THERMAL AND MORPHOLOGICAL ANALYSES OF HAP/β-TCP BIPHASIC BIOMATERIALS

Nay Win Tun[1], Aye Aye Thant[2] and Win Kyaw[3]

Abstract

This research has been embarked to prepare hydroxyapatite by co-precipitation method to provide an accurate understanding of the behavior of biphasic biomaterials with HAP and β-TCP. Raw materials of calcium sulphate dihydrate ($CaSO_4.2H_2O$, or Gypsum) and di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) solution have been used as the starting materials to synthesize high purity hydroxyapatite in the first step. The effect of reaction temperature on conversion efficiencies of gypsum to HAP and reaction kinetics has been reported in the previous work. At heat-treatment of 1100℃, HAP has converted partially into beta-tricalcium phosphate (β-TCP, $Ca_3(PO_4)_2$). The phase formations of these samples have been confirmed by using X-ray Diffraction (XRD) technique. Surface morphology and particle size of HAP and HAP/β-TCP samples have been studied by Scanning Electron Microscope (SEM). The effect of the reaction temperature on the morphology of biomaterials has been investigated. The thermal stability studies of the co-precipitated dry powder have been conducted by using Thermo-gravimetric and Differential Thermal analysis (TG/DTA).

Keywords: calcium sulphate, hydroxyapatite, β-TCP, XRD, SEM, TG/DTA,

Introduction

Among all biomaterials, hydroxyapatite: the mineral component of hard tissues in vertebrates is the most biocompatible material. Hydroxyapatite shows excellent biocompatibility not only with hard tissue but also with soft tissue. This material is capable of integrating biologically when directly implanted into a bone defect. Furthermore, it is not toxic and produces no harmful effect on the immune system with excellent osteoconductive behavior. Tricalcium phosphate is also one of the most important biomaterials based on phosphates, currently recognized as ceramic material that significantly simulates the mineralogical structure of bone. Theoretically, the resorbable β-TCP is an ideal implant material.

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The mineral gypsum precipitated in the evaporation of sea water since 100 to 200 million years ago. From a chemical point of view it is calcium sulphate dihydrate ($CaSO_4.2H_2O$) deposited in sedimentary layers on the sea bed. Under high pressure and temperature gypsum turns into anhydrite $CaSO_4$. When gypsum ($CaSO_4.2H_2O$) is ground to form a powder and heated at 150°C to 165°C, three-quarters of its combined water is removed producing hemi-hydrate plaster ($CaSO_4.0.5H_2O$), commonly known as the 'Plaster of Paris' (PoP). When this PoP powder is mixed with water, the resulting paste sets hard as the water recombines with anhydrite $CaSO_4$ to produce gypsum again. This process can be repeated almost indefinitely, with important implications for recycling.

In this work, the phase formations of these samples have been confirmed by using X-ray Diffraction (XRD) technique and the synthesized HAP and HAP/β-TCP samples have been characterized by Scanning Electron Microscope (SEM) to observe their surface morphology and particle size. Thermo-gravimetric and Differential Thermal analysis (TG/DTA) has been used to study thermal stability of the co-precipitated dry powder. The effect of calcination temperature on the morphology and thermal properties has been discussed.

Materials and Method

Experimental Procedure

Laboratory grade gypsum ($CaSO_4.2H_2O$) has been used for starting material to synthesize hydroxyapatite (HAP) in the first stage. HAP synthesized from gypsum powder has been achieved by co-precipitation method at 90°C. Figure 1 shows HAP and HAP/β-TCP pellets before sintering. The flow chart in Figure 2 shows the details for conversion of gypsum powder to HAP. This reaction conversion has been achieved according to the reaction below.

$$10CaSO_4.2H_2O + 6(NH_4)_2HPO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 6(NH_4)_2SO_4 + 4H_2SO_4 + 18H_2O$$

1.6 M of gypsum solution has been prepared with 11.5 g of gypsum and 40 ml of deionized water. Then the gypsum solution has been mixed with 40 ml of 1 M - $(NH_4)_2HPO_4$ solution in conical flask with water bath at the reaction

temperature of 90° with magnetic stirring. The reaction time is for 4 hours. At the end of the reaction period, the solid products have been washed with DI-water for 5 times and filtered to eliminate any water soluble remains. After washing, the solid residue has been put in drying oven operating at 75^{o}C for 24 hours. Again, the dry powder has been heat-treated at 500 ^{o}C, 800 ^{o}C, 1100 ^{o}C and 1150 ^{o}C for 2 hours each in a furnace. The HAP phase has been formed at 500 ^{o}C and 800 ^{o}C for 2 hours. However, HAP converts into β-tricalcium phosphate (β-TCP) at 1100 ^{o}C and beyond. After sintering 1200 ^{o}C of HAP/β-TCP pellet partially converts into biphasic HAP/α-TCP. The α-TCP is brittle and more soluble than HAP and β-TCP. Therefore, this research focus on biphasic HAP/β-TCP. The process of sample preparation of HAP is presented. Morphology study has been conducted using JEOL-JSM 5610LV scanning electron microscope. The thermal behavior of the sample has been investigated by using Thermo-gravimetry and Differential Thermal Analysis (TG/DTA).

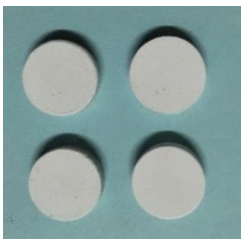

Figure 1: HAP/β-TCP pellets before sintering temperature

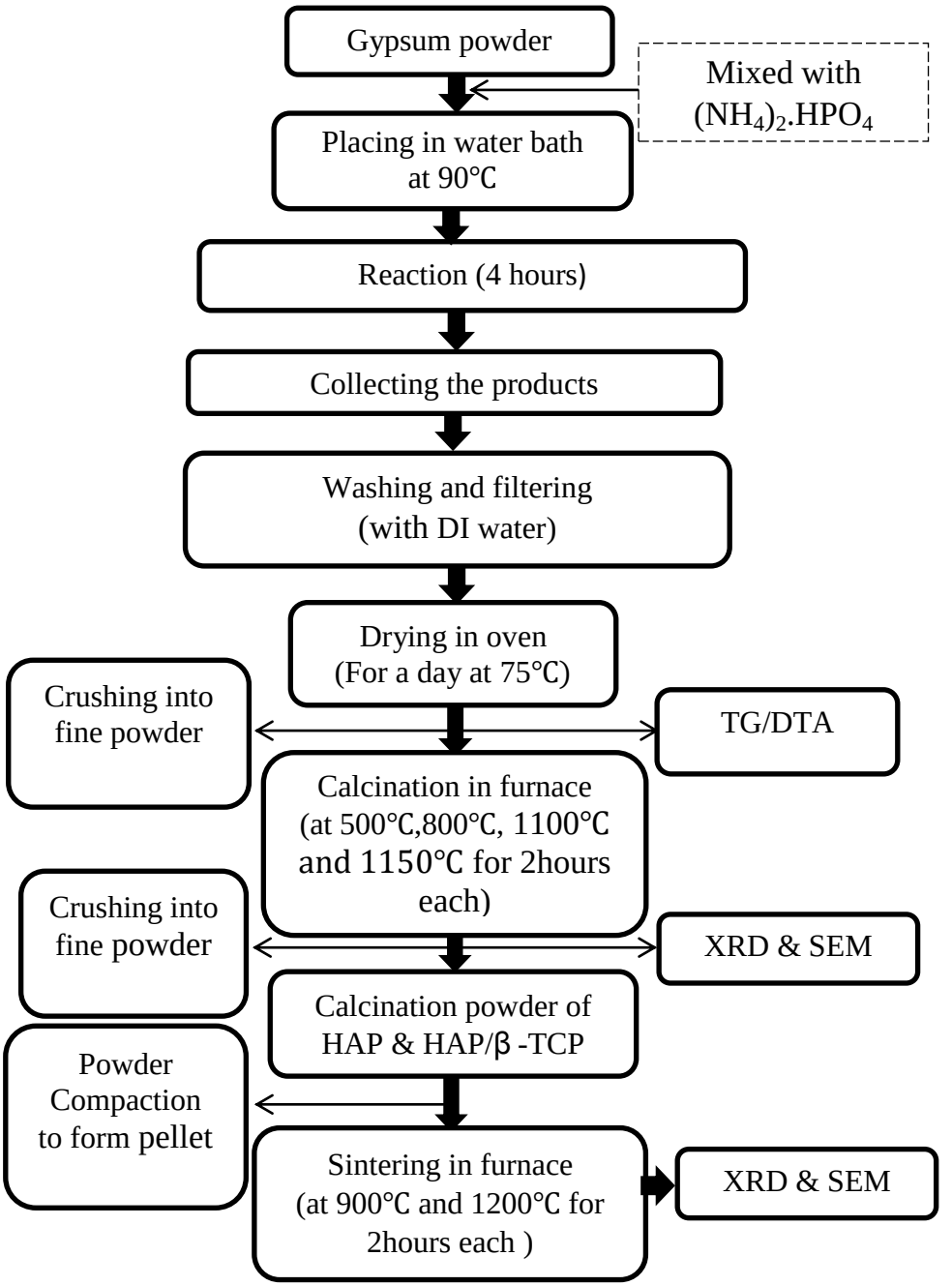

Figure 2: Flowchart of HAP and HAP/β -TCP sample

Results and Discussion

Thermal analysis

Thermal Analysis (TA) is a group of analytical techniques that measures properties or property changes of materials as a function of temperature. But Thermogravimetry (TG) is mainly used to examine the decomposition of materials by monitoring mass change with temperature. In this research, the thermal properties of co-precipitated compound of gypsum and di-ammonium hydrogen phosphate are investigated. A sample of 51.72 mg was placed in a semi-hermetically aluminum sealed container with a pinhole in the lid. The flow rate was 50 ml/min of nitrogen and the heating rate was 15°C/min.

Figure 3 shows the TG/DTA plots for the co-precipitated gypsum and di-ammonium hydrogen phosphate compound. In this semi-hermetic state, the TG curve showed a two-stage weight decrease corresponding to the evaporation of water. The weight loss starts from 34.36°C to 601.58 °C and it is about 35.336% over heating time. From the DTA curve, the decomposition has been investigated at about 122.52°C and 169.68°C to be endothermic reaction. It is important information for the transformation temperature of HAP to β-TCP. From TG curve, the final weight is 33.44 mg and so weight loss is 18.28 mg from an ambient temperature up to 250°C. Beyond that temperature, the synthesized co-precipitated gypsum and di-ammonium hydrogen phosphate compound are stable in thermal analysis.

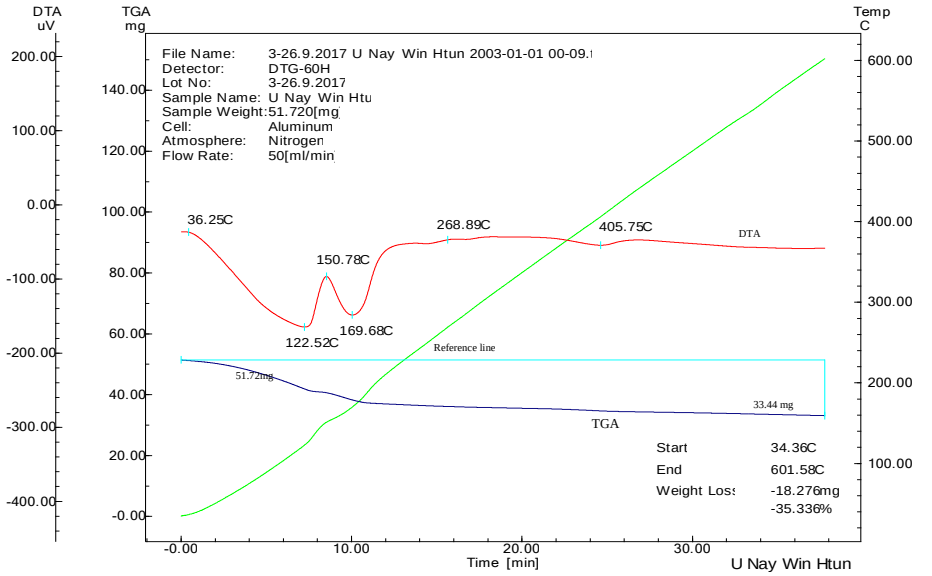

Figure 3: A plot of TG/DTA for the thermal behavior of the co-precipitated gypsum and di-ammonium hydrogen phosphate compound

Phase Formation by XRD analysis

HAP powder has been synthesized from gypsum powder by co-precipitation method at 90°C. After heat-treatment of powder at 500°C and 800°C and that of pellet after sintering at 900°C, HAP phase formed. After heat-treatment of powder at 1100°C and 1150°C, HAP/β-TCP biphasic formed. At 1200°C, the pellet shows the formation of HAP,β-TCP and α-TCP. The XRD diffractograms of powder and pellets samples at different temperatures are shown in Figures 4 to Figures 6.

The pattern in Figures 4 to Figures 6 reveals that the phase precipitated out in the sample is hexagonal structure. There is no trace of starting materials. Therefore, it has been identified that a single phase structure of HAP from gypsum has been formed via the co-precipitation method.

After heat-treatment 1100°C, some of the HAP converts into β-TCP. The lattice parameters ‘a’ and ‘c’ have been calculated by using ‘d’ value of

the diffraction peaks. These lattice constants well agree with the typical values for HAP and β-TCP structures.

The crystallite size has also been estimated from FWHM values and it is found that the HAP and β-TCP crystallites have been formed in the nanometer scale. For HAP, the typical standard value of lattice parameter a, b is 9.432 Å and that of lattice parameter c is 6.8814 Å. For β-TCP, the typical standard value of lattice parameter a, b is 10.439 Å and that of lattice parameter c is 37.375 Å. The average lattice vales and crystallite sizes of HAP and β-TCP are shown in Table 1 and Table 2. From all XRD diffractograms, the lattice parameters values well agree with the typical values.

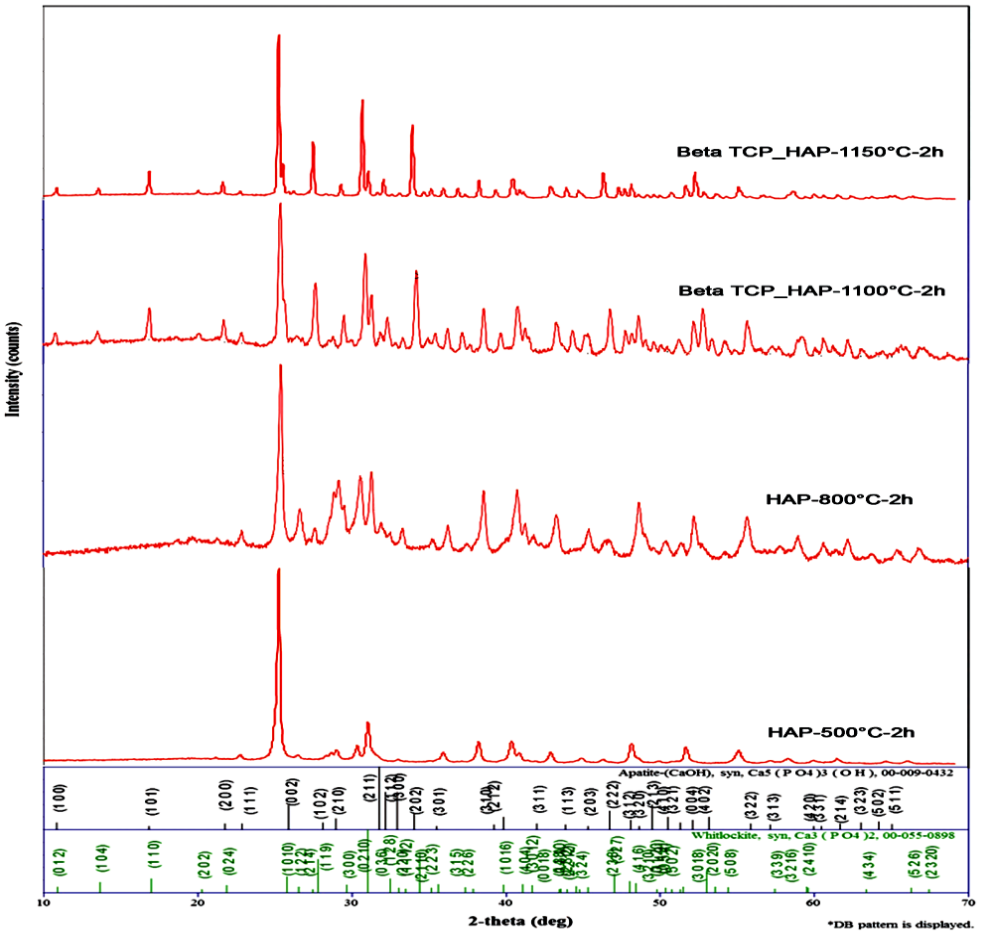

Figure 4: XRD diffractograms of HAP and β-TCP powder for different temperatures

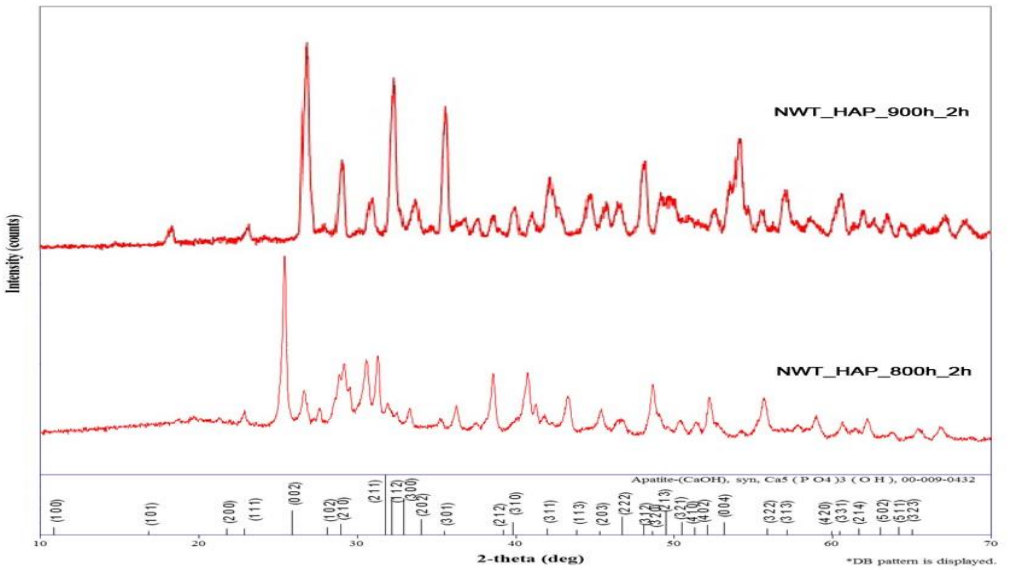

Figure 5: XRD diffractograms of HAP compare with calcination temperature (800℃) and sintering temperature (900℃)

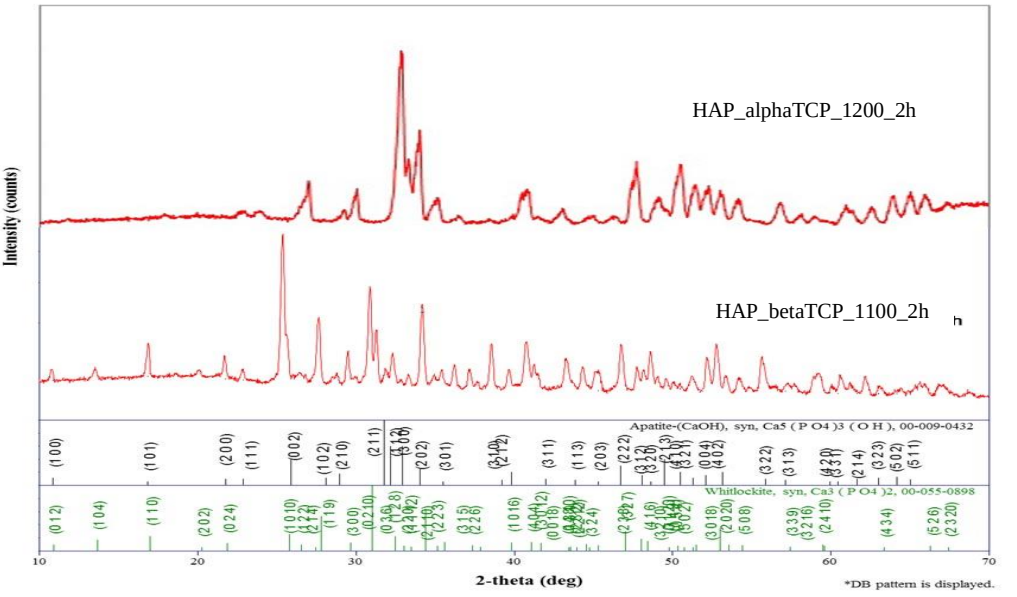

Figure 6: XRD diffractograms of HAP, β-TCP and α-TCP compare with calcination temperature (1100℃) and sintering temperature (1200℃)

Table 1: The lattice parameters (a, b and c) and crystallite size (D) of heat-treatment HAP powder and pellet

Sr. No.	Sample	Heat-treatment temperature (°C)	a (Å)	b (Å)	c (Å)	D (nm)
1	HAP	500(Calcination)	9.409	9.409	7.023	31.48
2	HAP	800(Calcination)	9.251	9.251	6.707	26.56
3	HAP	900(Sintering)	9.220	9.220	6.699	24.01

Table 2: The Lattice parameters (a, b and c) and crystallite size (D) of heat-treatment HAP/ □-TCP powder and pellet

Sr. No.	Sample	Heat-treatment temperature(°C)		a (Å)	b (Å)	c (Å)	D (nm)
1	HAP/ β - TCP	1100 (Calcination)	HAP	9.317	9.317	7.026	41.47
			β -TCP	10.486	10.486	37.561	46.98
2	HAP/ β - TCP	1150 (Calcination)	HAP	9.412	9.412	6.839	66.09
			β -TCP	10.471	10.471	37.469	66.95
3	HAP/ β - TCP	1200 (Sintering)	HAP	9.138	9.138	6.658	19.92
			β -TCP	10.123	10.123	37.761	20.60

Morphological Analysis by SEM Technique

The SEM micrographs of powder and pellets samples at different temperature are shown Figures 7 and Figures 8.

According to the SEM micrograph, the grain sizes of HAP after heat-treatment at 500°C are found to be in the range of 0.50 μm to 1.00 μm. It is observed that the small grains are being agglomerated with the small crystallites which are in nanometer range. The homogeneity of the topography exhibits the formation of pure HAP powder which agrees well with the XRD analysis.

From the SEM micrograph of HAP after heat-treatment at 800°C for 2 hours in a furnace, the grain sizes are estimated by using Line Intercept

Method and found to be 1.22μm. According to the microstructure of the sample heat-treated at 1100°C, it is found that some parts of the HAP has transformed into β-TCP. Therefore, the smaller grains of HAP are more numerical than the larger grains of β-TCP. However, after heat-treatment at 1150°C, most of the HAP has transformed into β-TCP and so the larger grains of β-TCP are more numerical than the smaller grains of HAP. From the SEM micrograph of HAP after sintering 900°C, the average grain size is about 1.45μm and that of HAP/ β-TCP pellet after sintering 1200°C, the average grain size of HAP is about 2.01μm and that of β-TCP is about 6.55 μm. It is worth to note that the grain sizes in biphasic pellets are about two and half times larger than those in biphasic powder. The comparison on grain sizes of HAP powder and pellet and that of HAP/β-TCP powder and pellets are shown in Tables 3 and 4.

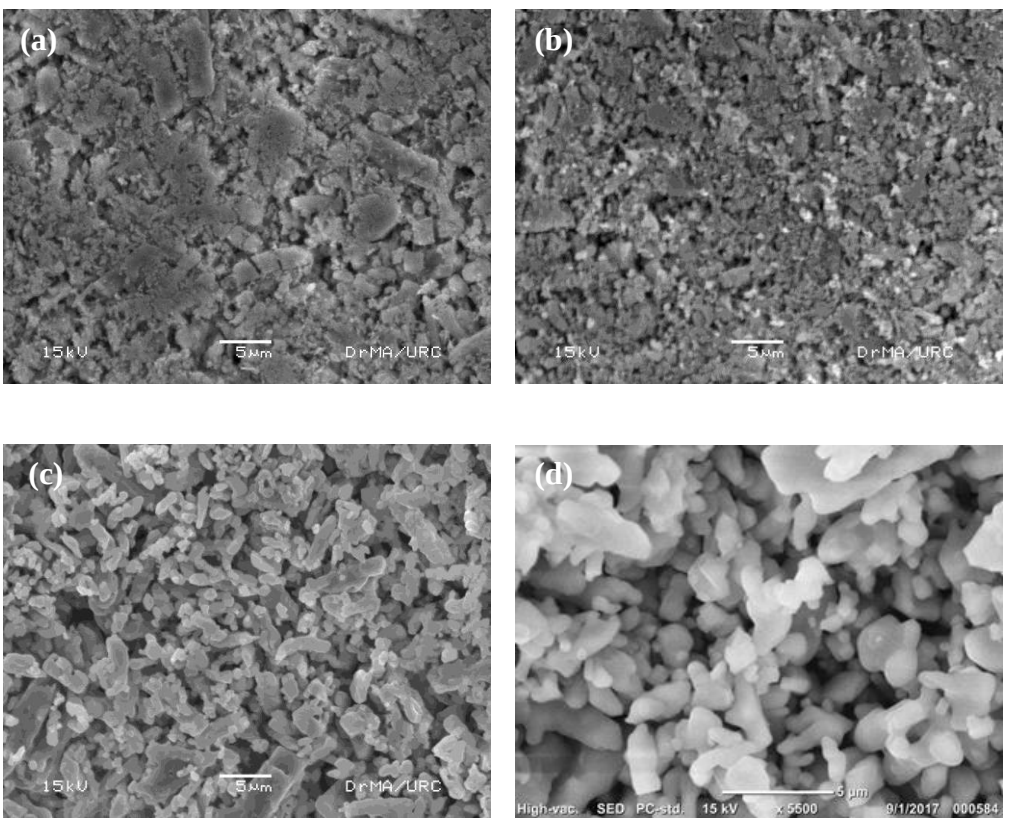

Figure 7: The SEM micrographs of the HAP powder at (a) 500°C, (b) 800°C and that of HAP/β-TCP powder at (c) 1100°C, (d) 1150°C for 2hours

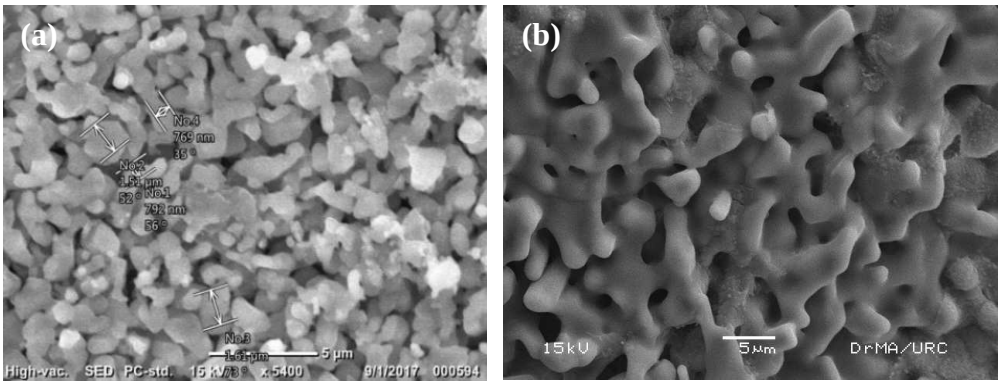

Figure 8: The SEM micrographs of the HAP pellet at (a) 900°C and that of HAP/β-TCP pellet at (b) 1200°C for 2 hours

Table 3: The average grain sizes of heat-treatment HAP powder and pellet

Sr. No.	Sample	Heat-treatment Temperature(°C)	Grain Size (□m)
1	HAP	500(Calcination)	0.50-1.00
2	HAP	800(Calcination)	1.22
3	HAP	900(Sintering)	1.45

Table 4: The average grain sizes of heat-treatment HAP /□-TCP powder and pellet

Sr. No.	Sample	Heat-treatment Temperature(°C)	Grain Size (□m)	
			HAP	□-TCP
1	HAP/β -TCP	1100(Calcination)	0.84	2.51
2	HAP/β -TCP	1150(Calcination)	0.74	1.75
3	HAP/β-TCP	1200(Sintering)	2.01	6.55

Conclusion

Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ has been prepared from gypsum by co-precipitation method. The raw materials have been well characterized prior to the preparation of HAP. A single phase structure of HAP from gypsum has been successfully formed via the co-precipitation method after heat-treated at 500°C and 800°C for 2 hours. The average lattice constants well agree with the typical values for HAP structure. It is worth to note that some parts of HAP converts to β-TCP phases after heat-treated at 1100°C for 2 hours. These average lattice constants well also agree with the typical values for β-TCP structure. It is interesting to note that transformation to β-TCP has started by the heat treatment at 1100°C and the transformation rate has increased with increase in temperature. From the TG/DTA curves, the decomposition temperature has been found about 122.52°C and 169.68°C in endothermic reactions. The synthesized co-precipitated gypsum and di-ammonium hydrogen phosphate compound are found to be stable beyond 250°C.

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