XRD Analysis of Calcined Magnesium Substituted Biphasic Calcium Phosphate (Mg-BCP)

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Abstract. The incorporation of magnesium (Mg) in biphasic calcium phosphate (BCP) was prepared through precipitation method. The concentration of added Mg was varied with respect to calcium (Ca) precursor molarity as such Mg/Ca molar ratio were 0.05 and 0.1, while the (Ca+Mg)/P ratio was maintained at 1.59 throughout the experiment to ensure that calcium deficient apatite was formed. Precipitate obtained was aged for 24 h in ambient condition followed by decantation, centrifugation and drying at 90°C overnight. The as-synthesized powders were calcined at 600°C and characterized by X-ray diffraction (XRD) via Rietveld refinement (X'Pert HighScore Plus software). Both as-synthesized and calcined Mg-BCP powder contains hydroxyapatite (HA) and beta-tricalcium phosphate (β-TCP) phase with Mg in its lattice. The substitution of Mg in calcium-deficient apatite resulted in the formation of biphasic mixtures of β-TCP/HA after calcinations with shifted peaks β-TCP when compared to reference β-TCP peaks. High deficiency of calcium in apatite enables more substitution of magnesium thus stabilizing β-TCP phase when subjected to high temperature.

1. Introduction

For the past few decades, calcium phosphate-based bioceramics are materials of choice for bone tissue engineering applications because of their composition similarity with bone mineral; which are excellent bioactivity and osteoconductivity [1]. One of the most common calcium phosphate used in biological applications is biphasic calcium phosphate (BCP) which contain the hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂, HA) and beta-tricalcium phosphate (Ca₃(PO₄)₂, β-TCP) phases. Mixture of these two phases ensures that BCP would have ideal biodegradability and biocompatibility compared to the applications of HA or β-TCP alone in bone healing process. Lack of magnesium (Mg) in bone may cause patient to suffer from osteoporosis disease [2]. Doping of calcium phosphate with required amount of Mg gives improvement on mechanical and biological properties of BCP. Due to the smaller size of Mg compared to calcium (Ca), it easily enter Ca lattice and controls the crystallization of HA, affecting the stability of apatite [3]. The synthesis of Mg doped calcium apatites can be achieved through different preparation route as such sol-gel, hydrothermal or precipitation method [4–5].

Current trend of studies focusing on the structural analysis of Mg doped BCP have been discussed via X-ray powder diffraction (XRD) in parallel with Rietveld refinement. So, in this study, we focused on the preparation of Mg substituted BCP through precipitation method as well as to investigate the effect of Mg substitution on XRD peaks. The amount of Mg required for BCP doping usually in between 1-3 wt% of total BCP wt%. Only a few papers have reported and studied magnesium doped BCP obtained via this method.
2. Experimental

2.1 Powder Preparation

The sources for calcium (Ca), phosphorus (P) and, magnesium (Mg) precursors are calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O, Merck), diammonium hydrogen phosphate ((NH₄)₂HPO₄, Merck) and magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O, Merck) respectively. Pure biphasic calcium phosphate (pure BCP) and Mg substituted BCP (Mg-BCP) samples were synthesized through precipitation method. To prepare pure BCP powder, an appropriate amount of Ca(NO₃)₂·4H₂O was dissolved in water and stirred at the rate of 1000 rpm. (NH₄)₂HPO₄ solution was slowly added into the mixture through titration process in a fixed molar ratio (Ca+Mg)/P of 1.59. The pH of the mixture was controlled between 10-11 with the addition of 25% ammonia solution (NH₄OH). The precipitated suspension was allowed to age to maturity for 24 h at room conditions. After aging, precipitates were decanted and undergo centrifugation followed by drying at 90°C overnight. The dried cakes were ground to fine powders using agate mortar and calcined at 600°C in air for 2 h with heating rate of 5°C/min.

To prepare Mg-BCP powders, same preparing approach of pure BCP was implemented with the subsequent addition of Mg(NO₃)₂·6H₂O whilst stirring. The Mg/Ca molar ratio was varied between 0.05 and 0.1 (coded M-MgBCP1.59 and H-MgBCP1.59 respectively). (NH₄)₂HPO₄ solution was added into mixture by titration with the same molar ratio of (Ca+Mg)/P as mentioned above. 25% ammonia solution (NH₄OH) was added to control pH at 10-11. Precipitated product was aged for 24 h at room conditions, decanted, centrifugated and dried at 90°C overnight. The dried cakes were ground to fine powders and kept for calcinations. All of the as-synthesized and calcined samples were submitted for characterizations.

2.2 Characterization

The phase formation of the as-synthesized and calcined sample was characterized using X-ray diffraction (XRD) with Rietveld refinement. X-ray diffraction spectra of the Mg doped BCP powders were analysed over 2θ range of 10-70°C, copper Kα radiation (λ=1.5418Å), with a step scan of 2°/min. The accelerating voltage and current were 40kV and 30mA respectively. Crystallographic identification of the synthesized phases was accomplished by comparing the experimental XRD patterns to International Centre for Diffraction Data (ICDD); #98-010-2187 for hydroxyapatite (HA), #98-000-5558 for monetite, and #98-000-0800, beta-tricalcium phosphate (β-TCP).

3. Results and discussion

3.1 As-synthesized powders

The XRD patterns for the as-synthesized powders are presented in Fig. 1 and Fig. 2. Both pure biphasic calcium phosphate (BCP) and magnesium (Mg) substituted BCP powders indicated the presence of HA except for the difference in phases and peak intensities. As can be seen in Fig.1, the phase with highest intensity in pure BCP powder were monetite. This phase normally exists predominantly before HA formation due to its high phase stability under acidic condition compared to HA [7]. This condition being monitored through pH value (pH less than 5). Mg substitution is characterized by the broad diffraction patterns which indicate the formation of calcium deficient HA; which can be observed in Fig. 2. A little amount β-TCP phase can be found in the as-synthesized Mg substituted BCP powders. Various study report that the diffraction pattern usually resembles that of HA although the Ca/P molar ratio was not fixed at 1.67 [8].
3.2 Calcined powders and formation of biphasic phases

Calcinations of the powders at 600°C as shown in Fig. 3 indicated the improvement in crystallinity by the resolution of peaks when compared to the as-synthesized powders in Fig. 2. These peaks assigned to the β-TCP phase are viewed by the difference in intensities which related to the level of calcium.
deficiencies. Higher amount of \( \beta \)-TCP phase formed denotes the higher deficiencies of calcium in powders [9]. Considering the substitution of Mg inside BCP lattice, there is slight shift in 2\( \theta \) and d-spacing in (0 2 1 0) plane of the highest intensity (refer Table 1). The 2\( \theta \) for both Mg doped BCP samples were higher than pure BCP sample with 31.2573\( ^{\circ} \) and 31.2591\( ^{\circ} \) for H-MgBCP and M-MgBCP samples respectively; and 30.6063\( ^{\circ} \) for pure BCP sample. This shift is mainly caused by stabilization effect of Mg when this ion (ionic radius ~0.65 Å) being introduced into Ca ion (ionic radius ~0.99 Å) sites; thus resulted in peak displacement toward higher 2\( \theta \) angles of \( \beta \)-TCP peaks. However, there is no exact match found for the powders peaks with those \( \beta \)-TCP peaks. [5]. As for the d-spacing of these three samples, pure BCP sample happen to have bigger d-spacing with 2.9186Å compared to Mg doped BCP samples with 2.8591Å and 2.8593Å. It suppose that Mg substitute the Ca sites in BCP lattice. While Mg ion have slightly smaller size than Ca ion, the substitution would trigger lattice stresses which later causes an increase in d-spacing of Mg doped samples [10].

\[
\text{Ca}_{10-x}(\text{Mg}_x\text{P}_2\text{O}_7)_x(\text{PO}_4)_{6-x}(\text{OH})_x + x/2\text{H}_2\text{O} \rightarrow (1-x)\text{Ca}_{10}\text{(PO}_4)_{6}(\text{OH})_2 + 3x(\text{CaMg}_{2/3})_3(\text{PO}_4)_2 + x\text{H}_2\text{O} \quad (\text{Eqn. 1})
\]

The above Eqn. 1 explains that the higher substitution of Mg in Ca sites is in parallel with the transition of HA to \( \beta \)-TCP phase. Higher content of Mg causes HA phase to convert into \( \beta \)-TCP phase. These cause high amount of \( \beta \)-TCP produce in heat treated Mg substituted BCP powder when compared to heat treated pure BCP. It is correlated to the high amount of \( \beta \)-TCP formed in Mg substituted powder compared to pure BCP powder as observed in Table 1. Small difference in the values tabulated in Table 1 probably effect of different Mg concentrations substituted into \( \beta \)-TCP phase. Quantitative determinations of the \( \beta \)-TCP/HA phase ratios of calcined pure BCP, M-MgBCP1.59 and H-MgBCP1.59 powders were found to be 90.5/9.5, 99.2/0.8 and 98.7/1.3 respectively in phase compositional percentage obtained via Rietveld refinement.

![Figure 3. XRD patterns of pure BCP and magnesium substituted BCP powders after calcined at 600°C](image-url)
Table 1 Comparison of diffraction angle (2θ) and d-spacing values in XRD patterns of calcined samples

| Sample        | 0 2 1 0 plane | 2θ (°)  | d-spacing (Å) |
|---------------|---------------|---------|---------------|
| Pure BCP      | 30.6063       | 2.9186  |
| M-MgBCP1.59   | 31.2591       | 2.8591  |
| H-MgBCP1.59   | 31.2573       | 2.8593  |

4. Conclusion

Mg substituted BCP with varying Mg content has been successfully synthesized through wet precipitation method. After calcinations at 600°C, most of HA phase has been converted into β-TCP denotes the formation of biphasic mixtures. The addition of Mg in BCP structure causes lattice contraction which can be observed from the larger 2θ of Mg doped BCP samples with 31.2591° and 31.2573° compared to the 2θ of pure BCP sample with 30.6063°. The effect of lattice contraction which causes stresses in lattice was proved from the smaller d-spacing of Mg doped samples with 2.8591Å and 2.8593Å than pure BCP sample with 2.8592Å. The stresses is a result of the substitution of Mg with smaller ionic size into the Ca sites with larger ionic size.

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