Synthesis and thermal behavior of Mg-doped calcium phosphate nanopowders via the sol gel method

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Abstract The aim of this study was to investigate the thermal behavior of Mg-doped calcium phosphate compounds. Nanocrystalline HA and β-TCP mixtures containing different magnesium contents were synthesized via an alkoxide sol gel method. The ratio of (Ca + Mg) / P was kept constant at 1.67, and the Mg content ranged between 0 and 3 mol%. The influence of magnesium on the phase composition, chemical structure, thermal behavior and morphological characteristics of nanopowders was analyzed using X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), Simultaneous Thermogravimetry and Differential Thermal Analysis (STA/DTA), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Based on the results of this research, the presence of magnesium led to the formation of Mg-doped hydroxyapatite (Mg-HA) and Mg-doped tricalcium phosphate (β-TCP) phases. The characteristic peaks of apatite structures have been identified in the FTIR spectra. It was found that both the presence of magnesium and low Ca/P ratio caused the formation of a biphasic mixture, even at 470 °C. In addition, the β-TCP to α-TCP transformation temperature increased due to the presence of magnesium ions. Morphological investigations showed that the synthesized powders were composed of nanoparticles, with sizes ranging from 40 to 100 nm.

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1. Introduction

Hydroxyapatite (HA, Ca₁₀(PO₄)₆(OH)₂) 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]. 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 [2]. Biphasic Calcium Phosphate (BCP), a mixture of nonresorbable HA and resorbable β-TCP are well known for their applications in the field of bone and tooth augmentation programs. Their different dissolution behaviors make them versatile, in comparison to single-phase HA or β-TCP components [3]. The unique dissolution characteristics of BCP promote new bone formation at the implant site [1].

On the other hand, all properties associated with hydroxyapatite, such as bioactivity, biocompatibility, solubility and adsorption, can significantly improve by modifying its composition through ionic substitutions [4]. Biological apatites are characterized by nanosized crystals, low crystallinity, nonstoichiometric chemical formula and several ionic substitutions [5,6]. Small quantities of cations (i.e. K⁺, Mg²⁺, Sr²⁺, Al³⁺) and/or anions (i.e. F⁻, SiO₄⁴⁻ and CO₃²⁻) in the apatite structure play a pivotal role in its overall biological performance [2,7,8].

Magnesium is one of the most important bivalent ions in the biological apatite [9] and is the fourth most abundant cation in the human body (0.44–1.23 wt%) [8]. Enamel, dentin and bone contain 0.44, 1.23, and 0.72 wt% of magnesium, respectively [4].
Recently, this element, as a dopant in both apatite and \( \beta \)-TCP structures, has been the subject of specific interest, due to its important role in biological processes upon implantation [3]. Magnesium plays an essential role in the formation of dental caries and bone deposition [10]. Mg ions are able to promote bone mineralization and to control the growth of HA crystals in \( \text{in vivo} \) conditions [11]. Magnesium indirectly influences bone resorption and directly stimulates osteoblast proliferation with an effect comparable to that of insulin (a known growth factor for osteoblast) [11,12]. In addition, magnesium doped BCP has shown more thermal stability than BCP and higher \( \beta \)-TCP to \( \alpha \)-TCP transition temperatures [13]. Incorporation of this ion in the biphasic calcium phosphate structure could result in improving mechanical properties [14]. Thus, magnesium containing calcium phosphates are more appropriate for biomaterials and their applications. A brief summary of previous studies including precursors, stoichiometric ratio and the amount of added-magnesium, along with the final product, is described in Table 1.

### Table 1: Summary of previous studies on the synthesis of Mg containing calcium phosphates.

<table>
<thead>
<tr>
<th>Mg content</th>
<th>((\text{Ca} + \text{Mg})/\ce{P})</th>
<th>(\text{Ca}/\ce{P})</th>
<th>Phase</th>
<th>Precursors</th>
<th>Method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x = 0–3^a)</td>
<td>Initial: 1.67</td>
<td>Calculated: 1.66–3.2</td>
<td>(\beta)-TCP</td>
<td>(\text{Ca(NO}<em>2))(</em>{2} \cdot 4\text{H}_2\text{O}) (\text{Mg(NO}<em>2))(</em>{2} \cdot 6\text{H}_2\text{O}) (\text{P}_2\text{O}_5) (\text{Ca(NO}<em>2))(</em>{2} \cdot 4\text{H}_2\text{O})</td>
<td>Sol–gel</td>
<td>[15]</td>
</tr>
<tr>
<td>5–15 mol%</td>
<td>–</td>
<td>Initial: 1.8</td>
<td>(\text{Mg-BCP})</td>
<td>(\text{Mg(NO}<em>2))(</em>{2} \cdot 6\text{H}_2\text{O}) ((\text{NH}_4))(2\text{HPO}_4) (\text{Ca(NO}<em>2))(</em>{2} \cdot 4\text{H}_2\text{O})</td>
<td>Sol–gel</td>
<td>[14]</td>
</tr>
<tr>
<td>–</td>
<td>Initial: 1.51–1.63</td>
<td>1.42–1.62</td>
<td>(\text{Mg-BPC})</td>
<td>(\text{Mg(NO}<em>2))(</em>{2} \cdot 6\text{H}_2\text{O}) ((\text{NH}_4))(2\text{HPO}_4) (\text{Na}_2\text{HPO}_4)</td>
<td>Precipitation</td>
<td>[16]</td>
</tr>
<tr>
<td>–</td>
<td>Initial: 1 Calculated: 1.207</td>
<td>0.5</td>
<td>(\text{Brushite}) (\beta)-TCP</td>
<td>(\text{CaCl}_2 \cdot 2\text{H}_2\text{O}) (\text{MgCl}_2 \cdot 6\text{H}_2\text{O})</td>
<td>Precipitation</td>
<td>[13]</td>
</tr>
<tr>
<td>1–10 wt%</td>
<td>Initial: 1.67–1.7 Calculated: 1.5–1.56</td>
<td>–</td>
<td>(\beta)-TCP</td>
<td>(\text{Mg(NO}<em>2))(</em>{2} \cdot 6\text{H}_2\text{O}) ((\text{NH}_4))(2\text{HPO}_4) (\text{NH}_4\text{OH})</td>
<td>Precipitation</td>
<td>[17]</td>
</tr>
<tr>
<td>0.905–4.32 mol%</td>
<td>Initial: 1.45 Calculated: 1.39–1.4</td>
<td>–</td>
<td>(\beta)-TCP</td>
<td>(\text{Ca(OH)}_2)</td>
<td>Wet chemical</td>
<td>[18]</td>
</tr>
<tr>
<td>0–6 wt%</td>
<td>–</td>
<td>–</td>
<td>(\alpha)-TCP</td>
<td>(\text{MgO}) (\text{H}_2\text{PO}_4) (\text{CaCO}_3)</td>
<td>Wet mixing</td>
<td>[19]</td>
</tr>
<tr>
<td>0.03–0.6 wt%</td>
<td>–</td>
<td>–</td>
<td>(\beta)-TCP</td>
<td>(\text{HA} + \text{MgO})</td>
<td>HA powder</td>
<td>[20]</td>
</tr>
<tr>
<td>2.3–10.1 mol%</td>
<td>1.5</td>
<td>–</td>
<td>(\beta)-TCP</td>
<td>(\text{MgO}) (\text{H}_2\text{PO}_4) (\text{CaCO}_3) (\text{Mg(NO}_2))(2 \cdot 6\text{H}_2\text{O}) (\text{CaCO}_3) (\text{Mg(NO}_2))(2 \cdot 6\text{H}_2\text{O}) ((\text{NH}_4))(2\text{HPO}_4)</td>
<td>Precipitation</td>
<td>[21]</td>
</tr>
<tr>
<td>0–10 mol%</td>
<td>1.5</td>
<td>–</td>
<td>(\beta)-TCP</td>
<td>(\text{MgO}) (\text{H}_2\text{PO}_4) (\text{CaCO}_3) (\text{Mg(NO}_2))(2 \cdot 6\text{H}_2\text{O}) ((\text{NH}_4))(2\text{HPO}_4) (\text{MgO}) (\text{H}_2\text{PO}_4) (\text{CaCO}_3) (\text{Mg(NO}_2))(2 \cdot 6\text{H}_2\text{O}) ((\text{NH}_4))(2\text{HPO}_4)</td>
<td>solid-state reaction</td>
<td>[22]</td>
</tr>
<tr>
<td>1.8–3.6 mol%</td>
<td>1.5–1.56 1.5</td>
<td>–</td>
<td>(\beta)-TCP</td>
<td>(\text{MgO}) (\text{Ca(NO}_2))(2 \cdot 4\text{H}_2\text{O}) (\text{Mg(NO}_2))(2 \cdot 6\text{H}_2\text{O}) ((\text{NH}_4))(2\text{HPO}_4) (\text{CaCO}_3) (\text{Mg(NO}_2))(2 \cdot 6\text{H}_2\text{O}) ((\text{NH}_4))(2\text{HPO}_4) (\text{CaCO}_3) (\text{Mg(NO}_2))(2 \cdot 6\text{H}_2\text{O}) ((\text{NH}_4))(2\text{HPO}_4) (\text{CaCO}_3) (\text{Mg(NO}_2))(2 \cdot 6\text{H}_2\text{O}) ((\text{NH}_4))(2\text{HPO}_4) (\text{CaCO}_3) (\text{Mg(NO}_2))(2 \cdot 6\text{H}_2\text{O}) ((\text{NH}_4))(2\text{HPO}_4)</td>
<td>Aqueous precipitation</td>
<td>[7]</td>
</tr>
<tr>
<td>(x = 0–10)</td>
<td>1.67</td>
<td>Varied</td>
<td>(\beta)-TCP</td>
<td>(\text{Mg-HA}) (\beta)-TCP (\beta)-Ca(2\text{P}_2\text{O}_7) (\beta)-TCP (\text{Mg-HA})</td>
<td>Mechanocohemical hydrothermal</td>
<td>[14]</td>
</tr>
<tr>
<td>0.6–2.4 wt%</td>
<td>1.67</td>
<td>–</td>
<td>(\beta)-TCP</td>
<td>(\text{Mg-HA}) (\beta)-TCP</td>
<td>Precipitation</td>
<td>[8]</td>
</tr>
<tr>
<td>(x = 0–10)</td>
<td>–</td>
<td>–</td>
<td>(\text{Mg-HA}) (\text{Mg}_2\text{O}_4\text{HPO}_4\cdot3\text{H}_2\text{O}) (\text{Na}_2\text{HPO}_4)</td>
<td>(\text{CaCl}_2 \cdot 2\text{H}_2\text{O}) (\text{MgCl}_2 \cdot 6\text{H}_2\text{O}) (\text{Ca(OH)}_2)</td>
<td>Precipitation</td>
<td>[23]</td>
</tr>
<tr>
<td>1 wt%</td>
<td>1.7</td>
<td>–</td>
<td>(\text{Mg-HA})</td>
<td>(\text{H}_2\text{PO}_4) (\text{MgCl}_2 \cdot 6\text{H}_2\text{O})</td>
<td>Wet chemical</td>
<td>[24]</td>
</tr>
</tbody>
</table>

\(^a\text{x refers to }\text{(Ca}_{10–x}\text{Mg}_x\text{PO}_4\text{)}\text{H}_2\text{O})\text{ formula.}\)

Synthesis methods, such as precipitation [5,7,24,16], wet mixing [19,20], mechanochemical–hydrothermal synthesis [4,12], in-situ synthesis [13], solid state reactions [22] and sol gel [14,25], have been applied. Among the synthesis methods of biomaterial nanopowders, the sol gel process has been widely studied due to its promising advantages in producing products with higher purity and more homogeneous composition [26,27]. However, there are very few studies available in literature on the synthesis and thermal characterization of calcium phosphate bioceramics containing magnesium prepared via the sol gel process [14,25]. Some researchers have analyzed the influence of magnesium incorporation in HA or the \( \beta \)-TCP structure on the physicochemical properties of these phases, such as phase composition and crystallinity [4], solubility [21], mechanical behavior and final microstructure [19], but some deficiency exists in literature about the thermal behavior of Mg-doped single phase or biphasic calcium phosphate.

As previous work was based on precipitation and mechanochemical hydrothermal methods, this study introduces a sol gel
procedure through which all advantages associated with this method can be obtained, along with the simultaneous presence of magnesium in the structure. The purpose of this study is to clarify the thermal behavior of the synthesized Mg-doped calcium phosphate, such as the best calcination temperatures and transition temperatures, as well as effects of Mg content on the processes.

2. Experimental procedure

2.1. Powder preparation

Calcium nitrate tetrahydrate \((\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}; \text{Merck})\), triethyl phosphate \((\text{C}_3\text{H}_7\text{O}_3)\cdot \text{P}; \text{Merck})\) and magnesium nitrate hexahydrate \((\text{Mg(NO}_3)_2 \cdot 6\text{H}_2\text{O}; \text{Merck})\) were used as Ca, P and Mg precursors, respectively. Triethyl phosphate sol was diluted in the absolute ethanol (98%; Merck) with a small amount of deionized water. The designated amount of Mg and Ca precursors was first mixed in the absolute ethanol and then vigorously stirred in a glass container at ambient temperature. After 24 h, the Ca–Mg solution was added drop-wise into the phosphorous containing precursor, while stirring vigorously. The ratio of \((\text{Ca} + \text{Mg})/\text{P}\) were kept constant at 1.67. The degree of substitution of \(\text{Ca}^{2+}\) by \(\text{Mg}^{2+}\) in the mixture was indicated by the \(x\) value in the general formula of \((\text{Ca}_{10-x}\text{Mg}_x\text{PO}_4)_6(\text{OH})_2\), where \(x = 0, \ 1.5\) and 3. The subsequent powders were labeled as X0, X1.5 and X3, respectively (Table 2). The transparent stable sol was then aged under until a white dried gel was obtained. The dried gels were further calcined at 600 °C for 1 h and then were ground to fine powder and used for characterization studies.

2.2. Characterization techniques

The thermal behaviour of the samples was investigated by simultaneous thermogravimetry and differential thermal analyses (PL STA 1640, England) at a heating rate of 20 °C/min from ambient temperature to 1200 °C. The phase analysis was carried out by X-ray diffraction analysis (XRD: Philips PW 3710) using Cu Kα radiation with a step size of 0.020° and 20.029° s per step. Crystallographic identification of phases and determination of phase compositions were evaluated via XPert High Score 1.0 d, PANalytical B.V, using the International Center for Diffraction Data (2003) database. The crystallinity degree (\(X_c\)), corresponding to the fraction of crystalline apatite phase present in the examined volume, was calculated from Eq. (1) [18], where \(V_{300}\) is the intensity of the peak diffracted from the (300) crystallographic planes of HA, and \(V_{112/300}\) is the intensity of the valley between the peaks of the planes (112) and (300) of HA:

\[ X_c = 1 - \frac{V_{112}}{V_{300}} \]  

(1)

The chemical structure of powders was evaluated in the vibration range of 400–4000 cm\(^{-1}\), using an Infrared Fourier Spectrometer (FT-IR, Bruker-V33, 22 scans and resolution 4 cm\(^{-1}\)).

![Figure 1: DTA plots for the dried gel of X0, X1.5 and X3 samples.](image1)

![Figure 2: TGA plots for the dried gel of X0, X1.5 and X3 samples.](image2)

The microstructure of samples was studied by scanning electron microscopy (SEM, S360, Cambridge 1990). The average grain size of the particles was estimated from the SEM micrographs, using Manual Microstructure Distance Measurement software. Transmission electron microscopy (TEM, Philips, EM 2085, 100 kV) was used to analyze the morphology and crystallite size of the synthesized nanopowders.

3. Results and discussion

3.1. Thermal analysis

To study the effect of magnesium on the phase transformations and thermal stability of synthesized powders, STA analysis (Figures 1 and 2) of the dried gel, of X0, X1.5 and X3 samples, was performed. The relatively strong endothermic peaks up to 200 °C indicated the evaporation of ethanol and physically adsorbed water [14,28–30]. The corresponding weight losses in this region were around 11%, 27% and 24% for X0, X1.5 and X3 samples, respectively. The evaporation of solvent, along with the hydrolytic products of triethyl phosphate, mainly occurred in this step [31]. The second stage took place within the temperature range between 200 and 330 °C, with 10%, 10% and 14% of weight loss for X0, X1.5 and X3 samples, respectively. These sharp exothermic peaks can be attributed to decomposition of nitrate [28]. This conclusion can be corroborated by the FTIR

| Table 2: Ca/P ratio and the amount of magnesium (wt%) in different samples. |
|-----------------|----------------|----------------|
| \(x\)            | \((\text{Ca} + \text{Mg})/\text{P}\) | \(\text{Ca}/\text{P}\) | Mg (wt%) |
| 0               | 1.67           | 1.67           | 0         |
| 1.5             | 1.67           | 1.41           | 3.52      |
| 3               | 1.67           | 1.16           | 7.29      |
Table 3: The observed absorption peaks in the FTIR spectra of synthesized samples.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Frequency (cm$^{-1}$)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO$_4^{3-}$ ($v_1$)</td>
<td>960–962</td>
<td>[35,36]</td>
</tr>
<tr>
<td>PO$_4^{3-}$ ($v_2$)</td>
<td>470–474</td>
<td>[35]</td>
</tr>
<tr>
<td>PO$_4^{3-}$ ($v_3$)</td>
<td>1037–1049, 1076–1080</td>
<td>[8,35–37]</td>
</tr>
<tr>
<td>PO$_4^{3-}$ ($v_4$)</td>
<td>563–567, 601–603</td>
<td>[8,35–37]</td>
</tr>
<tr>
<td>CO$_2^{−}$</td>
<td>1415, 1445–14450</td>
<td>[24,35,38]</td>
</tr>
<tr>
<td>CO$_2^{−}$</td>
<td>870–873</td>
<td>[28,39]</td>
</tr>
<tr>
<td>OH$^−$</td>
<td>630, 3566</td>
<td>[40,36,37]</td>
</tr>
<tr>
<td>P$_2$O$_4^{−}$</td>
<td>740–720</td>
<td>[29,41]</td>
</tr>
<tr>
<td>NO$_3^{−}$</td>
<td>820, 1380</td>
<td>[28,32–34]</td>
</tr>
<tr>
<td>HPO$_4^{2−}$</td>
<td>870–873</td>
<td>[8,28,39]</td>
</tr>
</tbody>
</table>

spectra of the X3 sample (Figure 3), in which one of the characteristic absorption peaks of the nitrate [28,32–34] was observed at 820 cm$^{-1}$ up to 370 °C, whereas the intensity of this peak decreased with temperature. Another characteristic peak of the nitrate group at 1380 cm$^{-1}$ [28,32–34] also decreased with temperature; however, a small amount of this group was still observed up to 534 °C. The complete list of the main vibration modes of hydroxyapatite observed in Figure 3 are shown in Table 3.

It should be noted that the amount of samples for STA analysis was selected in such a way that all samples have almost the same weight at 390 °C. STA peaks corresponding to crystallization and phase transformation, hence, can be compared regarding their shift or intensity. XRD patterns of the X3 and X0 samples, calcined at different temperatures, are shown in Figures 4 and 5. Based on these figures, the powders were composed of pure and Mg-substituted hydroxyapatite (ICDD PDF #010841998), β-TCP (ICDD PDF #000030681), Mg-substituted β-TCP (ICDD PDF #010871582), α-TCP (ICDD PDF #010700364), MgO (ICDD PDF #010870651) and CaO (ICDD PDF #000481467) phases.

The relative intensity of the main peaks of each phase (denoted, hereafter, as relative intensity) were determined using semi-quantitative XRD [8,42–46] by comparing the peaks of apatite (211), β-TCP (0210), α-TCP (034), MgO (200) and CaO (200) from the XRD patterns (Figures 6 and 7). The XRD pattern of the X3 sample at 370 °C showed a XRD pattern of an amorphous compound, while at 470 °C, a crystalline XRD pattern appeared. In addition, in the FTIR spectra of this sample, at 200 and 370 °C, characteristic peaks of amorphous calcium phosphate were observed [28,47–49]. With the increase in temperature and completion of the crystallization process, the phosphate bands at 600–500 and 1030–1080 cm$^{-1}$ split into doublet peaks. Moreover, the apatite characteristic peak at 3566 cm$^{-1}$ appeared at the FTIR spectra of this sample, only after 470 °C. The OH$^−$ characteristic bands in the amorphous calcium phosphate do not appear [49]. So, comparison of XRD patterns related to the samples heat treated at 370 and 470 °C, as well as the presence of exothermic peaks between 370 and 470 °C in the DTA plots and the appearance of characteristic crystalline hydroxyapatite bands in the FTIR (Figure 3), revealed that the crystallization of the apatite phase occurred through this temperature period. The DTA plots indicated that substitution of magnesium could accelerate the crystallization process of the apatite phase.

In the case of the X3 sample, from 470 to 510 °C, the relative intensity of Mg-HA and β-TCP phases decreased, and the MgO phase was formed. With the increase in temperature up to 534 °C, the relative intensity of Mg-HA decreased and the relative intensity of β-TCP increased. So, this region in the DTA curve can be due to the decomposition of the Mg-HA to β-TCP phase. However, when the powder was
of the MgO phase increased. It can be concluded that in this region, magnesium ions formed the stable MgO phase, likely through the decomposition of phosphate groups. The degree of crystallinity, corresponding to the apatite phase of the X3 and
Based on previous results, HA can be decomposed into \( \beta \)-TCP at and above 800 °C [50]. As reported elsewhere [23], HA to \( \beta \)-TCP dissociation, can occur at lower temperatures, taking into account the nonstoichiometric nature of HA or the presence of secondary phases, like hydrogen phosphate. In addition, it is found that when magnesium is substituted, the Calcium-Deficient Hydroxyapatite (CDHA) to \( \beta \)-TCP transition temperature shifted from 700–800 to 600–700 °C [7]. The destabilizing effect of magnesium is ascribed to the smaller ionic radius of Mg\(^{2+}\) (0.65 Å), in comparison with that of Ca\(^{2+}\) (0.99 Å). Substitution of the smaller ion gives rise to lattice strain, which favors the HA→\( \beta \)-TCP transition [17].

In a good agreement with literature, a decreased decomposition temperature was detected in the X3 and X0 samples. In the case of pure HA (the X0 sample), this decrease in temperature could be attributed to nonstoichiometric hydroxyapatite, as the FTIR spectra of this sample confirmed the presence of CO\(^{3-}\)\_ and HPO\(^4-\)\_ groups (Figure 3). However, in the X3 sample, Mg-HA and \( \beta \)-TCP were formed simultaneously at 470 °C (Figures 4 and 6) and the relative intensity of \( \beta \)-TCP increased with temperature. It is known that the crystallization of different calcium phosphates, like HA and \( \beta \)-TCP, depends on the Ca/P ratio, temperature and presence of water and impurities [26]. At 700 °C, the CDHA powders with 1.50 \( \leq \) Ca/P \( \leq \) 1.667 dissociated into a mixture of HA and \( \beta \)-TCP according to [53]:

\[
\text{Ca}_{10-x} \text{(HPO\(_4\))}_x \text{(PO\(_4\))}_6-x \text{(OH)}_{2-x} \rightarrow (1-x) \text{Ca}_{10} \text{(PO\(_4\))}_6 \text{(OH)}_2 + 3x\beta\text{-Ca}_3 \text{(PO\(_4\))}_2 + x\text{H}_2\text{O}.
\] (1)

Although the (Ca + Mg)/P ratio of all synthesized powders was equal to 1.67, it is quite reasonable to say that both the presence of magnesium and a Ca/P ratio lower than 1.5 caused the formation of the biphasic mixture, even at 470 °C. In the case of the X3 sample, the Ca/P ratio was equal to 1.16. Another possible reason for the decreased transition temperature is the nano-scale structure of the synthesized powders. As reported in the literature, the equilibrium phase diagram of nanoparticles differs from that of the corresponding bulk [54], which is a result of their size and shape [55] (for example, lower melting temperature for smaller particles [54]).

In the X0 sample, pure HA was the principle phase up to 600 °C. At 600 °C, the \( \beta \)-TCP was formed and the relative intensity of this phase increased with temperature. In the case of the X3 sample, the maximum intensity of the main peaks corresponding to \( \beta \)-TCP also increased (at above 600 °C). Furthermore, the XRD pattern of the X3 sample, besides the decomposition of Mg-HA, showed the formation of a new type of \( \beta \)-TCP (\( \text{Ca}_3\text{Mg}_x\text{(PO}_4\right)_x\_\text{ICDD PDF # 000110234} \_\), which is labeled as \( \beta \)-TCP(2) –. This phase was stable up to 1150 °C. Hence, the weak exothermic peaks at about 650–750 °C in DTA curves could be attributed to the formation of tricalcium phosphate phases [4,18,29]. Suchanek et al. [12] have reported that slightly below 700 °C, HA and \( \beta \)-TCP have crystallized from the amorphous calcium phosphate.

The FTIR spectra of the X3 sample (Figure 3) is also a supporting evidence for this result. The presence of hydrogen phosphate groups (HPO\(^4-\)) was observed from the peak at 870 cm\(^{-1}\) in all spectra up to 600 °C. However, the intensity of this peak was very low at 800 °C, and it was not apparent above 800 °C. Meanwhile, the other characteristic peaks of CDHA [56], pyrophosphate groups (P\(_2\)O\(_{6-}\))\_1, were observed in the region around 740 cm\(^{-1}\) up to 800 °C, while they were not
detected for the spectra of higher temperatures. This result is in agreement with the condensation mechanism proposed by Mortier et al. [57]:

\[
\begin{align*}
\text{Ca}_{10-2z}^\infty (\text{PO}_4)^{3-z} \cdot \text{(OH)}_2 \rightarrow \text{Ca}_{10-z}^\infty (\text{P}_2\text{O}_7)\cdot (\text{PO}_4)^{3-z} \cdot (\text{OH})_2 + 2\text{H}_2\text{O}, \\
\text{Ca}_{10-z}^\infty (\text{P}_2\text{O}_7)\cdot (\text{PO}_4)^{3-z} \cdot (\text{OH})_2 + 2\text{H}_2\text{O} \\
\rightarrow (1 - z)\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 3z\text{Ca}_3(\text{PO}_4)_2 + 2\text{H}_2\text{O}.
\end{align*}
\]

On the other hand, the band at 870–3 cm\(^{-1}\) is also ascribed to \(v_2\) stretching vibrations of the carbonate groups [40, 35]. It is generally difficult to distinguish between HPO\(_4^2\) and CO\(_3^2\) groups, due to the overlapping of the characteristic peaks around 870 cm\(^{-1}\) [48]. If the existence of this peak is attributed to the presence of carbonate groups, the peak in the temperature range of 600–900 °C in the DTA curve could be attributed to the removal of carbonate and resumption of the formation process of tricalcium phosphate groups [12]. This carbonate can be originated due to the intake of CO\(_2\) from the air or due to the presence of alkyl groups [28]. The intensities of characteristic carbonate bands in the FTIR spectra of the X3 sample (Figure 3) decreased at higher calcination temperatures, because they were released as volatile gases [34].

Transformation of apatite to tricalcium phases continued up to 1200 °C. Figure 8 compares the XRD patterns of the X3 and X0 samples heat-treated at 1200 °C, in detail. As deduced from this figure, the X0 sample at 1200 °C was composed of \(\alpha\)-TCP (60%) and pure HA (35%), and no peak related to \(\beta\)-TCP was detected, while the \(\beta\)-TCP to \(\alpha\)-TCP allotropic transformation was not observed in the X3 sample. As reported, the \(\beta\)-TCP, \(\alpha\)-TCP and \(\alpha'\)-TCP are the stable phases of pure HA up to 1125, 1125–1430 °C and above 1430 °C, respectively [53, 58]. Therefore, based on the results obtained from Figure 8, the \(\beta\)-TCP to \(\alpha\)-TCP transformation temperature increased with the presence of magnesium ions. The phase equilibrium diagram of the system, Mg\(_3\)(PO\(_4\))\(_2\)–Ca\(_3\)(PO\(_4\))\(_2\) [59], is another supporting evidence for this result. According to this diagram, as the magnesium content of the X3 sample was equal to 3 mol\%, the \(\beta\)-TCP to \(\alpha\)-TCP transformation occurred above 1280 °C, and this temperature rose with the magnesium content. In the DTA curve of the X0 sample, the endothermic peak related to the allotropic retransformation from \(\beta\) to \(\alpha\)-TCP was not detected. It might be due to the low weight of the sample used for DTA analysis.

Cacciotti et al. [8] reported the \(\beta\)-TCP → \(\alpha\)-TCP and \(\alpha\)-TCP → \(\alpha'\)-TCP allotropic transformation temperature for Mg-HA samples around 1380 and 1470 °C, respectively. In contrast, Kannan et al. [29] suggested that the two sharp endothermic peaks in DTA curve of the magnesium containing powders around 1350 and 1460 °C are due to the occurrence of partial dehydroxylation of HA and \(\beta\)-TCP → \(\alpha\)-TCP transformation, respectively. The amount of magnesium in both these studies was less than 1.5 mol%.

According to Wang et al. [60], the dehydroxylation of synthesized hydroxyapatite powder includes four successive conversion stages,

1. OH\(^{-}\) anion diffusion through HA,
2. OH\(^{-}\) anion debonding from hydroxyapatite lattice,
3. The lattice constitution of oxyapatite,
4. 2OH\(^{-}\) → H\(_2\)O\(+\) + O\(^2\) \(^{-}\) at the reaction interface.

The decomposition of HA includes two stages,

1. Dehydroxylation producing oxyapatite [O\(_A\), Ca\(_{10}(\text{PO}_4)_6\)] after the appearance of hydroxyoxyapatite [O\(_{HA}\), Ca\(_{10}(\text{PO}_4)_6(\text{OH})_2\)_2] as a transition product,
2. The following decomposition of OHA (and remained HA) resulting in calcium phosphates [60].

In accordance with the results shown in Figures 1, 3 and 6, it is possible to assume that the weak endothermic peak in the DTA curve of the X3 sample around 1124 °C is attributed to the dehydroxylation of apatite [29, 34, 57, 60].

3.2. Microstructure analysis

The morphology of powders at high magnification is provided in Figure 9. All powders exhibited tiny agglomerations of nanosphere particles. The particle size was studied via Manual Microstructure Distance Measurement software. The presence of particles with spherical grains in the range of 40–150 nm was observed in all samples. Figure 9 also illustrates the MAP of calcium and magnesium component for the X3 sample calcined at 600 °C. From these images, it can be concluded that magnesium has homogenously been dispersed in the structure of the sample, thus regions full of magnesium and without calcium were not found.

The TEM images of this sample showed the particles formed by several nanocrystallites (Figure 10). As observed, particles are well separated, and hexagonal apatite particles are visible. The average size of these particles was determined to be in the range of 40–100 nm.

4. Conclusion

Pure and Mg-doped calcium phosphate compounds were synthesized via the sol gel method. The thermal behavior of synthesized powders was closely studied with the help of FTIR and XRD data. Based on the results of this research, Mg-HA and \(\beta\)-TCP were the two main phases in Mg-doped sample. In the magnesium containing sample, the MgO phase was produced during heat treatment, which was stable up to 1200 °C, while in the case of pure hydroxyapatite, production of CaO was observed. It was also determined that the presence of magnesium shifted the \(\beta\)-TCP to \(\alpha\)-TCP transformation temperature to higher temperatures. Reduced decomposition temperature of apatite to \(\beta\)-TCP was also observed. Admittedly, the desired properties of synthesized samples make them suitable for use as biomaterials.
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References


