

Synthesis of Zinc Doped-Biphasic Calcium Phosphate Nanopowder via Sol-Gel Method

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Abstract. Biphasic calcium phosphate powders doped with zinc (Zn-doped BCP) were synthesized via sol-gel technique. Different concentrations of Zn have been successfully incorporated into biphasic calcium (BCP) phases namely: 1%, 2%, 3%, 5%, 7%, 10% and 15%. The synthesized powders were calcined at temperatures of 700-900°C. The calcined Zn-doped BCP powders were characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), differential and thermogravimetric analysis (TG/DTA) and field-emission scanning electron microscopy (FESEM). X-ray diffraction analysis revealed that the phases present in Zn-doped are hydroxyapatite, β -TCP and parascholzite. Moreover, FTIR analysis of the synthesized powders depicted that the bands of HPO_4 increased meanwhile O-H decreased with an increase in the calcination temperature. Field emission scanning electron microscopy (FESEM) results showed the agglomeration of particles into microscale aggregates with size of the agglomerates tending to increase with an increase in the dopant concentration.

Introduction

Calcium hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, commonly referred to as HA, is a synthetic biomaterial similar to biological HA, which forms the structural component of the human bone and teeth. It has been used widely for various bone and tooth implants due to its excellent biocompatibility and bioactivity. It bonds strongly to the bone and favours osseointegration of bone implant, necessary for minimizing the damages to the surrounding tissues. BCP ceramics, consisting of a mixture of hydroxyapatite and beta-calcium phosphate (β -TCP, $\text{Ca}_3(\text{PO}_4)_2$) are considered to be effective in promoting bone formation at the implant site. The properties of BCP bioceramics can be attributed to the fact that they comprise of a more stable phase of HA and highly soluble TCP [1]. It has been observed that most natural apatites in the bone are non-stoichiometric (Ca-deficient apatite crystals) and consist of a number of substituted elements viz cations (Mg^{2+} , Mn^{2+} , Zn^{2+} , Na^+ , Sr^{2+}) or anions (HPO_4^{2-} or CO_3^{2-}) [2]. Among all these ions, zinc is considered to be the most essential metal ion since its involved in bone formation in vitro and in vivo [3]. Zinc is analogous to most of the transition metals in terms of bioinorganic properties [4]. Zinc is one of the bone growth factor and has a stimulatory effect on bone growth [5]. The essential roles of Zn involve prevention of bone loss, increase in bone density, stimulation of bone metabolism and growth [6]. Synthesis of Zn substituted hydroxyapatite has been carried out by many researchers using several techniques such as chemical co-precipitation and hydrothermal mechanisms. However all these synthesis routes result in the products that are irregular and easy to agglomerate [7]. Moreover it is difficult to incorporate Zn^{2+} into HA structure using these mechanisms [8]. On contrary, Sol-gel method has many advantages over these mechanisms as it involves low temperatures and the products so produced are highly pure [9]. In the present investigation Zn-doped BCP nanopowders have been synthesized via sol-gel method and characterization of the obtained powder has been done by XRD, FTIR, FESEM and TG/DTA.

Experimental Procedures

Several chemicals were used in the synthesis of zinc-doped BCP powders via sol-gel technique [9] such as calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) (System), diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) (Merck), zinc nitrate hexahydrate (Friendemann & schmidt), urea (System), EDTA (titriplex) (Merck) and ammonium solution (NH_4OH) (B&M Chemical). While calcium nitrate tetrahydrate and di-ammonium hydrogen phosphate (reagent grade) were used as calcium and phosphorus precursors respectively, zinc nitrate hexahydrate was used as the dopant source viz zinc. EDTA was used as a chelating agent to prevent the spontaneous precipitation of calcium ions during the gel formation and Urea (analytical grade) was used for gelling and as an ammonium donor. The whole reaction was carried out in the ammonia solution and heated at 60°C . Different mole percentages of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as per the general formula $\text{Ca}_{10-X}\text{Zn}_X(\text{PO}_4)_6(\text{OH})_2$ where $X = 0\%, 1\%, 2\%, 3\%, 5\%, 7\%, 10\%$ and 15% , were used in the process. The resulting black powders were calcined at $700, 800$ and 900°C (Protherm, PLF 160/5) by maintaining a heating rate of $10^\circ\text{C}/\text{min}$. For the evaluation of phases, the calcined Zn-doped BCP powders were characterized using X-ray diffractometer (Shimadzu, XLab XRD 6000), Fourier Transform Infrared Spectrometer (Parkin Elmer, Spectrum 100), Thermogravimetric Analysis Parkin Elmer apparatus (Pyris Diamond TG/DTA) and Field emission scanning electron microscope (JEOL, JSM 6700 F).

Results and Discussion

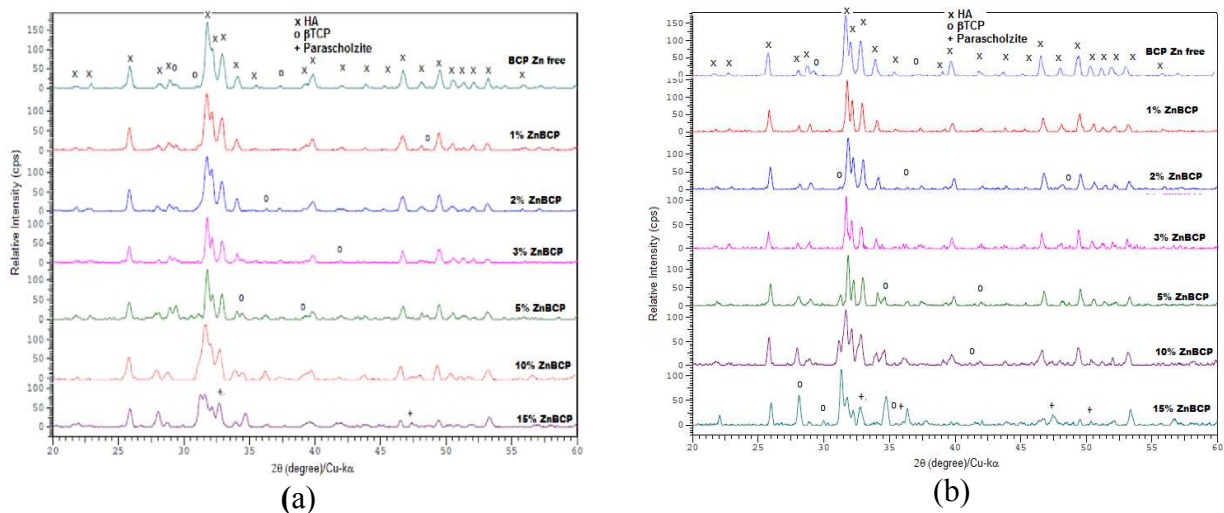


Fig. 1 XRD patterns of various Zn-doped BCP Powder calcined at a) 700°C and b) 800°C

Fig. 1 presents the XRD pattern of various Zn-doped BCP powders calcined at 700°C and 800°C . The figure shows peaks attributed to ICCD standard data of HA (JCPDS 09-432) as the main phase and β -TCP (JCPDS 09-169) as the secondary phase. It is evident from the figure that the intensity of the peaks become more less as the amount of dopant, Zn is increased. The present results are in agreement with previous report by Ren et al [10]. It is indicating that crystallinity decreased due to the Zn content in the solution increased and the ionic radius in Zn^{2+} is smaller than that in Ca^{2+} by 0.074 nm and 0.099 nm respectively. On the other hand, a new phase parascholzite ($\text{CaZn}_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$) (JCPDS 35-0495) starts to appear in 15 mol% rather than 18 mol% as reported by Miyaji et al [7]. By comparing the XRD patterns for different calcination temperatures, it is inferred that with an increase in calcination temperature the intensity of the HA peaks increase and peaks become narrower. It is indicative of an increase in crystallinity with an increase in the calcination temperature [11].

Fig. 2 shows FTIR spectra of 5 mol% Zn-doped BCP calcined at $700, 800,$ and 900°C . The spectra show vibrational characteristic of apatite phase. The characteristic phosphate (mode ν_4) vibrations of HA are spotted at 563 and 600 cm^{-1} and other mode ν_1 , and mode ν_3 of PO_4^{3-} peaks at

961, 1024 and 1085 cm^{-1} respectively. The bands at 3500-3600 cm^{-1} and 630 cm^{-1} could be attributed to the presence of hydroxyl group (OH^-). Furthermore the bands at 1380-1550 cm^{-1} correspond to CO_3^{2-} groups while 1420 and 875 cm^{-1} to HPO_4^{2-} [12]. The band at 1085 cm^{-1} which is attributed to PO_4^{3-} of TCP becomes narrower and sharper as the temperature is increased. It likely indicates the increment of TCP content of the powder. The effect of increased temperature can also be observed on the HPO_4 peak which becomes obscure and is compensated by the hydroxyl (OH^-) peak at 630 cm^{-1} . The stronger vibrational mode of OH^- indicates high crystallinity of the powder [10, 11]. Moreover, the intensity of PO_4^{3-} band also increases with temperature and a decrease in CO_3^{2-} band at 1600 cm^{-1} is observed with the simultaneous increase in OH^- and PO_4^{3-} . It indicates that the formation of the Zn-doped BCP phase involves the substitution of carbonate for hydroxyl (A-type) and phosphate (B-type) groups.

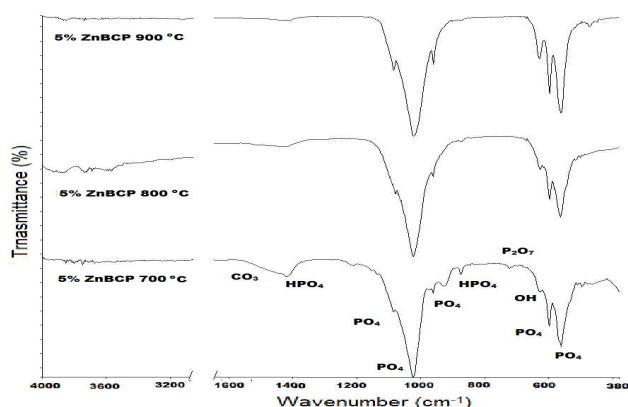


Fig. 2 FTIR spectra of 5 mol% Zn-doped BCP at various calcination temperatures

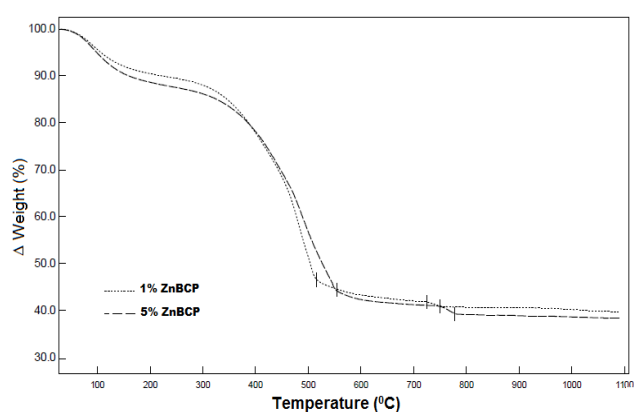


Fig. 3 TGA curve of BCP doped with 1% and 5% Zn

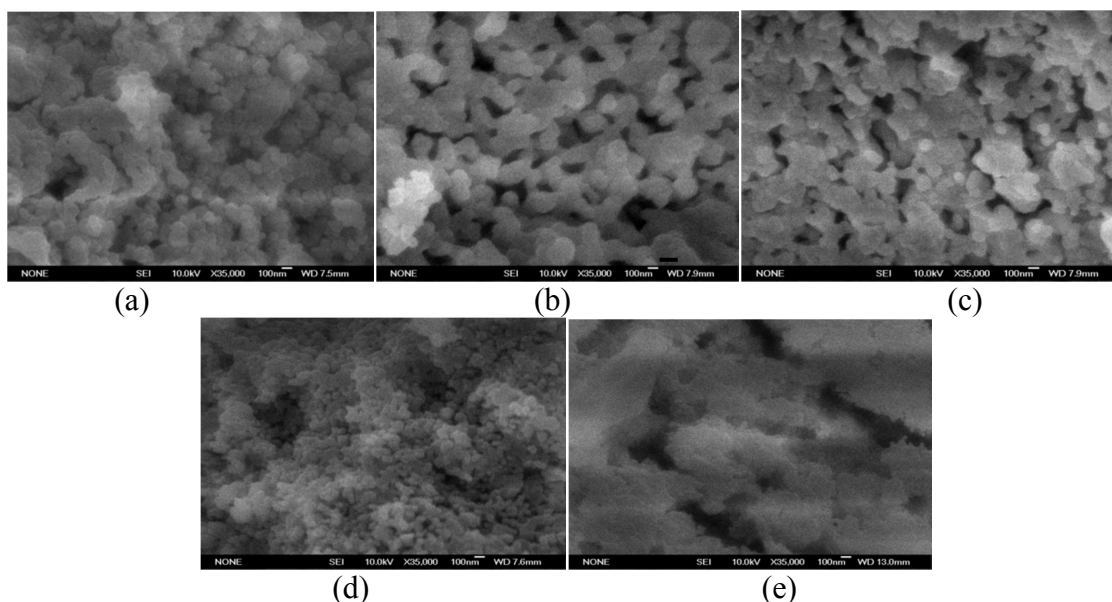


Fig. 4 FESEM micrograph of Zn-doped BCP powders calcined at 900°C: (a) 2 mol% ZnBCP (b) 3 mol% ZnBCP (c) 5 mol% ZnBCP (d) 7 mol% ZnBCP (e) 10 mol% ZnBCP

Fig. 3 shows TGA curve of Zn-doped BCP at 1 mol% and 5 mol%. It can be observed that TCP is formed in the temperature range of 700-800°C [12]. This is verified by steps of weight loss between 700 and 800°C. It is in agreement with FTIR results that the decomposition of HPO_4^{2-} and $\text{P}_2\text{O}_7^{4-}$ into biphasic phase takes place at temperatures beyond 700°C.

Fig. 4 shows the morphology of Zn-doped BCP powders at different Zn molar percent calcined at 900°C. It is shown that the particles of Zn-doped BCP agglomerates are globular in shape. Moreover the powders show the agglomeration of fine particles into microscale aggregates. The size of the agglomerates tends to increase as the amount of dopant increases. The micrograph of 10 mol% ZnBCP showed a flat-like structure which resulted from the fusion of the spherical-particle aggregates. The fusion of the aggregates was being observed to start at 3 mol% ZnBCP, which increased with an increase in the dopant concentration.

Summary

Zn-doped BCP fine powders have been successfully synthesized using sol-gel method. The effect of dopant concentration and calcination temperature on its phase behavior was studied. XRD results confirmed the formation of HA as main phase and β -TCP as the secondary phase in the as calcined Zn-doped BCP powders. The formation of parascholzite occurred at the high dopant concentration 15 mol% ZnBCP. From the FTIR analysis of the calcined powders, it was analyzed that on an increase in the calcination temperatures O-H band appeared whereas HPO_4 peak disappeared implying an increase in the crystallinity. The morphology of the samples showed agglomeration and densification of the powders with an increase in Zn concentration.

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