mention that since the synthesis was carried out by the aqueous precipitation method, the excess Ca^{2+} ions replaced by Mg^{2+} ions would readily form the HAP phase. Therefore, one should expect a higher amount of HAP for the powder tcp-5 than for the powder tcp-4, which contains low level of replaced Ca^{2+} ions.

The lattice constant values presented in Table 2 confirm the formation of rhombohedral β-TCP space group for the powders tcp-1, tcp-2 and tcp-3. It is significant from the values that the incorporation of Mg in β-TCP has shown significant contraction in both *a*- and *c*-axis with respect to the pure β-TCP phase. The reason may be due to the difference in size of Ca^{2+} (0.96 Å) ions and Mg^{2+} (0.69 Å) ions. Increasing amounts of added Mg gave rise to enhanced contractions as indicated for the sample tcp-3. Additionally, the obtained *d*-spacing and 2θ values from the X-ray patterns have also indicated significant differences due to the incorporation of Mg in the β-TCP. Although all the values have indicated significant changes, Table 2 reports only the values for the maximum intensity plane of β-TCP (0 2 1 0). The given data also tend to agree with the role played by Mg, where the tcp-3 powder has shown considerable decrease in the *d*-spacing value with corresponding increase in the 2θ value in comparison with the powder tcp-2, which has indicated the values in vice versa.

4. Conclusion

The synthesis of Mg-stabilized β-TCP has been achieved by the aqueous precipitation method. The transformation took place within the temperature range of 600–700 °C for Mg substituted def-apatites, which is about 100 °C lower than that recorded for pure β-TCP (700–800 °C). For the precursors molar ratio of Ca/P = 1.5, small amounts of the HAP phase were detected, accounting for the excess of replaced Ca^{2+} ions by the substituted Mg^{2+} ions. The Mg-stabilized β-TCP powders have indicated higher density values when compared to that of pure β-TCP powder. Finally, the calculated lattice constants and unit cell volumes have shown significant contraction for Mg-stabilized β-TCP powders with respect to that of pure β-TCP powder.

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