Synthesis and characterization of magnesium substituted biphasic mixtures of controlled hydroxyapatite/β-tricalcium phosphate ratios

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Abstract

The present paper investigates the preparation of magnesium (Mg) substituted biphasic mixtures of different hydroxyapatite (HAP)/β-tricalcium phosphate (β-TCP) ratios through aqueous precipitation method. The concentrations of added magnesium (Mg) were varied with the calcium in order to obtain constant (Ca + Mg)/P ratios of 1.67 ranging from $1.62 + 0.05$, $1.58 + 0.09$ and $1.54 + 0.13$, respectively. The as prepared powders were calcined at different temperatures to study the phase behaviour and thermal stability. The powders were characterized by the following analytical techniques: TG–DTA, X-ray diffraction and FT-IR. The results have shown that substitution of Mg in the calcium-deficient apatites resulted in the formation of biphasic mixtures of different HAP/β-TCP ratios after heating above 700 °C. The ratios of the formation of phase mixtures were dependent on the calcium deficiency in the apatites with the higher deficiency having the strongest impact on the increased formation of β-TCP and the substituted Mg was found to stabilize the β-TCP phase.
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Keywords: Magnesium; HAP; β-TCP; Calcium-deficient apatite; Biphasic mixtures

1. Introduction

Biphasic ceramics (a mixture of hydroxyapatite (HAP) and β-tricalcium phosphate (β-TCP)) have been considered as potential substitutes for bone replacement surgical operations for the past two decades owing to its favourable features like: (a) difference in dissolution properties (HAP, non-resorbable and β-TCP, resorbable); (b) rapid bone formation around the implant site and (c) its close matches with the inorganic component of living bone [1–3]. Recently, the addition of magnesium (Mg) to the apatite phase has attracted the researchers due to its significant impact on the mineralization process and also its influence in the HAP crystal formation and growth [4,5]. Additionally, the deficiency of Mg in bone has suggested as a possible risk factor for osteoporosis in humans [6]. Since then, the development of Mg sub-stituted apatites has been the subject of interest among the material scientists. Some research results have been dealt with the synthesis of Mg substituted apatites by different preparation methods [7–9]. It was also shown that Mg found to stabilize the β-TCP phase while calcination at higher temperatures [10]. However, so far no clear emphasis has been made quantitatively on the formation of biphasic mixtures with substituted Mg in the structure. The advantage of controlled formation of phase mixtures could be an essential factor, which will serve as choices for clinical trials.

Generally, calcium-deficient apatites [d-HAP, $Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$; $0 \leqslant x \leqslant 1$] possessing the Ca/P ratio varying between 1.67 and 1.5 lead to the formation of biphasic mixtures of HAP and β-TCP (Eq. (1)) when calcined above the temperature of 700 °C [11,12]:

$$Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$$
$$\rightarrow (1-x)Ca_{10}(PO_4)_6(OH)_2 + 3xCa_3(PO_4)_2 + xH_2O.$$
$$(1)$$
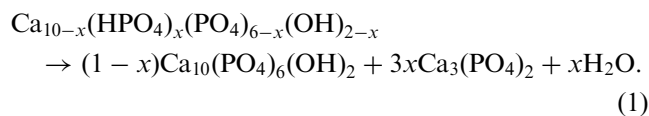
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It was found that the proportions of HAP/β-TCP formed during heat treatment reflected the original Ca/P ratio of the precursors. In the present study, substitution of Mg was carried out on three different types of d-HAP of varying Ca/P ratios through a wet chemical method of preparation. The phase changes on the formation of phase mixtures upon heat-treating magnesium substituted calcium-deficient apatites were studied systematically.

2. Experimental

2.1. Preparation method

Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$), diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) and magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$) were used as starting chemicals precursors for calcium, phosphorous and magnesium. For the preparation of magnesium substitution in the calcium-deficient apatite (d-HAP), an appropriate amount of $Ca(NO_3)_2 \cdot 4H_2O$ was dissolved in water by vigorously stirring at a rate of 1000 rpm. $(NH_4)_2HPO_4$ solution was slowly added to the $Ca(NO_3)_2 \cdot 4H_2O$ solution to achieve predetermined Ca/P molar ratios of 1.62, 1.58 and 1.54. Different amounts of $Mg(NO_3)_2 \cdot 4H_2O$ solution were added individually to attain the $(Ca + Mg)/P$ molar ratios of $1.62 + 0.05$ (coded as Mhap-1), $1.58 + 0.09$ (coded as Mhap-2) and $1.54 + 0.13$ (coded as Mhap-3), respectively. The pH of the mixed solution was maintained at 8–9 by the addition of 8 M ammonium hydroxide (NH_4OH) solution. After the completion of addition, the reaction was performed at 60 °C for 2 h under a constant stirring condition of 1000 rpm. The precipitated suspension was discharged from the reactor and allowed to settle down for 24 h for the maturation of precipitate. After 24 h, the 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. Sample characterization

The as dried powders were subjected to thermal analysis using a heating rate of 10 °C min^{-1} between 30 and 1500 °C in air atmosphere (Labsys Setaram TG–DTA/DSC, France) to analyse the thermal behaviour during heating. The prepared powders were calcined at different temperatures varying from 700 to 1400 °C to study the phase changes. Lattice parameters (a and c) and phases present in the powders calcined at different temperatures were determined with X-ray diffraction (XRD) (using a high-resolution Rigaku Geigerflex D/Mac, C Series diffractometer). Copper Kα radiation ($\lambda = 1.5406$ nm) produced at 30 kV and

25 mA scanned the diffraction angles (2θ) between 20° and 60° with a step size of 0.02° 2θ per second. The volume V of the hexagonal unit cell was determined for each Hap formulation from the relation $V = 2.589a^2c$. Quantitative determinations of the phase compositions of biphasic mixtures were made using X'Pert High Score 1.0f, PANalytical B.V using International Center for Diffraction Data (2004) database. 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), namely the following card numbers: # 09-0432 for HAP [13], # 09-0169 for whitlockite [14] and # 70-0682 for $Ca_{2.81}Mg_{0.19}(PO_4)_2$ [15]. Densities of the powders were determined by helium gas multi-pycnometry with an Accupyc Quantachrome apparatus (Florida, USA). Infrared spectra of the as prepared powders and powders calcined at different temperatures were obtained using an infrared Fourier Spectrometer (FT-IR, model Mattson Galaxy S-7000, USA). For this purpose each powder was mixed with KBr in the proportion of 1/150 (by weight) for 15 min and pressed into a pellet using a hand press. Elemental analyses for the presence of Ca, Mg and P were made using X-ray fluorescence spectroscopy (Philips PW2400 X-ray Fluorescence Spectrometer). The concentration of the same elements in the solutions above the precipitates was also analysed by atomic absorption spectroscopy (AAS–GBC Scientific Equipment, Avanta).

3. Results and discussion

3.1. Synthesized powders

The XRD patterns for the as synthesized powders are presented in Fig. 1. All the powders have indicated the formation of HAP phase except for the difference in peak width and absolute intensity of the diffraction patterns. The increase in the concentration of Mg with the simultaneous increase in calcium deficiency is characterized by the broad diffraction patterns indicative of poor crystallinity of the as prepared powders. It seems that the substitution of Mg did not appear to affect the diffraction pattern of the apatite phase of the as prepared powders. In fact, this results tend to agree with those reported in some previous works showing that XRD analysis of an as-precipitated apatite powder can result in diffraction patterns resembling that of Hap even though the Ca/P ratio is greater or less than the stoichiometric molar ratio of 1.67 [16]. Similar observations were made also for the apatites with elements substituted in trace levels [17]. FT-IR spectra for the as dried powders presented in Fig. 2 have indicated the vibrational modes of PO_4 groups at 475, 574, 609, 966

and 1020–1120 cm^{-1} and OH groups (630 and 3570 cm^{-1}) of apatite phase for all the powders. FT-IR patterns also tend to coincide with the results from XRD by the way that the intensity of peak resolution of OH and PO$_4$ bands are viewed with less intensity with the increase in Mg concentration. The presence of adsorbed water could also be detected from FT-IR spectra in the region around 3300–3600 cm^{-1}. Other information from the FT-IR spectra of the powders is the presence of carbonates (CO$_3$) groups at 1660 cm^{-1}, which are due to the adsorption of species remaining from the aqueous precipitation [18]. The presence of nitrates (NO$_3$) in the as dried powders is clearly witnessed in the FT-IR patterns in the region around 1320–1480 cm^{-1}. The presence of nitrates and the band at 875 cm^{-1} resulting from the residual species (NO$_3^-$, NH$_4^+$) in the as synthesized powders tend to agree with the previous study [19]. Hence, a more precise and complete characterization of the precipitated powders requires thermal treatments.
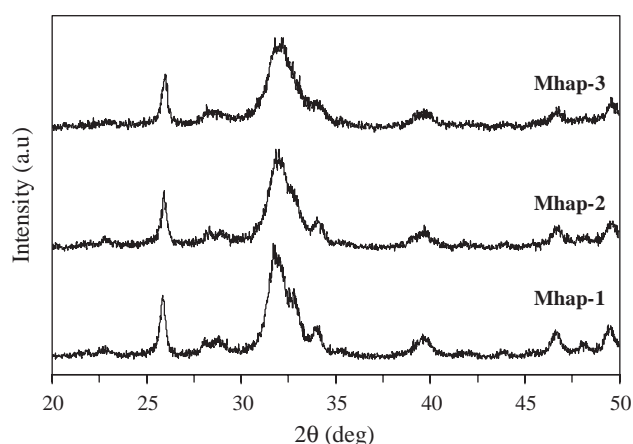

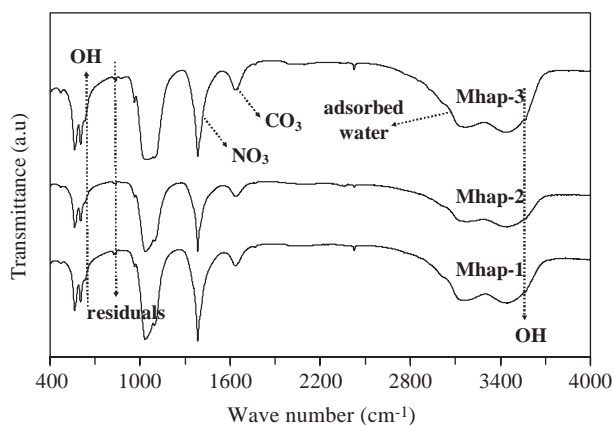Fig. 1. XRD patterns for as prepared Mg substituted apatitic powders.

Fig. 2. FT-IR spectra for as prepared Mg substituted apatitic powders heat treated at 1400 °C.

3.2. Calcined powders

The TG and DTA plots illustrated in Figs. 3 and 4 report the weight loss and the thermal effects along the investigated temperature range for the precipitated powders with different concentrations of added Mg. The mass loss during heating could be classified into three different stages. The first stage occurs within the temperature range between 30 and 250 °C in which all the samples have indicated a similar weight loss of about 5% thus accounting for the removal of physically adsorbed water. Differences in mass loss among the three samples could be witnessed in the second region (250–800 °C) attributed to the structural changes associated with the different incorporation levels of Mg and Ca ions in the biphasic mixtures. FT-IR spectra for the selected sample Mhap-3 calcined at different temperature conditions are presented in Fig. 5. The weight loss observed in this particular region from the thermal analysis accounts for the loss of residual nitrates and carbonates, which are observed by the decrease in intensity of the corresponding peaks on heating. From the FT-IR spectra presented in Fig. 5, the presence of hydrogen phosphate groups (HPO$_4^{2-}$) is apparent at 400 °C from the peak at around 880 cm^{-1}, while at 650 °C the peak observed at 728 cm^{-1} accounts for the pyrophosphate groups (P$_2$O$_7^{4-}$). Although the (Ca + Mg)/P ratio of all the synthesized powders was equal to 1.67, the obtained results are somewhat similar to those reported elsewhere for calcium-deficient apatites [11,12]. It seems that the stoichiometric ratio of pure HAP (Ca/P = 1.67) was not retained in the presence of Mg. The presence of HPO$_4^{2-}$ ions and P$_2$O$_7^{4-}$ ions within the temperature range of 350–720 °C tend to agree with the condensation mechanism proposed by Mortier et al. [20]. The decomposition of pyrophosphates (P$_2$O$_7^{4-}$) to biphasic mixtures is obvious by the observed sharp weight losses of about 1.3–1.8% in the temperature range around 750–800 °C and also from the absence of corresponding peaks for P$_2$O$_7^{4-}$ at
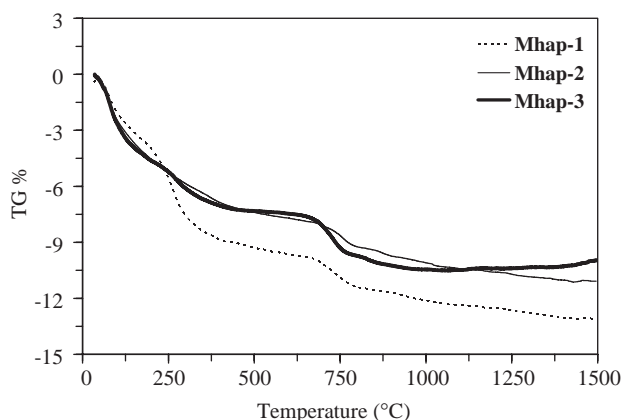

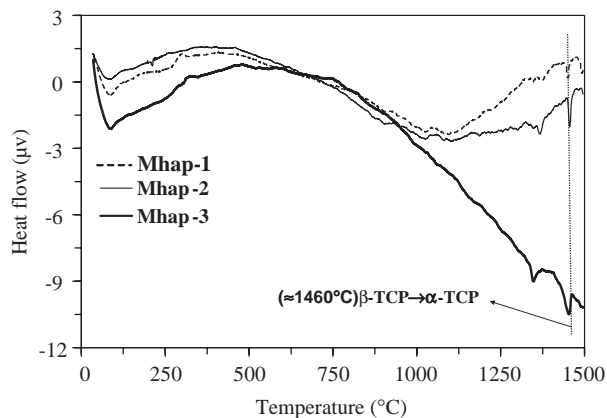Fig. 3. TG plots for the different Mg substituted apatitic powders.

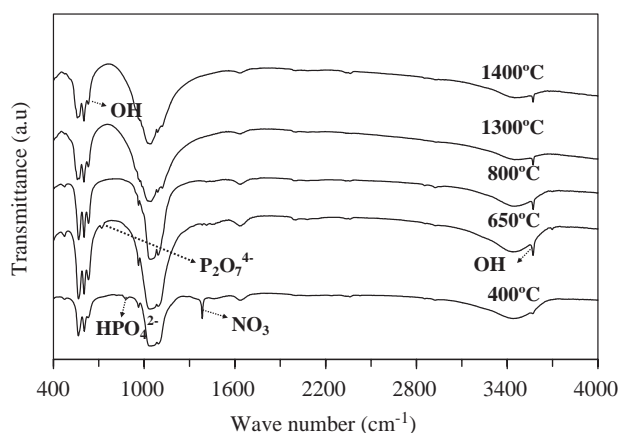Fig. 4. DTA plots for the different Mg substituted apatitic powders.

Fig. 6. XRD patterns for Mg substituted apatitic powders calcined at 700 °C.

Fig. 5. FT-IR spectra for Mhap-3 heat treated at different temperatures.

Fig. 7. XRD patterns for the powder Mhap-1 powder heat treated at different temperatures (unmarked peaks refer to HAP).

800 °C. The weight loss in the third region (800–1500 °C) will be discussed in Section 3.3.

3.3. Formation of biphasic mixtures with substituted Mg

The XRD patterns for all the powders calcined at 700 °C are presented in Fig. 6. Calcination of the powders at this temperature has indicated the improvement in crystallinity by the increase in the resolution of peaks when compared to the as prepared powders. It is well seen from the patterns that only HAP phase is present in all the Mg substituted powders. At 800 °C, all the powders (Figs. 7–9) have indicated the formation of β-TCP phase in addition to that of HAP phase thus confirming the formation of biphasic mixtures. These peaks assigned to the β-TCP phase are viewed by the difference in intensities corresponding to the degree of calcium deficiency of precursors. Thus, an increase in the calcium deficiency is characterized by the increased formation of β-TCP phase. However, the peaks pertaining to this β-TCP have not shown exact matches
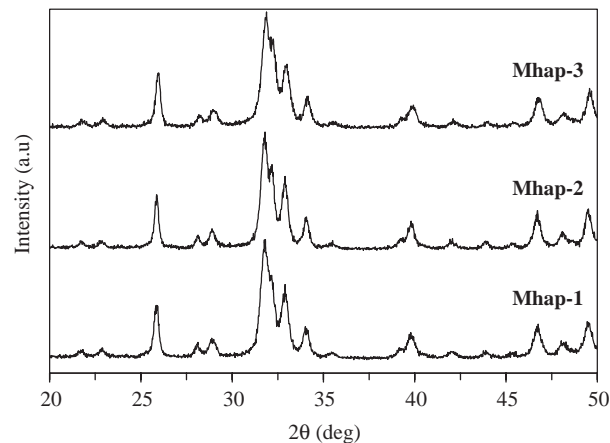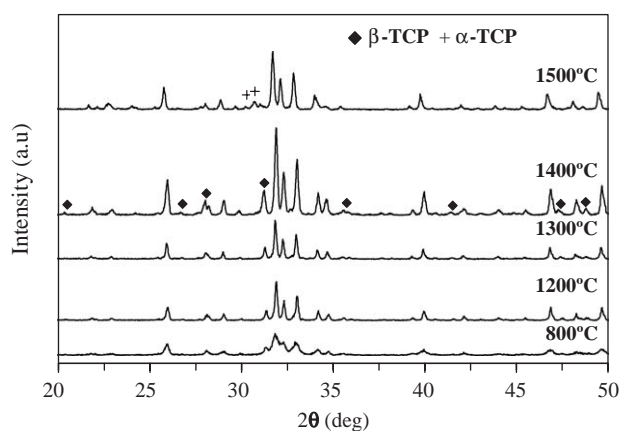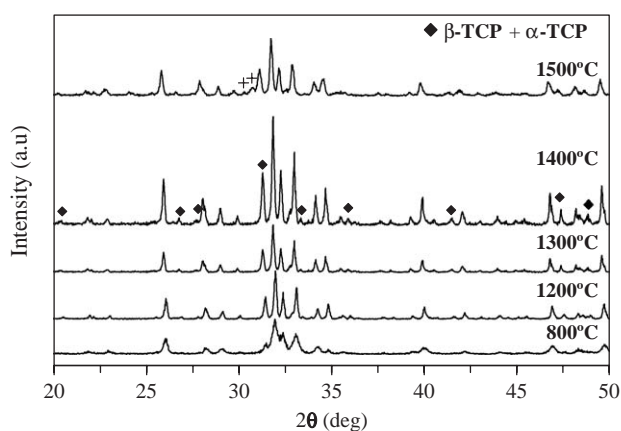

Fig. 8. XRD patterns for the powder Mhap-2 powder heat treated at different temperatures (unmarked peaks refer to HAP).

with those of JCPDS PDF # 09-169, which in fact have indicated considerable shift in the 2θ and d-spacing values of maximum intensity plane (0210), as repre-

sented in Table 1. This observed shift is solely due to the stabilization effect of Mg on β-TCP as explained by the previous works [21,22]. The 2θ and d-spacing values show considerable shift with that of JCPDS PDF # 09-169 but tend to behave closer towards JCPDS PDF # 70-0682 of phase $Ca_{2.81}Mg_{0.19}(PO_4)_2$, thus confirming the stabilization of Mg on β-TCP phase. However, the observed small discrepancies in the values illustrated in Table 1 may be due to the different levels of Mg incorporation into the β-TCP which can be expressed as $(CaMg)_3(PO_4)_2$.

The elemental analysis for the three powders presented in Table 2 also confirms the varied levels of Mg in the powders. In the case of as-precipitated powders, it is
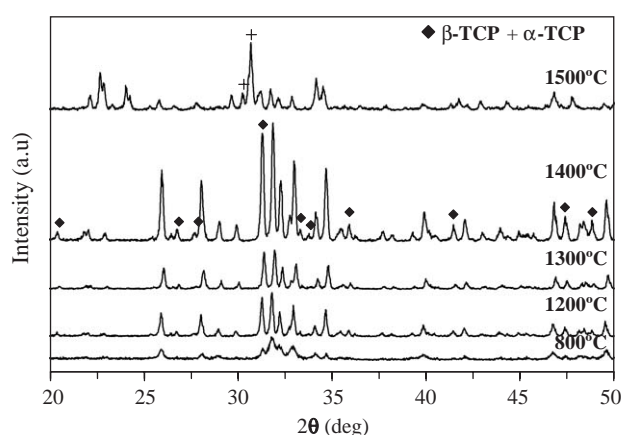

Fig. 9. XRD patterns for the powder Mhap-3 powder heat treated at different temperatures (unmarked peaks refer to HAP).
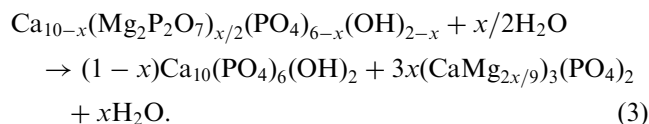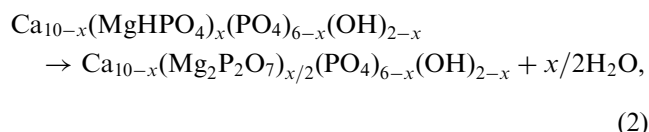
not possible to state whether all retained Mg has been incorporated into the lattice structure or partially adsorbed at the surface of the particles. However, the observed discrepancies in the 2θ and d-spacing values given in Table 1 for the powders heat treated at 1400 °C confirm the incorporation of Mg into the structure of (β-TCP). The difference in weight loss (250–800 °C) with varied Mg substitution witnessed in the TG curves is also a supporting evidence for the stabilization role of Mg and hence it is reasonable to explain the assistance of Mg in the condensation of HPO_4^{2-}. Hence, a qualitative expression of Mortier equation [20] could be used to explain the role of Mg in the formation of $Mg_2P_2O_7$ for temperatures <700 °C (Eq. (2)); and in the formation a mixture of stoichiometric HAP and Mg-stabilized β-TCP $(CaMg)_3(PO_4)_2$ for temperatures >720 °C (Eq. (3)):

$$Ca_{10-x}(MgHPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$$
$$\rightarrow Ca_{10-x}(Mg_2P_2O_7)_{x/2}(PO_4)_{6-x}(OH)_{2-x} + x/2H_2O, \tag{2}$$

$$Ca_{10-x}(Mg_2P_2O_7)_{x/2}(PO_4)_{6-x}(OH)_{2-x} + x/2H_2O$$
$$\rightarrow (1-x)Ca_{10}(PO_4)_6(OH)_2 + 3x(CaMg_{2x/9})_3(PO_4)_2$$
$$+ xH_2O. \tag{3}$$

Quantitative determinations of the HAP/β-TCP phase ratios of the powders Mhap-1, Mhap-2 and Mhap-3 were found to be 82/18, 73/27 and 62/38, respectively. Although the stabilization effect of Mg on β-TCP phase has been explained by previous workers, the present findings on the formation of different proportions of β-TCP with respect to the HAP phase are related with the different degrees of calcium deficiency while the added Mg is found incorporated into the β-TCP phase. Another supporting evidence for the Mg in β-TCP is the maintenance of phase stability even at temperatures as high as 1400 °C. The XRD patterns also have revealed considerable increase in the peak intensity while heating from 1300 to 1400 °C. This is due to the occurrence of partial dehydroxylation of HAP around 1350 °C that are witnessed by the sharp endothermic peak in the DTA curves of all the powders within this particular temperature range that coincide with the results of

Table 1
Comparison of diffraction angle (2θ) and d-spacing values of experimental X-ray patterns with respect to standard JCPDS values

Sample	0 2 1 0 Plane	
	d-Spacing	2θ
JCPDS PDF # 09-0169 (β-TCP)	2.8800	31.026
JCPDS PDF # 70-0682 ($Ca_{2.81}Mg_{0.19}(PO_4)_2$)	2.8549	31.306
Mhap-1	2.8610	31.237
Mhap-2	2.8609	31.239
Mhap-3	2.8554	31.300

Table 2
Elemental concentration (wt%) of three different powders after synthesis and after calcinations at 1400 °C

Sample	After synthesis			After calcinations at 1400 °C		
	Ca	P	Mg	Ca	P	Mg
Mhap-1	38.870	18.600	1.215	38.534	19.571	0.736
Mhap-2	37.900	18.600	2.182	37.643	19.642	1.319
Mhap-3	36.950	18.600	3.150	36.673	19.555	1.905

Table 3
Calculated lattice parameters for the different Mg substituted powders calcined at 1300 and 1400 °C[a]

Sample	Temperature (°C)	a-Axis (Å)	c-Axis (Å)	Unit cell volume (Å^3)
Mhap-1	1300	9.4105	6.8684	1574.75
Mhap-2		9.4153	6.8692	1576.55
Mhap-3		9.4124	6.8324	1567.13
Mhap-1	1400	9.4086	6.8541	1570.84
Mhap-2		9.3965	6.8582	1567.87
Mhap-3		9.4082	6.8588	1571.78

[a]HAP JCPDS PDF # 09-432 [$a = 9.418$, $c = 6.884$ and $V = 1586.3$ Å^3].

previous work [23]. The small and gradual weight losses observed especially for the samples richer in HAP phase (Mhap-1, Mhap-2) for temperatures > 800 °C can also partially support the dehydroxylation of this phase. Accordingly, comparisons of FT-IR patterns obtained at 1300 and 1400 °C have indicated the decrease in intensity of OH groups at 1400 °C. Another possible reason for the gradual weight loss witnessed for the powders over this wide temperature range could be due to the loss of Mg.

The presence of pure HAP phase even after heating at 1400 °C is confirmed for all the powders by the observed fundamental vibrational modes of PO_4 groups in the regions at 960 cm^{-1} (v_1), 605 and 575 cm^{-1} (v_4), 480 cm^{-1} (v_2), 1080 and 1020 cm^{-1} (v_3) and for OH groups at 3570 and 630 cm^{-1}. Heat treating at 1500 °C has indicated the formation of α-TCP phase in all the powders, thus attributing the delay of this allotropic transformation [22] to the influence of Mg. In usual cases, pure β-TCP without any additions on its lattice is not stable beyond 1120 °C and tends to transform into α-polymorph of β-TCP, which is not desirable for biomedical applications [24–26]. The influence of Mg in the phase stability can also be evaluated by the measured density values of Mg substituted biphasic powder mixtures after heat treating at 1400 °C. However, a significant Mg loss of about 40% was witnessed on comparing the concentrations measured in powders before and after calcinations at 1400 °C. It is known that Mg inhibits the crystallization of HAP phase [27,28]. Therefore, the weight changes due to the loss of Mg upon heat treatment at high temperature have seemingly enhanced the crystallinity of HAP, that are clearly evident from the XRD patterns obtained at 1400 °C. On the other hand, the improved thermal stability of the β-TCP phase with substituted Mg resulted in a marginal increase of density of the biphasic powders Mhap-1, Mhap-2 and Mhap-3, which have indicated the values of 2.919, 3.060 and 3.062 g cm^{-3}, respectively.

The calculated lattice parameters for the HAP phase for all the powders heat treated at 1300 and 1400 °C are presented in Table 3. The measured values have indicated presence of hexagonal apatite phase. However, a significant contraction has been observed in all the lattice parameters with respect to that of stoichiometric HAP JCPDS PDF # 09-432, that tends to coincide with some previous research works [29,30].

4. Conclusions

Our goal of synthesizing biphasic ceramic mixtures of varying HAP/β-TCP with substituted Mg through a wet chemical preparation technique has been successfully achieved. The presence of Mg in the β-TCP (CaMg)$_3$ (PO$_4$)$_2$ phase of the biphasic mixtures was evidenced from the marginal shift in the 2θ and d-spacing values. A good correlation between the Mg addition to d-HAP of varying Ca/P ratios and the composition of biphasic HAP/β-TCP mixtures was also observed. Mg substitution enhanced phase stability of β-TCP even at 1400 °C thus exhibiting better densification behaviour with increasing Mg concentrations showing a marginal increase in the density value. The present work demonstrates that biphasic ceramics of different HAP/β-TCP ratios with the substitution of Mg at varying concentrations can be prepared by adjusting the Ca/P ratios of the precursors. However, occupancy and behaviour of Mg in the substituted biphasic mixtures cannot be determined quantitatively from the present results, which need extensive structural investigation. As a conclusion, these biphasic mixtures will be a welcome feature for a material to be applied in biomedical applications.

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