EFFECT OF SINTERING TEMPERATURE ON STRUCTURAL PROPERTIES OF BETA-TRICALCIUM PHOSPHATE*

Cho Cho Khin[1], Nay Win Tun[2], Aye Aye Thant[3] and Khin Khin Win[4]

Abstract

Beta-tricalcium phosphate material (β-TCP) has excellent biocompatibility for medical science applications as bone substitutes. In this research,β-tricalcium phosphate powders, β-TCP, were prepared by the wet chemical precipitation method with calcium nitratetetrahydrate, $Ca(NO_3)_2.4H_2O$, and diammonium hydrogen phosphate, $(NH_4)_2HPO_4$. The pH of the system was controlled by adding sodium hydroxide solution. The dry precipitate was calcined at 700°C and the pellets were sintered at 800°C, 900°C, 1000°C and 1100°C for 6h each. The phase formations of these samples were characterized by using X-ray Diffraction (XRD) analysis. The crystallite sizes and lattice parameters were estimated from the XRD data. The rhombohedral structure of β-TCP phase has been stable after sintering upto 1100°C.The crystallite size is in nano-range and increased with increasing temperatures. The morphological feature of theβ-TCP samples were studied by Scanning Electron Microscope (SEM). Importantly, the dense microstructure without pores could be obtained at sintering temperature of 1100°C.Fourier Transform Infrared Spectroscopy (FTIR) was applied to study the molecular vibrations of functional groups in β-TCP. The presence of β-TCP with the same vibrational modes in all samples has been proved consistently.

Keywords: β-tricalcium phosphate, wet chemical precipitation, XRD, SEM, FTIR

Introduction

Tricalcium phosphate is one of the most important biomaterials and currently recognized as ceramic material that significantly simulates the mineralogical structure of bone.β-tricalcium phosphate powders are widely applied in the biomedical fields because of their biocompatibility and osteoconductivity [Behzad, M., et al., 2012].β-TCP is found to be resorbable in vivo with new bone growth replacing the implanted β-TCP. Theoretically, resorbable β-TCP is an ideal implant material. After implantation, β-TCP will degrade with time and be replaced with natural tissues. It leads to the regeneration of tissues instead of their replacement and so the problem of interfacial stability has been solved[Behzad M., et al, 2014]. β-TCP is known to have significant biological affinity, activity and hence responds well to physiological environments. Because of these positive characteristics, β-TCP is regarded as an ideal bone substitute. In the physiological environment, they are able to gradually degrade, absorb and promote bone growth. They are capable of replacing damaged bone with new tissue [Asmae, M., et al., 2014]. In the present research, a wet chemical precipitation method was carried out to prepare β-TCP and the effect of sintering temperature on its structural properties was investigated.

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Materials and Method

Experimental Procedure

β-TCP powders have been synthesizedby the reaction of calcium nitrate tetrahydrate$Ca(NO_3)_2.4H_2O$ with diammonium hydrogenphosphate $(NH_4)_2HPO_4$. The chemical equation that describes the reaction is as shown below.

$$2(NH_4)_2HPO_4+3Ca(NO_3)_2.4H_2O+2NaOH \rightarrow Ca_3(PO_4)_2+4NH_4NO_3+14H_2O+2NaNO_3$$

The Ca:P ratio for stoichiometric β-TCP is 1.5. Keeping that ratio constant, the amount of $(NH_4)_2HPO_4$ required was calculated and the solution was prepared by dissolving $(NH_4)_2HPO_4$ in distilled water. The prepared solution of $(NH_4)_2HPO_4$was added slowly in drop-wise into the $Ca(NO_3)_2.4H_2O$ solution. Throughout the mixing process, the pH of the mixed solution was maintained at pH value of 8 by adding sodium hydroxide (NaOH) solution. The obtained white suspension was stirred for 12 h. The synthesized precipitate was washed with distilled water for four times and then washed with ethanol for three times to improve the dispersion characteristics. After filtrating the compact, the filtered cake was dried at 80°C for 24 h. The dried powders were then crushed with A-gate mortar and pestle and calcined at 700°C for2 h. The synthesizedβ-TCP powders have been pressed into pellet by uniaxial hydraulic press. The pellets were sintered at 800°C, 900°C, 1000°C and 1100°C for 6h each. The phase formations of these samples were characterized by using X-ray Diffraction (XRD) analysis. The crystallite sizes and lattice parameters were estimated from the XRD data. The morphological feature of β-TCP samples was studied by Scanning Electron Microscope (SEM). Fourier Transform Infrared Spectroscopy (FTIR) was applied to study the molecular vibrations of functional groups in β-TCP. Figure 1 shows the flowchart of wet chemical precipitation process used for preparation of β-TCP sample.

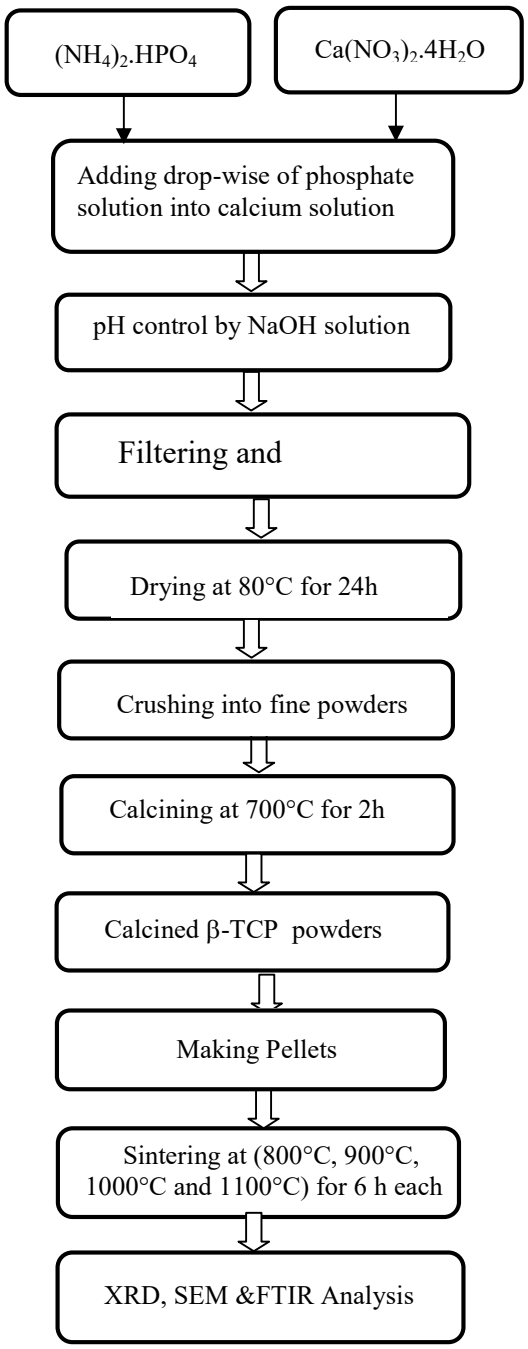

Figure 1 Flowchart of wet chemical precipitation process used for preparation of β-TCP sample

Results and Discussion

Phase Formation by XRD Analysis

Prior to the preparation of β-TCP, the phase of the raw materials was characterized by using XRD analysis. The XRD pattern of $(NH_4)_2HPO_4$ is shown in Figure 2. The pattern has confirmed that the powder can be considered as single phase, $(NH_4)_2HPO_4$. All diffractions could be indexed as $(NH_4)_2HPO_4$ according to ICDD card (76-0414). It is confirmed that there is no impurity and only the phase of $(NH_4)_2HPO_4$ presents in the sample. The XRD pattern of $Ca(NO_3)_2.4H_2O$ is shown in Figure 3. All diffractions could be indexed as $Ca(NO_3)_2.4H_2O$

according to ICDD card (73-0988). It is confirmed the presence of the phase $Ca(NO_3)_2.4H_2O$in the sample.

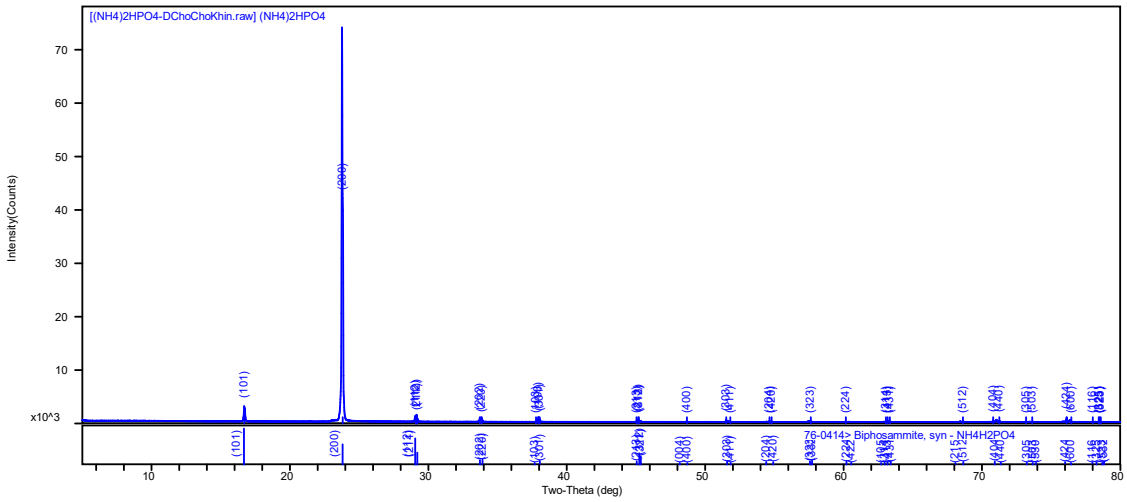

Figure 2 XRD pattern of raw $(NH_4)_2HPO_4$ powder

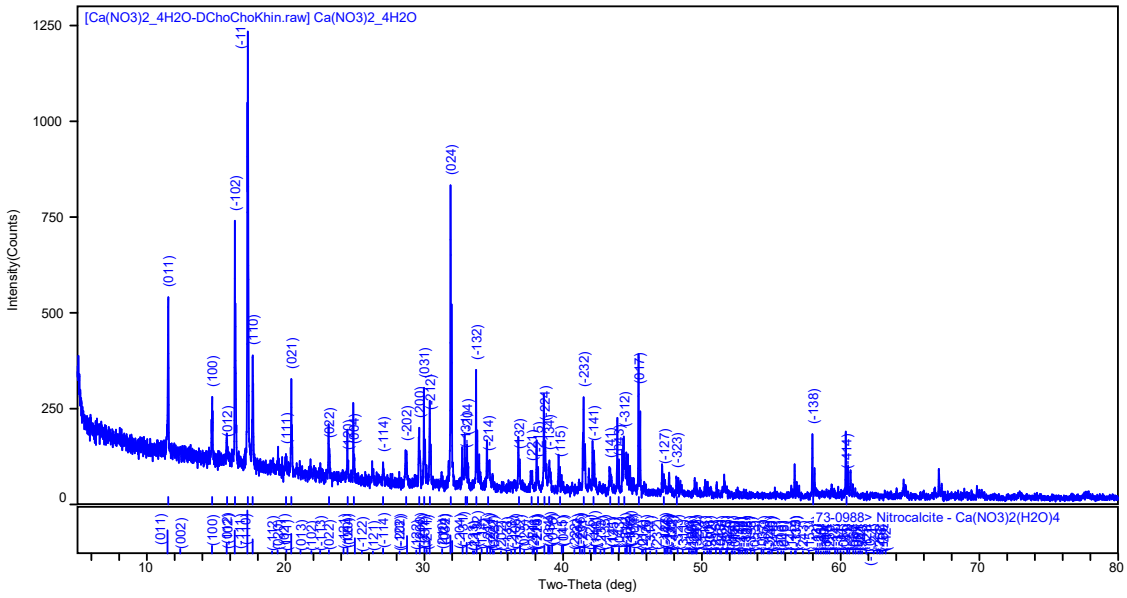

Figure 3 XRD pattern of raw $Ca(NO_3)_2.4H_2O$ powder

β-tricalcium phosphate powders were prepared by the wet chemical precipitation method with calcium nitrate tetrahydrate, $Ca(NO_3)_2.4H_2O$, and diammonium hydrogen phosphate, $(NH_4)_2HPO_4$.After drying at 80°C for 24 h, the dried powders were characterized by using X-ray diffraction to identify the phase formed after the processing. The pattern has revealed that the phase precipitated out in the samples is rhombohedral structure ofβ-TCP. The dried powders were calcined at 700°C for 2 h after crushing with A-gate mortar and pestle. XRD analysis was also conducted to check the phase of the calcined powders. The XRD patterns of dried and calcined β-TCP powder are shown in Figure 4. After calcination, the crystallinity becomes increased and the diffractions peaks are more distinct. The samples revealed the formation of single phase β-TCP structure.

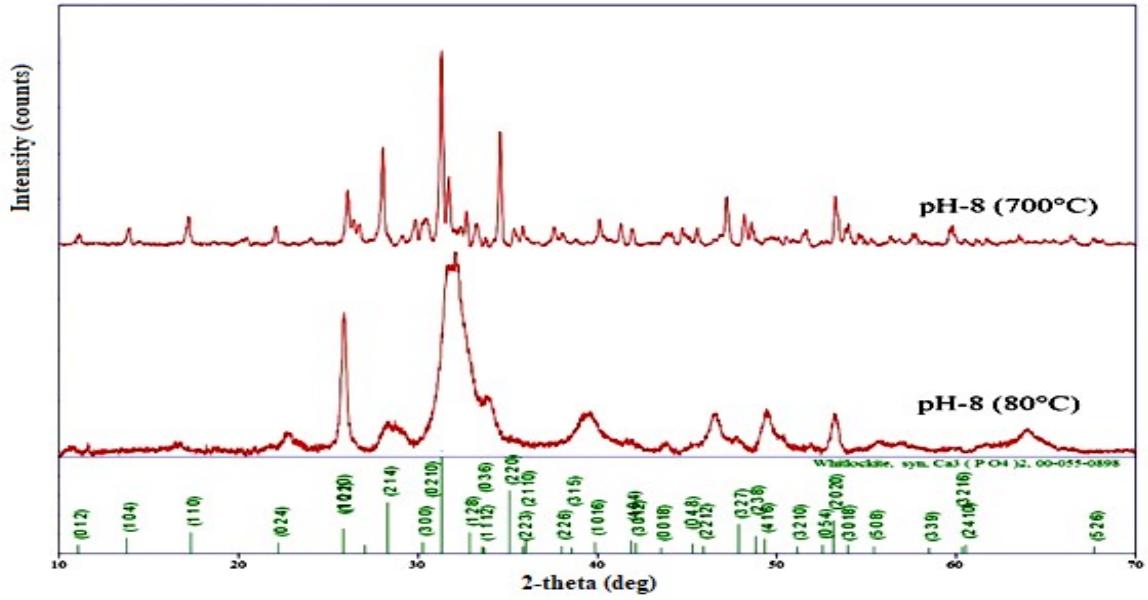

Figure 4 XRD patterns of β-TCP powder dried at 80°C and calcined at 700°C

The synthesized β-TCP powders were pressed into pellet by uniaxial hydraulic press. The β-TCP pellets were sintered at 800°C, 900°C, 1000°C and 1100°C for6 h each. The phase formations of these samples have been characterized by using X-ray Diffraction (XRD) analysis. The XRD patterns of sintered β-TCP pellets are shown in Figure 5.The XRD patterns exhibit that the phase in each sintered pellet is rhombohedral structure of β-TCP. The peaks were sharper as the sintering temperature was increased. The results show that the calcined powders and sintered pellets contain only a single phase β-TCP structure. Therefore, it has been confirmed that rhombohedral structure of β-TCP phase has been stable after sintering upto 1100°C.

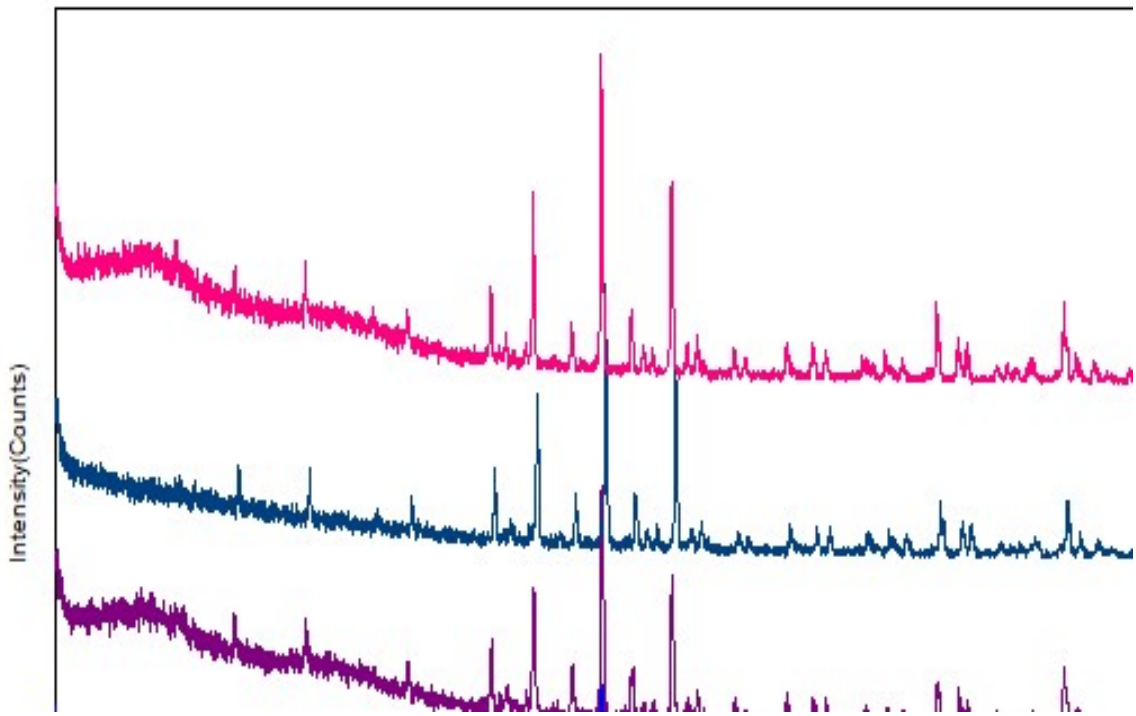

Figure 5 XRD patterns of β-TCP pellets sintered at 800°C, 900°C, 1000°C and 1100°C

Determination of Lattice Parameters and Crystallite Size

The lattice parameters 'a' and 'c' have been calculated by using 'd' value of the intense peak. The crystallite sizes have been estimated by the Scherrer equation. The values of crystallite size and lattice parameters of dried powders after drying at 80°C for 24 h, calcination at 700°C for 2 h and sintered pellets at 800°C, 900°C, 1000°C, 1100°C for 6 h are summarized in Table1. It has been investigated that the lattice parameters of the samples well agree with the typical values for β-TCP structure as discussed in other research of β-TCP [Yashima, M., et al., 2003].It is worth to note that the crystallite size is in nano-range and increased with increasing temperatures.

Table 1 The value of crystallite size and lattice parameter of β-TCP samples

Type of Heat Treatment	Crystallite Size D (nm)	Lattice Parameter	
		'a' (Å)	'c' (Å)
Dried at 80°C	18.58	10.36	36.77
Calcined at 700 °C	44.83	10.37	37.10
Sintered at 800°C	52.54	10.47	37.50
Sintered at 900°C	59.91	10.48	37.57
Sintered at 1000°C	61.93	10.42	37.29
Sintered at 1100°C	63.99	10.47	37.57

Morphological Analysis by SEM Technique

The surface morphology of β-TCP powders after heat-treatment at 80°C and 700°C have been investigated by using Scanning Electron Microscope. Figure 6(a) shows the SEM micrograph of the β-TCP powders for 80°C. It is seen that the as-prepared powders consists of aggregated particles with broad size distribution. Figure 6(b) shows the SEM micrograph of the β-TCP powders calcined at 700°C. The β-TCP powders are highly agglomerated with almost spherical particles having average size of approximately 0.57 μm. SEM micrographs of β-TCP pellets obtained by sintering at 800°C, 900°C, 1000°C and 1100°C for 6 h are shown in Figure 7. The value of average grain size for the pellets sintered at 800°C, 900°C, 1000°C and 1100°C have been estimated and presented in Table2. The SEM micrographs of pellets which were sintered at different temperatures exhibit that the average grain size is increased with increasing sintering temperature. The pores become smaller with increase in sintering temperature and finally the dense microstructure without pores could be obtained at sintering temperature of 1100°C.

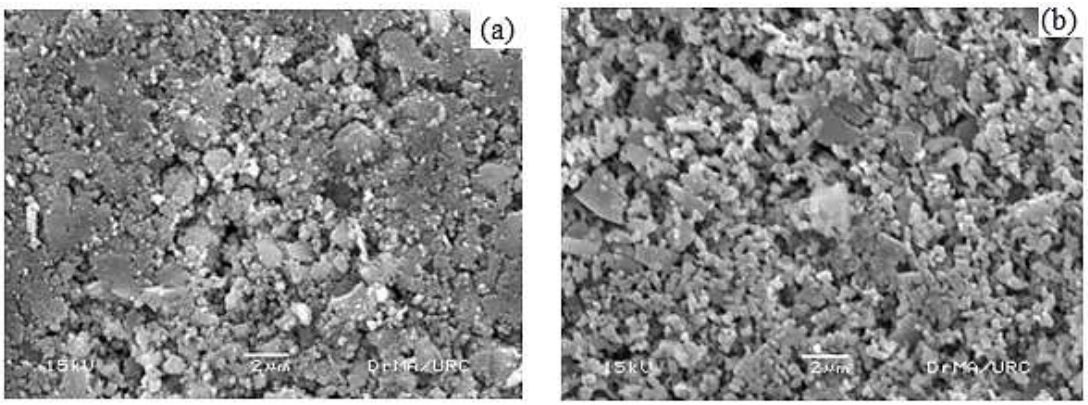

Figure 6 SEM micrographs of β-TCP powders at (a) 80°C and (b) 700°C

Table 2 The value of grain size of β-TCP pellets at different temperatures

Sintered Temperature (°C)	Grain Size (μm)
800	0.68
900	1.16
1000	2.05
1100	3.79

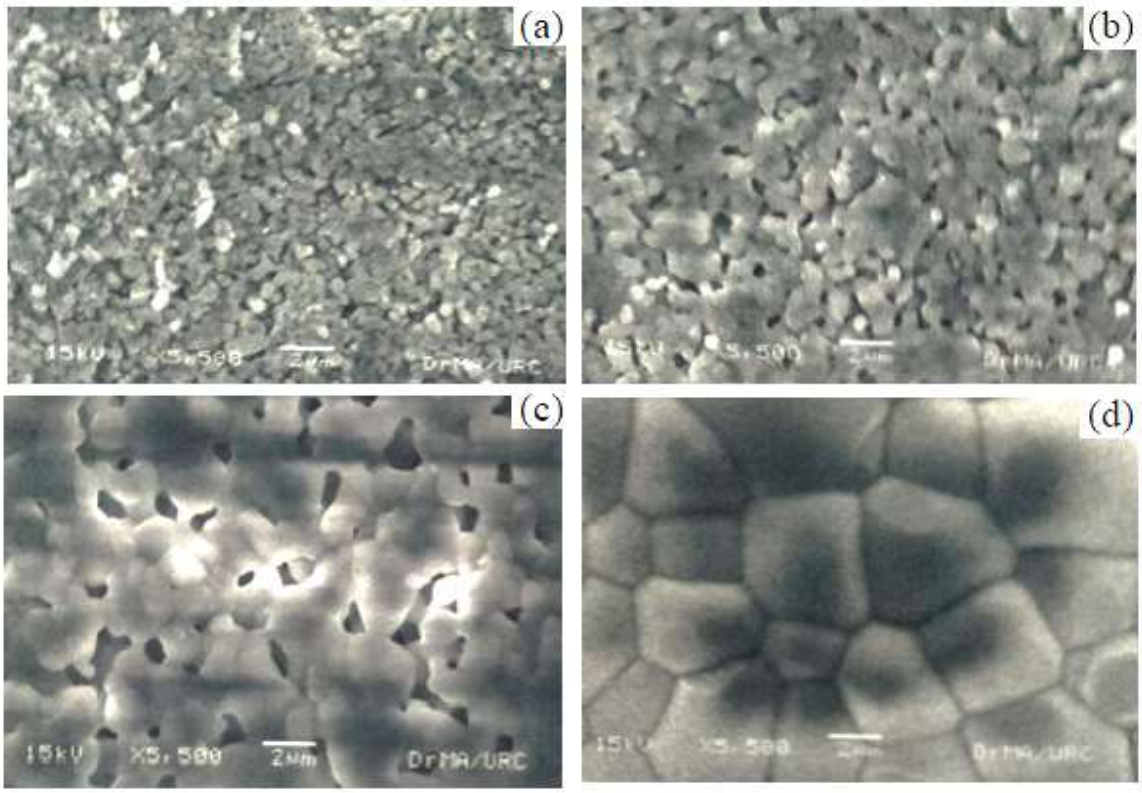

Figure 7 SEM micrographs of β-TCP pellets at (a) 800°C, (b) 900°C, (c) 1000°C and (d)1100°C

FTIR Analysis of Calcined and Sintered β-TCP samples

The functional groups present in calcined and sintered β-TCP were ascertained by Fourier transform infrared spectroscopy (FTIR). The transmission spectra have been recorded in the wavenumber region of 400-4000 cm^{-1}. The FTIR spectra of calcined and sintered β-TCP with different temperatures at700 °C, 800 °C, 900 °C, 1000 °C and 1100 °C are shown in Figure8. Transmission bands of chemical bonds in the calcined and sintered β-TCP are summarized in Table 3. The most characteristic chemical groups in the FTIR spectra of β-TCP are found to be PO_4^{3-}, $P_2O_7^{4-}$, hydroxyl and CO_3^{2-} groups. After sintering, the hydroxyl groups were disappeared.

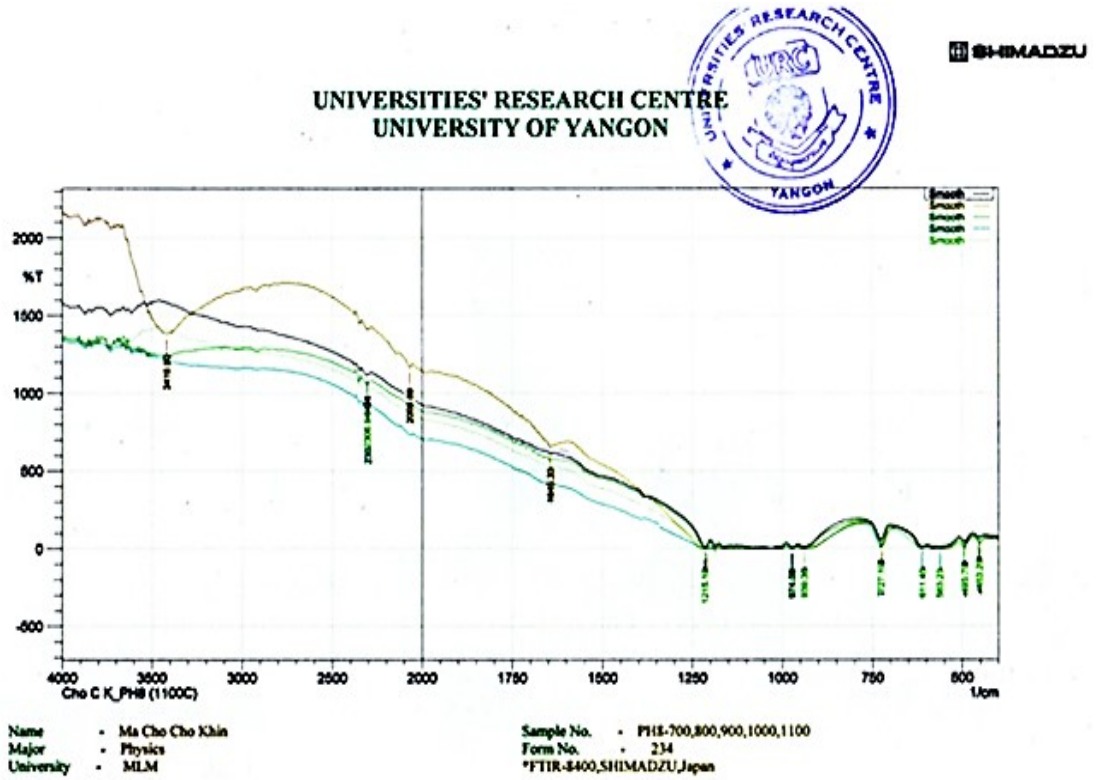

Figure 8 FTIR spectra of β-TCP samples at different temperatures

Table 3 The FTIR transmission bands of β-TCP samples at different temperatures

Chemical Group	Vibrational Mode	Wavenumber(cm^{-1})				
		Calcined temperature	Sintered temperature			
		700°C	800°C	900°C	1000°C	1100°C
PO_4^{3-}	ν_1 Symmetric P-O Stretching	939.36	974.08	939.36	939.36	939.36 974.08
	ν_2 O-P-O bending	453.29 493.79	453.29 493.79	453.29 493.79	453.29 493.79	453.29 493.79
	ν_4 O-P-O bending	611.45	611.45	563.23 611.45	563.23 611.45	563.23 611.45
$P_2O_7^{4-}$	Pyrophosphate	727.19 1215.19	727.19 1215.19	727.19 1215.19	727.19 1215.19	727.19 1215.19
CO_3^{2-}	Carbonate	2069.69	2306.94	2306.94	2306.94	2306.94
OH^-	Hydroxyl	1645.33 3419.9	-	-	-	-

Conclusion

β-TCP powders were prepared by wet chemical precipitation method. The XRD analysis has revealed that the phase precipitated out in the samples are rhombohedral. The lattice parameters of β-TCP well agree with the typical values for β-TCP structure. Moreover, the crystallite size of the particles in β-TCP powders estimated from diffraction intense peak (0 2 10) is obtained in nano-range and found to be increased with increasing temperatures. The XRD results proved that the single phase β-TCP was successfully obtained at different sintering temperatures with increased crystallite size. The SEM observation has confirmed the formation

of homogeneous powders via wet chemical precipitation method. The surface morphology of β-TCP powders after heat-treatment at 80°C consists of aggregated particles with broad size distribution. After calcination and sintering at different temperatures, the average grain size has increased with increasing temperature. This increase in grain size with temperature well agrees with the increase in crystallite size. This finding pointed out that the synthesis route is consistent with different sintering temperatures. Most importantly, the dense microstructure without pores could be obtained at sintering temperature of 1100°C.The various vibrational modes in the FTIR transmission bands have clearly revealed the presence of respective chemical groups in β-TCP. Based on the results obtained, it is concluded that the sintering temperature could effect on structural properties of beta-tricalcium phosphate and it can tune the applications for bone replacement.

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