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EFFECT OF SEVERAL CALCINATION TEMPERATURE ON DIFFERENT CONCENTRATION ZINC SUBSTITUTED CALCIUM PHOSPHATE CERAMICS

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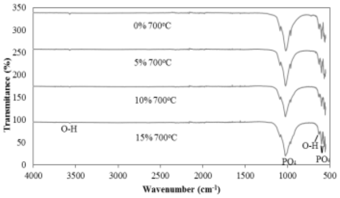
Graphical abstract



Abstract

Zinc substituted calcium phosphate ceramics powders were produced from precipitation method using calcium nitrate, zinc nitrate and ammonium dihydrogen phosphate solutions. Several zinc ions concentrations (5, 10, and 15 mole %) were substituted into calcium phosphate ceramics with the (Ca+Zn)/P initial ratio were set to 1.67. Calcium phosphate powders were then calcined at 600, 700, 800, 900, and 1000°C to observe its effect on the material phase behavior. By increasing the calcination temperature, XRD peaks changed from broad to narrower shape indicating that the powders are highly crystalline. Hydroxyapatite (HA) partly transformed to another phase which is tricalcium phosphate (β-TCP) at 700°C confirming the formation of biphasic calcium phosphate ceramics. FESEM observations clearly exhibit that the particles are in nanosized scale which explains why as zinc concentration increases, the particles tend to be agglomerated.

Keywords: Zinc substitution, calcium phosphate, precipitation, X-ray diffraction, calcination

1.0 INTRODUCTION

Calcium phosphate ceramics have been used as biomaterial in medical application for repair and rebuild damaged parts of the human bones. The most widely used calcium phosphate ceramics are hydroxyapatite (HA) and tricalcium phosphate (β-TCP) [1]. Calcium phosphate ceramics have similar chemical compositions with bones. Therefore, shows excellent properties of biocompatibility. Still, calcium phosphates ceramics degrade differently depending on types of calcium phosphate ceramics. HA has low degradability in human body and need years to be resorbed. On the contrary, β-TCP is more degradable [2]. It is important that the implanted material should not have higher degradation rate than bone ingrowth rate. Biphasic calcium phosphate ceramics (BCP) were developed in order to achieve optimum degradation rate [3]. BCP ceramics are considered to be effective as it consists of more stable HA and soluble β-TCP.

It has been observed that human bones are formed in biological environments and they commonly contain several ionic elements that contribute to specific properties. It is well known that human bone is non-stoichiometric and contains trace element of ionic compound such Mg, Si, Zn, and Na. Among several ionic elements, zinc ions are considered as one of the most important trace metal ions for bone repair and its beneficial effects have been mentioned in several papers [4, 5]. A study by Yamaguchi et al [6] demonstrated that zinc ions have stimulatory effect on bone mineralization and formation in vivo and in vitro studies. Furthermore, zinc plays significant role in bone mass preservation and improves biological properties [7]. Thus, studies about ionic substitution into HA have become the subject of interest of many researchers.

It is important to carry out essential characterizations of substituted calcium phosphates ceramic in order to understand the mechanism of incorporation of substituted elements. The aim of this study is to examine the effect of different calcination temperature on calcium phosphate ceramics and zinc ions incorporation in calcium phosphates ceramics. The substitution of ionic ions in the apatite structure affects the particles morphology, stoichiometry and crystallinity. In this study ZnBCP was prepared via precipitation method and characterization techniques such as XRD, FTIR, FESEM were used to evaluate the chemical composition of the precipitated powders.

2.0 EXPERIMENTAL METHOD

2.1 Calcium Phosphate Samples Preparation

Calcium phosphate ceramics (CaP) were produced by precipitation method. About 0.3M ammonium dihydrogen phosphate $NH_4H_2PO_4$ and 0.5M calcium nitrate tetrahydrate $Ca(NO_3)_2.4H_2O$ were used. The solution was added drop wise. Then, the pH of the mix solution was brought to 10 by adding NH_4OH solution. The mixture was stirred for 3 h at 90˚C. For zinc substitution, the solution was prepared with different concentration zinc nitrate hexahydrate $Zn(NO_3)_2.6H_2O$ solution (0.025M, 0.05M and 0.075M). The obtained precipitates were aged for overnight to allow complete reaction. Then, it was filtered and washed with deionized water. The precipitates were dried in hot air oven for 24 h at 100˚C and then ground to fine powders using pestle and mortar. Finally, the as-synthesized powders were calcined at 600˚C, 700˚C, 800˚C, 900˚C and 1000˚C.

2.2 Samples Characterization

The X-ray diffraction (XRD) measurements of the as-synthesized and calcined samples were carried out using Rigaku Ultima IV diffractometer. The diffraction spectra were recorded in the range between 25˚ to 36˚ using Cu Ka wavelength 1.5406Å. The scan speed was 2 degree/min. The identification of phase crystallographic was done by matching the samples with standard data of HA and β-TCP gathered by the International Centre for Diffraction Data (ICDD). Fourier transform infrared (FTIR) spectra for calcined were recorded using a Fourier transform spectrometer (Perkin Elmer Spectrum 400). The FTIR spectra were recorded from 400-4000 cm^{-1} with 4 cm^{-1} resolution. Furthermore, the morphology studies of the calcined powders were evaluated using field emission scanning electron microscope (FESEM) (HITACHI SU8000). Before the observation, the samples were first coated with gold.

3.0 RESULTS AND DISCUSSION

X-ray diffraction patterns calcium phosphates ceramics after calcination at several temperatures are shown in figure 1. The XRD patterns were found closely matched to the ICDD standard data (9-432) and (9-169), thus confirming the existence of both HA and β-TCP phases in the samples. The results indicate that HA remain as the main phase for synthesis until calcination temperature reached 700˚C. After that, the intensity of HA peaks started to decrease while β-TCP peaks increased. The XRD patterns for all different calcination temperature revealed that β-TCP phase was formed above 700˚C suggesting that the presence of more Zn ions might have inhibited the formation of HA phase. For all zinc concentration, the XRD patterns for zinc substituted calcium phosphate ceramics showed to be identical to the XRD pattern of HA and β-TCP standard data. The most distinct reflection for the HA peak was observed at (211) plane which is located at 31˚ (2θ).

As zinc concentration increased, the powders become less crystalline which is reflected by the broader HA peaks. A study by Devanand et al [8] shows similar observation as zinc concentration affects the XRD patterns of the samples. Although Zn and Ca share the same ionic charge, they have different ionic radius charge, which is 0.074 nm for Zn and 0.099 nm Ca. The size difference between these ions is believed to have distorted the crystal structure of calcium phosphate ceramics contributing to its degrading crystallinity. The disturbances in crystalline size in the samples have affected the thermal stability of the powder. From the XRD analysis HA is thermally stable up to 700°C. After that, the changes in the phase composition in the samples started to appear.

As calcination temperature increased, HA and β-TCP peaks become narrower implicating that the crystallinity increases. Based on XRD result, calcium phosphate ceramics starts to transform into a mixture of HA and TCP phase by thermal treatment above 700˚C. Biphasic calcium phosphate ceramics (BCP) can be produced by this conversion without the need of powder blending.

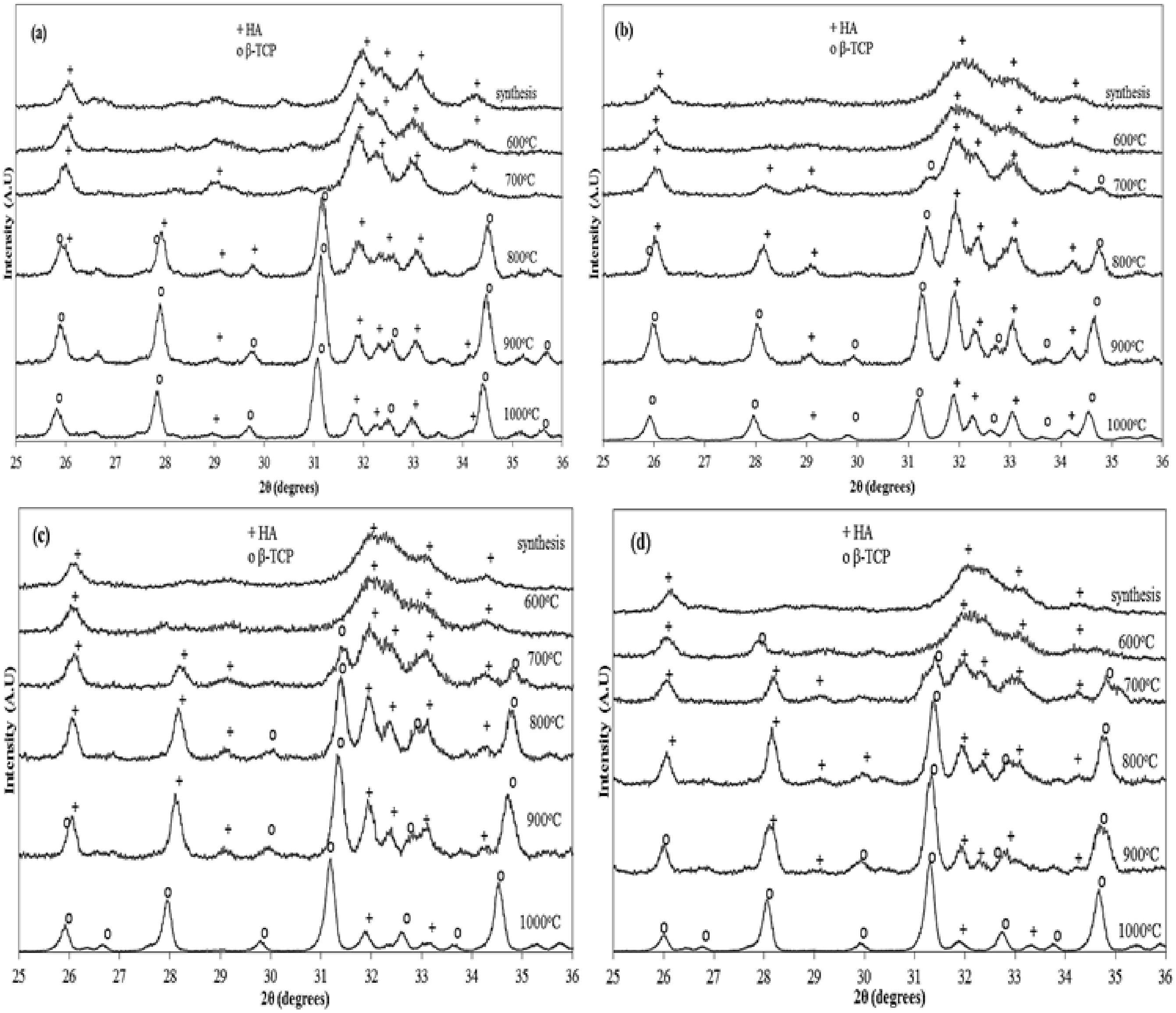


Figure 1 XRD patterns for the calcined samples (a) 0% (b) 5% (c) 10% (d) 15%

Figure 2 shows the FTIR spectra for calcination temperature at 700°C for all samples. The FTIR analysis was done to evaluate possible differences in the chemical composition of the calcium phosphate ceramics with different zinc concentration due to ionic substitution during precipitation and calcination. The characteristic PO_4 vibrations of HA are found at 565 and 600 cm^{-1}. The other modes of phosphate peaks are also found at 960, 1023 and 1090 cm^{-1}. The presence of hydroxyl group, OH is found at 630 cm^{-1} and 3600 cm^{-1} band as a very sharp peak, indicating the presence of characteristic O-H stretching and liberational mode in calcium phosphate ceramics [9]. These O-H bands identify in the samples are due to adsorbed water within the apatite structure. These results are indicating the typical of nanocrystalline HA. The substitution of ions into the HA structure probably disturbs the OH and PO_4 modes. As zinc concentration increased, the PO_4 band at 1090 cm^{-1} become narrower and sharper consistent with XRD results which shows crystallinity changes of HA due to formation of TCP phase [10].

A microstructural study has been performed on samples calcined at 700°C for different zinc mole concentration using field emission scanning electron microscope (FESEM) shown in figure 3. It can be seen that the samples particles are in the nanometer sized particles. The samples particles exhibit uniform globular shape with same morphology appeared.

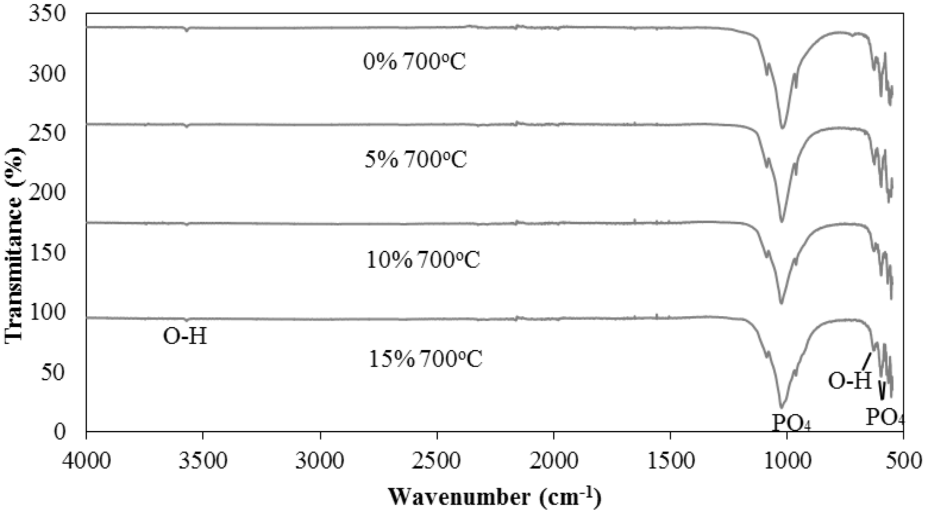


Figure 2 FTIR spectra of calcined samples

The particles sized in the figure 3(a)-(d) have a width of at least 50 nm and size of the individual particles could not be recognized precisely due to tightly agglomerated. Moreover, addition of more zinc ions into calcium phosphate ceramics has causing the particles with the tendency to highly agglomerate and appeared larger. Marchi et al [10] mentioned that the mechanism of agglomeration involves several steps which is nucleation, aggregation, agglomeration and growth. If the calcination temperature is below the temperature of neck formation, several particles agglomerate at comparable size in the nanometer range.

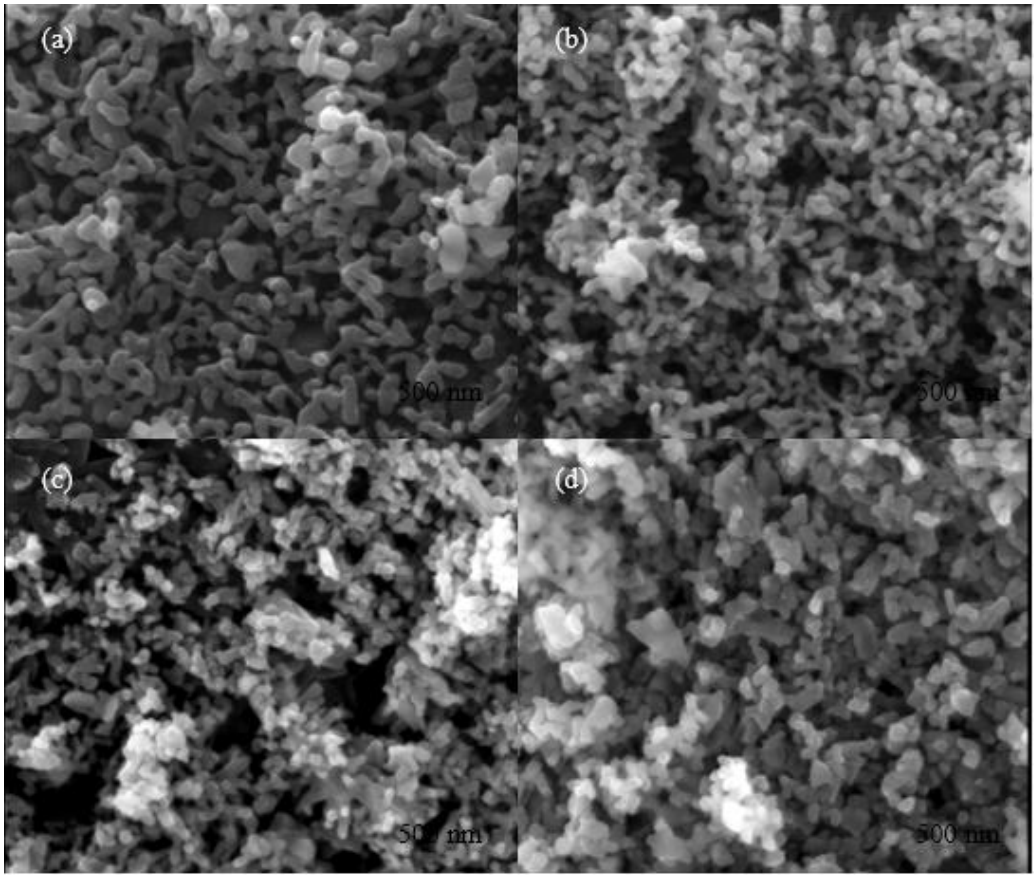


Figure. 3. FESEM of zinc substituted calcium phosphate ceramics calcined at 700ºC (a) 0% Zn (b) 5% Zn (c) 10% Zn and (d) 15% Zn

4.0 CONCLUSION

The effect of different calcination temperature and zinc mole concentration on phase behavior of ZnBCP was investigated. This study clearly showed that increasing zinc concentration at 700°C causing the crystallinity degree of ZnBCP to reduce. XRD patterns depicted that as calcination temperature increase from 600°C to 1000°C, the crystallinity increases significantly. However after 700oC, most of HA phase transformed to β-TCP as a secondary phase. With regard to this phenomenon, it can be deduced that Zn ions have an inhibitory effect on HA by promotion of the TCP formation. On the other hand, the micrograph of the samples showed that the particles are agglomerated and globular in shape with a diameter of about 50 nm for individual particle.

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