

## Synthesis and Characterization of Calcium Phosphate Ceramic

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### Abstract

Calcium phosphate ceramic consists of a mixture of hydroxyapatite (HAP) and beta-tricalcium phosphate ( $\beta$ -TCP) which is widely used for the repair and regeneration of bone tissues. In this study, calcium phosphate ceramic was synthesized by co-precipitation method. The calcium nitrate tetrahydrate  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and diammonium hydrogen phosphate  $(\text{NH}_4)_2\text{HPO}_4$  were used as calcium and phosphorus sources. The pH of the system was maintained up to (pH=11) by the adding of both sodium hydroxide and ammonium hydroxide bases. The synthetic sample was characterized by using X-ray diffractometry (XRD), Fourier transform-infrared spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM). These results show that hydroxyapatite phase was obtained at room temperature. Biphasic calcium phosphate (60% of  $\beta$ -TCP with respect to 40% of HAP) phase was attained at calcination temperature 950 °C. The formation of agglomeration of small particles could be obtained.

**Keywords:** Bioceramic materials, precipitation, XRD, FTIR and SEM.

### Introduction

Back pain, other spinal disorders and hip replacements are caused each year due to sports, road traffic injuries, and increased daily life activities. Recently, synthetic biomaterials have become the important materials for regenerative medicine and tissue engineering. Nowadays, different types of biomaterials were used, such as, natural or synthetic polymers, ceramics, metals, composites and hydrogels [1].

The most common ceramic biomaterials used for tissue regeneration are: (1) calcium phosphate group; including hydroxyapatite (HAP), beta-tricalcium phosphate ( $\beta$ -TCP), biphasic calcium phosphate (mixture of hydroxyapatite and beta-tricalcium phosphate), (2) bioglass, (3) alumina and (4) zirconia oxide [2].

Calcium phosphate is the common name of a family of minerals containing calcium cations ( $\text{Ca}^{2+}$ ) together with orthophosphate ( $\text{PO}_4^{3-}$ ), metaphosphate ( $\text{PO}_3^-$ ), or pyrophosphate ( $\text{P}_2\text{O}_7^{4-}$ ) anions and sometimes hydrogen ( $\text{H}^+$ ) or hydroxide ( $\text{OH}^-$ ) ions. Calcium phosphates with a Ca/P atomic ratio between 1.5 and 1.67 are called hydroxyapatites. According to the amount of different Ca: P molar ratio, the results would show in different types and properties of calcium phosphates. They are widely used in bone tissue engineering for hard tissues such as teeth or bone replacement, augmentation and regeneration [3].

Among various calcium phosphate groups, biphasic calcium phosphate (BCP) based bioceramics consisting of HAP and  $\beta$ -TCP are the most commonly used phases because their excellent bioactivity and composition are similar to bone mineral [4].

In this study, calcium phosphate ceramics were synthesized by co-precipitation method at room temperature and at calcined temperature 950 °C.

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## Materials and Method

### Materials

Calcium nitrate tetrahydrate and diammonium hydrogen phosphate were used as calcium and phosphorus sources. The pH regulation was performed by using inorganic bases; both sodium hydroxide and ammonium hydroxide during processing. Distilled water ( $H_2O$ ) was used as solvent.

### Method

There are various methods of calcium phosphate synthesis such as co-precipitation method, sol-gel approach, hydrothermal technique, multiple emulsion technique, microwave, electrode position technique and so on. Each employs various process parameters. Among them, co-precipitation method is a simple way to synthesize of nanomaterials. In particular, co-precipitation method is used to control particle size and shape, low working temperature, high percentages of pure products and inexpensive equipment requirement (E. Lerner, S. Sarig).

In this research, co-precipitation method has been used to synthetic calcium phosphate sample.

### Preparation of Calcium Phosphate Sample by Using both Sodium Hydroxide and Ammonium Hydroxide

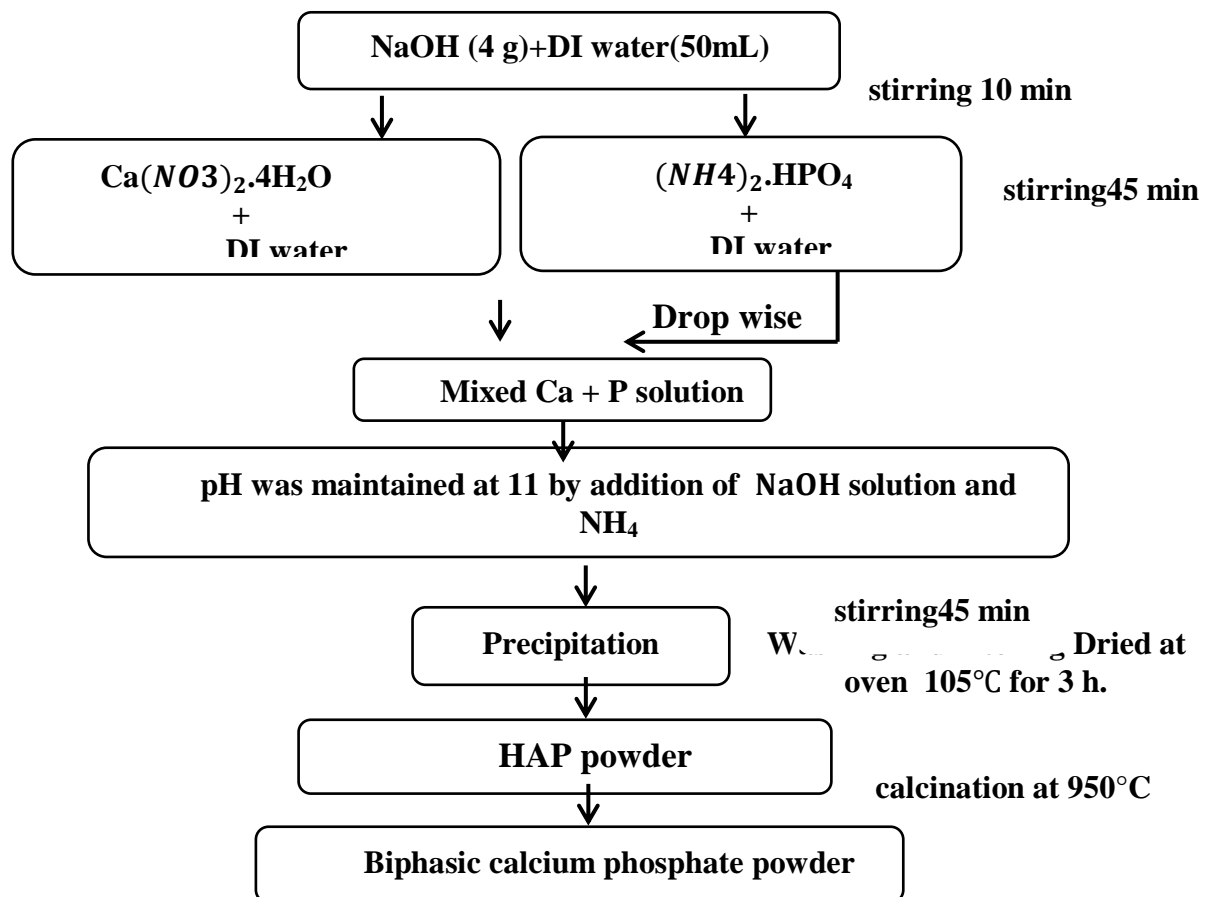


Figure 1. Flow chart of the preparation of calcium phosphate sample

## Results and Discussion

The synthetic samples have been characterized by X-ray diffractometry (XRD), Fourier Transform-Infrared Spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM).

### X-ray Diffractometry (XRD) Analysis

X-ray diffraction has been used to verify the phases, crystallite size, reference intensity ratio value, weight percentage of constituent of the sample powders.

#### Crystallite Size

The crystallite size can be calculated using the Scherer's equation

$$D = \frac{0.9\lambda}{B \cos \theta}$$

where, B = full width at the half maximum (radian)

$\lambda$  is the wavelength (Å),  $\theta$  is diffraction angle

#### Reference Intensity Ratio (RIR) Value and Weight Percentage

Reference Intensity Ratio (RIR) value and weight percentage of constituent of the sample has been calculated by using the following formula.

$$RIR_{HAP} = I_{HA} / (I_{HAP} + I_{\beta-TCP})$$

$$RIR_{\beta-TCP} = I_{\beta-TCP} / (I_{\beta-TCP} + I_{HAP})$$

$$\text{Weight \%} = (RIR \times 100)\%$$

where,  $I_{HAP}$  = maximum intensity of HAP phase

$I_{\beta-TCP}$  = maximum intensity of  $\beta$ -TCP phase

### XRD Analysis of Calcium Phosphate Sample by Using Both Sodium Hydroxide and Ammonium Hydroxide at Room Temperature and Calcined at 950°C

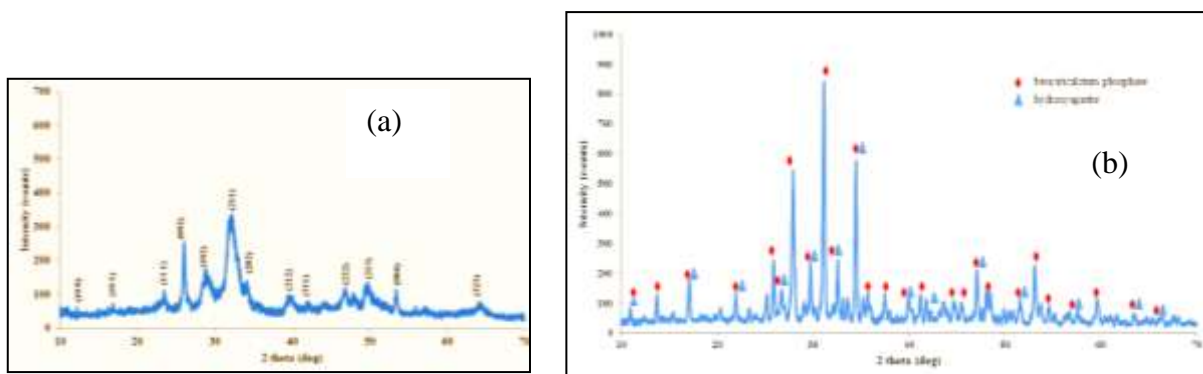


Figure 2. (a) XRD pattern of synthesized hydroxyapatite powder at room temperature and (b) XRD pattern of synthesized biphasic calcium phosphate powder calcined at 950°C

Figure 2(a) shows the XRD pattern of synthesized hydroxyapatite powder by using sodium hydroxide and ammonium hydroxide at room temperature. All the diffraction peaks of synthesized hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) are in agreement with the standard hexagonal structure has been reported in (ICDD-00-009-0432). The strong peaks appeared at angle  $2\theta$  values around  $26.02^\circ$ ,  $28.72^\circ$ ,  $31.96^\circ$ ,  $34.01^\circ$  and  $49.56^\circ$  have been well indexed to the crystal plane of hydroxyapatite (002), (102), (211), (202) and (213).

Figure 2(b) shows the XRD pattern of synthesized biphasic calcium phosphate powder by using sodium hydroxide and ammonium hydroxide calcined at  $950^\circ\text{C}$ . The formation of biphasic hydroxyapatite and beta tricalcium phosphate with hexagonal structure has been reported in (ICDD-00-009-0432).

The crystallite size has been calculated by Scherer's equation, 0.58 nm at room temperature and 4.10 nm at  $950^\circ\text{C}$  have been obtained.

Table 1. Crystallite Size from XRD result

Condition	FWHM	$2\theta$ -value	Crystallite size (nm)
room temperature	1.42	31.96	0.58
$950^\circ\text{C}$ ( $\beta$ -TCP)	0.22	31.14	4.10
$950^\circ\text{C}$ (HAP)	0.17	29.045	4.84

### RIR Value and Weight % of Calcium Phosphate

Table 2. RIR value and weight % of Biphasic Calcium Phosphate

Phase	$2$ (deg)	Plane	Relative Intensity	RIR value	Weight (%)
$\beta$ -TCP	31.50	(0210)	572	0.94	60
HAP	34.46	(202)	366	0.06	40

### FT-IR Analysis of Calcium Phosphate Sample by Using Both Sodium Hydroxide and Ammonium Hydroxide at Room Temperature and Calcined at $950^\circ\text{C}$

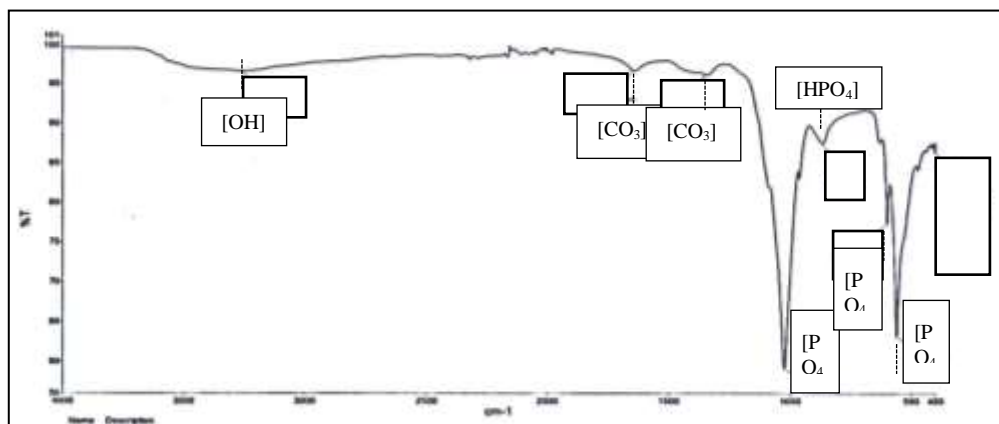


Figure 3. FT-IR spectrum of synthesized hydroxyapatite powder at room temperature

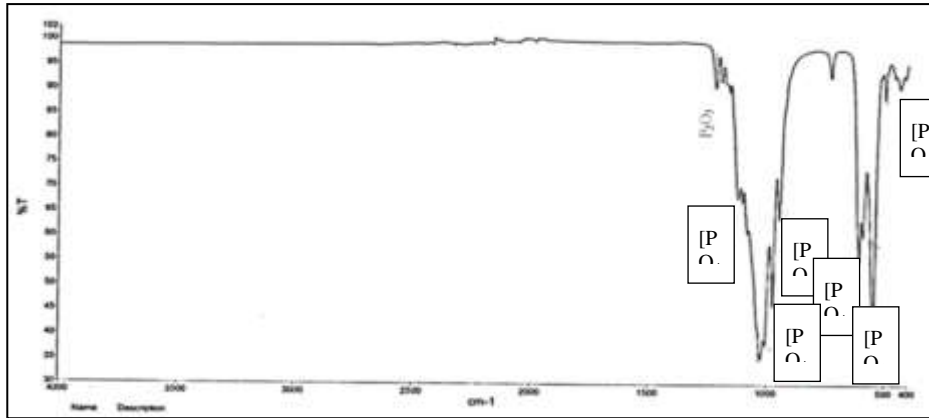


Figure 4. FT-IR spectrum of synthesized biphasic calcium phosphate powder calcined at 950°C

The functional groups generally observed in the FT-IR spectra of calcium phosphate based materials are  $\text{PO}_4^{3-}$ ,  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{P}_2\text{O}_7$  and  $\text{HPO}_4^{2-}$  groups in the range around 4000–400  $\text{cm}^{-1}$ .

Figure 3 shows FT-IR spectrum of synthesized hydroxyapatite powder at room temperature. The characteristic bands of phosphate groups have been appeared around 560–613  $\text{cm}^{-1}$  and 1000–1100  $\text{cm}^{-1}$ . There are sharp and well-separated peaks at 559.70  $\text{cm}^{-1}$ , 600.02  $\text{cm}^{-1}$  and 1023.30  $\text{cm}^{-1}$  have been all attributed to the  $\text{PO}_4^{3-}$  group of hydroxyapatite. The peak 3265.90  $\text{cm}^{-1}$  has been attributed to  $\text{OH}^-$  group and 1346.90  $\text{cm}^{-1}$  has been attributed to  $\text{CO}_3^{2-}$ .

Figure 4 shows FT-IR spectrum of synthesized biphasic calcium phosphate powder calcination at 950°C. The sharp and well-separated peaks at 495.80  $\text{cm}^{-1}$ , 541.65  $\text{cm}^{-1}$ , 1022.97  $\text{cm}^{-1}$ , 1118.03  $\text{cm}^{-1}$  and 1213.80  $\text{cm}^{-1}$  have been all attributed to the  $\text{PO}_4^{3-}$  group of beta tricalcium phosphate. The peak 604.13  $\text{cm}^{-1}$ , 944.50  $\text{cm}^{-1}$  and 971.45  $\text{cm}^{-1}$  have been assigned to  $\text{PO}_4^{3-}$  group of hydroxyapatite. These results are in good agreement with the X-ray diffraction analysis.

### Scanning Electron Microscopy (SEM) Analysis

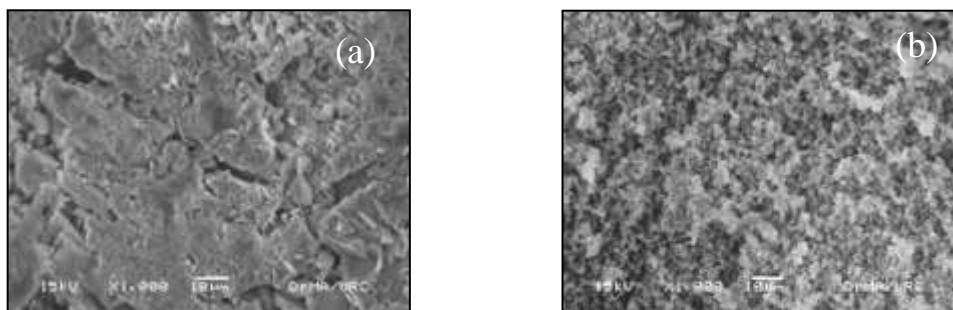


Figure 5. SEM micrographs of calcium phosphate powders

(a) at room temperature (hydroxyapatite) (b) at calcined at 950°C (biphasic)

Figure (5) shows SEM micrographs of the calcium phosphate powders at room temperature and calcined at 950°C. Figure 4(a) shows the hydroxyapatite particles which was highly agglomerated. Figure 5(b) shows the formations of biphasics calcium phosphate particles have been observed.

## Conclusion

The synthesis of calcium phosphate ceramic powders via co-precipitation method has been reported. Inorganic bases; Sodium hydroxide with ammonium hydroxide have been used for the pH regulation. The XRD analysis proved that the hydroxyapatite phase was formed at room temperature. The formation of biphasic (hydroxyapatite & beta-tricalcium phosphate) after calcination has been identified by XRD and FT-IR. The biphasic biomaterials with different phases involving different RIR values could be obtained. Note worthily, Observation on morphology proved that the formation of agglomeration of particles could be obtained in this research.

## Acknowledgements

The authors are grateful to Dr Nu Nu Yi, Pro-Rector and Dr Nay Thwe Kyi, Pro-Rector, Dagon University for their permission to submit this paper. We are also thankful to Physics Department, Dagon University and Taunggyi University for supporting facilities.

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