XRD and FTIR Analysis of Magnesium Substituted Tricalcium Calcium Phosphate Using a Wet Precipitation Method

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Abstract: The incorporation of magnesium (Mg) in tricalcium phosphate (TCP) was prepared through a precipitation method followed by calcination at 850 °C in air. Calcium hydroxide, (Ca(OH)₂), phosphoric acid, (H₃PO₄), and magnesium chloride (MgCl₂.6H₂O) with a Ca/P ratio of 1.5, were mixed as the precursor materials. The concentration of added Mg was varied with respect to calcium (Ca) precursor molarity as such Mg/(Ca +Mg) molar ratio was 0.05, 0.10, and 0.15, while the (Ca+Mg)/P ratio was maintained at 1.50 throughout the experiment. The influence of Mg-doped TCP on phase composition, chemical structure, and a functional group at different weight percentages were accomplished through X-ray diffraction (XRD), inductively coupled plasma optical emission spectroscopy (ICP-OES) and Fourier Transform Infrared Spectroscopy (FTIR) analyses. Based in the results of this research, the presence of magnesium led to the formation of Mg-doped calcium-deficient apatite (MgCDA) at 80°C and Mg-doped β-TCP at 850°C; the incorporation of Mg into the TCP phase causing an expansion of the lattice and increase in the lattice parameter. This result could be considered rather unusual.

Keywords: Tricalcium phosphate; Magnesium; precipitation method; XRD and FTIR.

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1. Introduction

Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂, HA) and β-tricalcium phosphate (β-TCP, β-Ca₃(PO₄)₂) have been considered the most promising materials for both dental and orthopedic applications, because of their chemical similarity to that of human hard tissue [1-5]. Owing to their favorable biological response, these materials have been applied in a wide range of typologies like cement [6,7]. Nevertheless, their applications are limited due to some disadvantages. For example, HA shows a limited ability to stimulate the development of new bone tissue and does not degrade significantly [8]. The weak mechanical properties of β-TCP ceramics, due to its brittleness and insufficient compaction, are limiting its use to non-load-bearing applications.

The most thoroughly investigated material considering ionic substitution is β-TCP [9-13]. In turn, magnesium is definitely the most widely incorporated dopant into its crystal lattice [14-16]. Magnesium (Mg) ion is an essential trace element where it is the fourth cation in the human body that plays an important role in preventing osteoporosis and increase the
regeneration of bone in biomedical applications. Generally, the magnesium content in the human body is known between 0.5 to 1.5wt% [17-20]. Bone contains 0.72wt% of magnesium that are required in the growth of osteoblast and osteoplastic activity of the bone. Mg and Ca provide strong and healthy bones and reduce osteoporosis. Osteoporosis happens due to the high content of calcium with low content of magnesium that affects the fracture of bone [21]. Also, doping β-TCP with Mg ions decreases its solubility [22]. Synthesis methods, such as precipitation [23,24], wet mixing [25,26], mechanochemical-hydrothermal synthesis [27,28], in-situ synthesis [29], solid-state reactions [30,31], sol-gel [32,33] and room temperature synthesis method [34] have been applied. The preparation of TCP through aqueous precipitation usually involves the synthesis of calcium-deficient apatite (CDA) by adjusting the initial Ca/P molar ratio of the precursors to 1.50 and subsequent calcination in the range of 700-800°C to form TCP with the loss of water as represented in the equation (1):

$$\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5\text{OH} \rightarrow 3\text{Ca}_3(\text{PO}_4)_2 + \text{H}_2\text{O}$$

However, there are very few studies available in the literature on the synthesis and characterization of tricalcium calcium phosphate-containing magnesium prepared via the wet precipitation method. In this work, precursor materials that are normally used to synthesize hydroxyapatite (HA) directly were adopted to obtain β-TCP and Mg-βTCP. The influence of the Mg substitution in the lattice parameters of the unit cell β-TCP was evaluated.

2. Materials and Methods

Tricalcium phosphate and Mg-substituted tricalcium phosphate with Mg/(Ca+Mg) ratio equal to 0 (TCP0), 0.05 (TCP1), 0.10 (TCP2) and 0.15 (TCP3) were synthesized by precipitation method [35] from an aqueous solution of calcium hydroxide [Ca(OH)_2] (Scharlau, Spain) orthophosphoric acid [H_3PO_4] (Riedel-de Haén, 85%) and magnesium chloride [MgCl_2.6H_2O] (Riedel-de Haén, Germany) at 40°C, pH = 9 (concentrations of the precursors are depicted in Table 1). A predetermined concentration of MgCl_2.6H_2O was added slowly to the continuously stirred solution of Ca(OH)_2. The aqueous solution of H_3PO_4 was added rapidly to the above solution containing calcium and Magnesium ions using a vigorous stirring. According to Table 1, the nominal composition, in terms of (Ca+Mg)/P ratio, was maintained at 1.50. Precipitates were aged in mother liquors at room temperature for 24 h, washed with distilled water, vacuum filtered, and finally dried 24h in an oven at 80°C. The dried samples were further calcined 12h at 850°C. In the case of the Mg-TCP precursor, it has been assumed that magnesium ions would substitute for the calcium site in the apatite lattice.

| Sample code | Molar Concentrations | Ca/P ratio (Ca + Mg)/P ratio |
|-------------|-----------------------|-----------------------------|
| TCP0        | 0.600 0.400 0.000   | 1.50 1.50                   |
| TCP1        | 0.570 0.400 0.030   | 1.42 1.50                   |
| TCP2        | 0.540 0.400 0.060   | 1.35 1.50                   |
| TCP3        | 0.510 0.400 0.090   | 1.27 1.50                   |

X-ray diffraction characterization of all batches of as-prepared and calcined Mg-TCP powders was performed using Cu Kα radiation. Samples were analyzed over a 20 range of 10–80° with a sampling interval of 0.07° (XRD, Kristalloflex D-500, Siemens Analytical X-ray Instrument Inc., Madison, WI). Crystallographic identification of the synthesized phases was accomplished by comparing the experimental XRD patterns to standards compiled by the Joint
Committee on Powder Diffraction and Standards (JCPDS), which were card #09-0169 for TCP (a=10.432(3)Å, b=10.432(3)Å, c=37.39Å, space group R3c (167), theoretical density 3.072g/cm³, V=3520.91Å³, Z=21) and #33-0297 for β-Ca₃P₂O₇.

The average crystallite size D(hkl) in nm was estimated following Debey–Scherrer equation [30]:

\[ D_{hkl} = \frac{k\lambda}{\beta \cos \theta} \]

where K is the shape factor equal to 0.9, λ is the X-rays wavelength (equal to 1.5406 Å for Cu Ka radiation), θ is the Bragg’s diffraction angle (in degrees), and β is the full width at half maximum (FWHM). The diffraction peak at 25.88 (2θ) corresponding to (0 0 2) Miller plane family of apatite lattice (JCPDS file #09-0432), was chosen to calculate the average crystal size along to the crystallographic axis c. The length of coherent domains D(2 0 10) in TCP crystallites was also calculated using the line broadening of the (2 0 10) peak (diffraction angle 2θ (31.08°)) [36], applying the Scherrer’s equation to XRD spectra of samples calcined at 850°C.

Cell parameters of the tricalcium phosphate phase were estimated through the algorithm DICVOL 06 (Fullprof-suite software), using XRD diffraction patterns of samples calcined.

The chemical structure of powders was evaluated in the vibration range of 400–4000 cm⁻¹, using an Infrared Fourier Spectrometer (VERTEX 70, Genesis Series, resolution 4, scans 20). For this, 1% of the powder was mixed and ground with 99% KBr.

3. Results and Discussion

XRD patterns of all as-prepared TCP and Mg-TCP powders are compared in Figure 1. All samples showed the typical diffraction pattern of the calcium-deficient hydroxyapatite (CDA) as from the perfect match with HA (#09-0432 card) characteristic reflections. In the pure TCP and the Mg-TCP samples, no other XRD peaks except for those derived from the CDA phase were observed. The substitution of Mg did not appear to affect the diffraction patterns of the as-prepared powders. Moreover, due to the existence of Mg, the diffraction peaks slightly shifted to larger angles in the pattern (figure 2), indicating the incorporation of Mg into β-TCP.

![Figure 1. XRD patterns of as-dried TCP and Mg-TCP precursors.](https://biointerfaceresearch.com/)

With increasing the amount of Mg in calcium-deficient apatite, the crystallinity of the apatite phase gradually decreased as manifested by the increased broadening of their XRD peaks. The gradual decrease of crystallinity is one of the indications suggesting increasing Mg incorporation in the CDA lattice. The calculated crystallite sizes are 25.5 nm (TCP0), 22.4 nm (TCP1), 20.7 nm (TCP2), and 20.5 nm (TCP3), respectively. The presence of Mg²⁺ ions seems to make the crystallization more difficult, as also observed in previous works for MgTCP powders [31, 37]. CDA powders are produced according to the reaction (1):
\[(9-3x)\text{Ca(OH)}_2 + 6\text{H}_3\text{PO}_4 + 3x\text{MgCl}_2.6\text{H}_2\text{O} \rightarrow \text{Ca}_{(9-3x)}\text{Mg}_{3x}(\text{HPO}_4)(\text{PO}_4)_5(\text{OH}) + 6x\text{HCl} + (17 + 12x)\text{H}_2\text{O}\]

Figure 2. X-ray diffraction showing peak shifts to larger angles after incorporation of Mg.

It is important to underline that TCP cannot be synthesized directly in aqueous solution by the wet method. The precipitate is an apatitic tricalcium phosphate \(\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH})\), consisting of calcium-deficient hydroxyapatite, \(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2\) where \(\text{HPO}_4^{2-}\) ion partially substitutes the \(\text{PO}_4^{3-}\) groups. The crystallization of anhydrous \(\beta\)-TCP requires further calcination of the apatitic compound at temperatures over 750°C [38]. For this reason, it is essential to carry out X-ray diffraction analysis on samples that have been heating treated at temperatures higher than 750°C in order to assess the effect of chemical changes on the phase composition and formation of pure \(\beta\)-tricalcium phosphate with Mg incorporation in its structure.

ICP was adopted to evaluate the actual Mg-doped amounts of the samples (TCP0, TCP1, TCP2, and TCP3). As shown in Table 2, the actual Mg-doped amounts of all the samples were closed to the designed ratios, but all were a little higher than that. Ca(4) in \(\beta\)-TCP has a lower occupancy factor of 0.43(4) [39]. Because of the shorter distance of Mg–O, after Mg is replaced with Ca, it altered the crystal lattice, which may intensify the vacancy of Ca ions, leading to the increase in Mg/(Ca+Mg) ratio.

Table 2. Molar ratio of (Ca+Mg)/P and Mg/(Ca + Mg) of the samples.

| Samples | (Ca+Mg)/P | Mg/(Ca+Mg) |
|---------|-----------|------------|
| TCP0    | 1.501     | 0          |
| TCP1    | 1.496     | 5.813%     |
| TCP2    | 1.478     | 11.744%    |
| TCP3    | 1.488     | 15.124%    |

Figure 3. XRD spectra of the TCP Mg-TCP precursors calcined at 850°C.
The XRD profiles (figure 3) of calcined undoped and Mg-doped CDA powders showed that all the calcined samples were completely transformed to β-TCP and Mg-β-TCP, respectively, according to equation (2):

\[
\text{Ca}^{(9-x)}\text{Mg}^x(\text{HPO}_4)(\text{PO}_4)\text{S(OH)} \rightarrow 3(\text{Ca}^{3-(x/3)}\text{Mg}^{x/3})(\text{PO}_4)_2 + \text{H}_2\text{O}
\]

In these powders, the precursors (Ca+Mg)/P molar ratio during synthesis was adjusted to 1.5 to ensure the incorporation of Mg into β-TCP. In the Mg-TCP samples with \( \text{Mg}/(\text{Ca}+\text{Mg}) = 0.05 \) and 0.15 (TCP1 and TCP3 samples), no other XRD peaks except for those derived from the TCP phase were observed, while peaks indicating the presence of \( \text{Ca}_3\text{P}_2\text{O}_7 \) (β-CPP) were observed in the sample with \( \text{Mg}/(\text{Ca}+\text{Mg}) = 0.10 \) (TCP2). When analyzing the vibrational bands of the samples doped with Mg\(^{2+}\), as observed in Figure 3, we realized that there were substitutions in the connection sites with phosphate, which would release Ca\(^{2+}\) ions and affect the chemical composition of the material, leading to the formation of new phases. Then, the substitution of Ca\(^{2+}\) by Mg\(^{2+}\) occurred at these sites and decreased the Ca/P ratio by changing the crystalline structure of β-TCP to β-CPP. With increasing Mg substitution, the XRD peaks became gradually broader and weaker. This effect could be explained by decreased crystallite size and increased lattice disorder associated with increasing Mg substitution in the TCP lattice. Peak positions shift to lower angles and are also observed (figure 4), which indicates lattice expansion caused by magnesium substitution. These observed peaks shift in the XRD pattern is a clear indication of the incorporation of Mg into the TCP phase, causing an expansion of the lattice and an increase in the lattice parameter. This could be considered somewhat unusual since Mg\(^{2+}\) is smaller in size (ionic radius ~0.65Å) compared to Ca\(^{2+}\) (ionic radius ~0.99Å). There are five crystallographically independent sites, \( \text{Ca}(1)-\text{Ca}(5) \), in the unit cell of β-TCP [40], but Ca\(^{2+}\) can be replaced by Mg\(^{2+}\) only on Ca(4) and Ca(5) sites in the β-TCP structure. According to Enderle et al. [41], the Ca\(^{2+}\) up to 10 mol% Mg\(^{2+}\) is preferably replaced on the six-fold coordinated Ca(5) site resulting in a decrease of both lattice parameters. Replacement of Ca\(^{2+}\) on the nine-fold coordinated Ca(4) site by Mg\(^{2+}\) does not significantly take place until the Ca(5) site is completely occupied by Mg\(^{2+}\). Above 10 mol% replacement by Mg\(^{2+}\), the nine-fold coordinated Ca(4) site is occupied by Mg\(^{2+}\), and the lattice parameters increase until maximum substitution. Hence the Mg\(^{2+}\) may be probably occupying an interstitial site rather than an actual lattice site causing increase cell parameter a.

![Figure 4. X-ray diffraction showing peak shifts after Mg is substituted indicative of lattice expansion.](https://biointerfaceresearch.com/)
850°C, i.e., TCP0, TCP1, TCP2, and TCP3 was estimated as about 47.1 nm, 46.7 nm, 42.9 and 31.9 nm, respectively.

| Sample | Mg/(Ca+Mg) | a(A˚)   | c(A˚)   | V (Å³)   |
|--------|------------|---------|---------|----------|
| TCP0   | 0          | 10.402(4)| 37.293(5)| 3495     |
| TCP1   | 0.05       | 10.412(4)| 37.403(2)| 3511     |
| TCP2   | 0.10       | 10.427(7)| 37.415(8)| 3522     |
| TCP3   | 0.15       | 10.440(5)| 37.424(3)| 3532     |

The FTIR analysis (Figure 5) of the as-prepared CDA and Mg-CDA powders was in good accordance with the results of the XRD analysis. Selected FTIR spectra to show the characteristic bands of Ca deficient apatite groups: ν4 PO₄³⁻ (560–600 cm⁻¹), ν1 PO₄³⁻ (960 cm⁻¹), and ν3 PO₄³⁻ (1020–1120 cm⁻¹). The band at 875 cm⁻¹ is ascribed to HPO₄²⁻ stretching mode of hydrogen phosphate groups. The very weak peaks located at 630 cm⁻¹ and 3568 cm⁻¹ were attributed to OH⁻. The amount of carbonate detected at 1420 and 1456 cm⁻¹. The presence of functional groups such as OH⁻, HPO₄²⁻ and PO₄³⁻ confirms that the powders prepared and then dried at 80°C are only DCA and Mg-DCA structures.

The FTIR spectra of TCP and Mg-TCP precursors calcined at 850°C are presented in Figure 6. As can be seen, the FTIR results of magnesium substituted tricalcium phosphate indicate the typical peaks characteristic of pure β-TCP [42]. The infrared absorption bands located at 1132, 1030, 990, 960, 610, and 560 cm⁻¹ contribute to the confirmation of PO₄ tetrahedra of β-Ca₃(PO₄)₂ structure [43]. The TCP2 sample showed additional peaks at 756 and 1213 cm⁻¹ ascribed to the symmetrical stretching vibration of the P–O–P group, which is characteristic of the calcium pyrophosphate phase Ca₂P₂O₇ in agreement with the previous XRD results.
4. Conclusions

Pure and Mg-doped calcium phosphate compounds were synthesized via the precipitation method starting from Ca(OH)₂, H₃PO₄, and MgCl₂·6H₂O. The thermal behavior at 80°C and 850°C of synthesized powders were studied with the help of FTIR and XRD data. Based on the results of this research, nanosized phase β-Mg-TCP powders were obtained by thermal treatment at 850°C. The crystallite size of Mg-CDA decreased with increasing Mg²⁺ content. It could be observed that both the cell parameters and cell volume increase, unusually, with Mg content.

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Conflicts of Interest

The authors declare no conflict of interest.

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