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Structural and Composition of Natural Hydroxyapatite (HA) at Different Sintering Temperatures

Saturo Baco^{1*}, Lisnawaty Bambang¹, Norlaila Joseph¹, Fouziah MD.Yassin¹ and Nur Fadzilah Basri²¹ Physics with Electronic Program, School of Science & Technology, Universiti Malaysia Sabah, Jalan UMS 88400 Kota Kinabalu² Preparatory Centre for Science and Technology, Universiti Malaysia Sabah, Jalan UMS 88400 Kota Kinabalu

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ABSTRACT

Hydroxyapatite (HA) is one of the most attractive biomaterials and widely used as a bone substitute due to its compositions are similar to the minerals in teeth and bones. Understanding of natural HA properties are useful in order to produces high quality of HA. In this paper, we report an easy and low cost method to extract the natural HA from femur cow bone and subsequently sintered at different temperature from 900 °C to 1300 °C. Structural, composition and surface morphology of natural Hydroxyapatite (HA) at different sintering temperatures (900 °C, 1000 °C, 1100 °C, 1200 °C and 1300 °C) were discussed. The HA structural, composition and surface morphology were studied by using X-Ray Diffractometer (XRD), Fourier Transform Infrared (FTIR) and Scanning Electron Microscope (SEM), respectively. The results show the main HA phases were detected in the range of 31.72° - 31.82° (2θ) for all sintered HA corresponding to 211 plane. The crystallite size of HA increases with sintering temperature from 900 °C to 1100 °C. Spectrums of FTIR revealed the existences of functional groups of carbonate (CO₃²⁻), phosphate (PO₄³⁻) and hydroxyl (OH) peaks. SEM micrographs presented small and homogenous grains from 900 °C to 1100 °C. The grains look interconnected as sintering temperature increased at 1200 °C and 1300 °C. From this study, sintering process was found to be an easy and low cost method to produce natural HA from femur cow bones.

| Natural hydroxyapatite | Sintering | Biomaterials | Crystallite size |

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1. INTRODUCTION

Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) is a bioceramic that attracted much attention to be used in biomedical application, since its compositions similar to the minerals in teeth and bone. This bioceramic can be used as a bone substitute materials due to their excellent osteoconductivity and non-toxicity properties. According to [1] hydroxyapatite can promote tissue growth and can bond directly to tissue, thus makes it as material to be applied in orthopedic and dental applications. Bone is a unique composite and comprises about 33–43% apatite minerals, 32–44% organics, and 15–25% water on a volumetric basis [2].

Hydroxyapatite (HA) powders can be produced either from natural sources or synthesis process. HA can be extracted from natural sources such as coral, egg shells [3] bovine bone [4-5] and fish scale [6]. In synthesis process, the HA can be prepared by hydrothermal process [7] wet precipitation or chemical precipitation [8] etc.

Extraction of natural HA from cow bone for instance, can be easily obtained and biologically safe and economic [9] compared to synthesizing process. Many studies were employed on the natural HA that sintered at low and high temperatures using synthesis process in order to study the temperature effect on physicochemical properties of HA [9-12].

Thus, in this study we report an easy and low cost method to extract the natural HA from femur cow bone and subsequently sintered at different temperature from 900 °C to 1300 °C. Structural and composition of natural HA at different sintering temperature were discussed. Surface morphology of sintered HA also presented in this paper.

2. EXPERIMENTAL

2.1 Materials, method and instruments

Material that has been used in this study was femur cow bone with the age around 2 years old. The cow bones collected from Pasar Besar, Kota Kinabalu Sabah and extracted to obtain the natural HA.

The bone firstly cleaned using water to remove visible tissue and substances on the bone surface before it was cut into small pieces. The bones then treated in sodium hydroxide solution to eliminate the organic and protein parts and subsequently neutralized by distilled water. The bones later heated at 800 °C for 4 hours under ambient condition to remove the protein completely (deproteinized) [13]. The bones turn to white color after heated and it is free from protein and then grounded into fine powder and sieved pass through 63 μm.

*Corresponding author. E-mail: saturi@ums.edu.my (Saturo Baco)

The HA powders were divided into 5 parts and were sintered at different temperature which are 900°C, 1000°C, 1100°C, 1200°C and 1300°C, for two hours. The structure analysis of HA phase was identified by X-Ray Diffractometer (PW 3040/60 X'pert Pro) using CuK α radiation with wavelength 1.5405 Å, 40 kV and 30 mA in the range of 20°-80° (2-theta). The composition of functional groups that presence in HA was analyzed by FTIR Spectrometer (Perkin Elmer Optima 100). Surface morphology of sintered HA examined by Scanning Electron Microscope (JEOL JSM-5610 LV).

3. RESULTS & DISCUSSION

3.1 Phase Identification and Structural analysis by XRD

The XRD patterns of HA phase for non-sintered sample, 900°C, 1000°C, 1100°C, 1200°C and 1300°C are depicted in Figure 1(a-f). Figure 1.0 (a) shows the broad peaks for sample without sintered and no HA phase was detected. This is because at low temperature the protein and organic compound still exist in bones thus it disperses the x-ray radiations [13]. A triangle symbol in the figure indicates most intense peaks of HA at 211 planes that match with the standard data of hydroxyapatite (XRD JCPDS-no.9-432) as shown in Table 1.0. Sintered HA are more crystalline than sample non-sintered. With increased of sintering temperature from 900°C to 1100°C, there was noticeable increase in the intensity. At 1100°C sintering temperature, the formation of HA was in optimum condition which is at highest intensity. This finding is consistent with [9].

The intensity of HA are found to be decreased when the sintering temperature greater than 1100°C [5]. The intensity of major peaks of HA decreases with increasing sintering temperature up to 1300°C and this finding also proved by [6]. In this study, the main HA phases were detected in the range of 31.72° - 31.82° (2 θ) for all sintered HA corresponding to 211 planes. At low intensity, several peaks of HA were also observed. Despite the change of sintering temperature, all sintered samples still shows similar XRD pattern. This is in agreement with Mezahi et al. (2011) [11] who found that the phases of natural HA from bovine bones were not affected by the heat treatment.

The HA phase at 211 planes is considered in order to calculate the crystallites size of HA using Scherer's equation:

$$d = \frac{0.9 \times \lambda}{B \cos \theta}$$

where d is crystallite size, B is full half width maximum (FWHM), λ is wavelength and θ is diffraction angle. Different crystallites sizes correspond to 211 planes are tabulated in Table 2.0. HA sintered at 1100°C has larger crystallite size than other temperature. For HA sintered from 900°C to 1100°C, the crystallite size increases with

sintering temperature and reduces when sintered beyond 1100°C. Research done by [14] presents the crystallite size of HA from bovine bone increased with temperatures which are 82 nm and 95 nm respectively to 900°C and 1200°C.

Table 1 HA on XRD JCPDS-no. 9-432

Plane			JCPDS 9-432	
<i>h</i>	<i>k</i>	<i>l</i>	2-Theta	<i>d</i>
2	0	0	21.819	4.0701
1	1	1	22.902	3.8800
2	0	1	25.354	3.5101
0	0	2	25.879	3.4400
1	0	2	28.126	3.1701
2	1	0	28.966	3.0801
2	1	1	31.773	2.8141
1	1	2	32.196	2.7780
3	0	0	32.902	2.7200
2	0	2	34.048	2.6311
3	0	1	35.48	2.5281
2	1	2	39.204	2.2961
3	1	0	39.818	2.2621
3	1	1	42.029	2.1481
1	1	3	43.804	2.0650
2	0	3	45.305	2.0000
2	2	2	46.711	1.9431
3	1	2	48.103	1.8900
3	2	0	48.623	1.8710
2	1	3	49.468	1.8410

Table 2 Crystallite sizes of HA corresponding to 211 planes at different sintering temperatures

Temperature (°C)	2 θ (211 plane)	FWHM ($^{\circ}$)	Crystallite Size (nm)	
			Present Study	Figuerdo <i>et al</i> , (2010) [14]
900	31.74	0.1744	54	82
1000	31.74	0.1696	55	-
1100	31.82	0.1446	65	-
1200	31.72	0.1836	51	95
1300	31.77	0.1623	58	-

3.2 Composition analysis by FTIR

FTIR analysis was carried out to analyze composition of functional groups in HA powders (63 μ m) that have been extracted from femur cow bone at different sintering temperatures. Figure 2.0 shows the FTIR transmittance spectrum of HA powders and the spectrum was recorded in range of 4000 - 600 cm^{-1} .

Generally, the FTIR spectrum of HA in annealed femur bone indicates the functional groups of carbonate (CO_3^{2-}), phosphate (PO_4^{3-}) and hydroxyl (OH^-) peaks (Ooi et al., 2007). In this study we found these functional groups as shown in the Figure 2. The sharp peaks of phosphate (PO_4^{3-}) observed in 1025.44 cm^{-1} , 1026.34 cm^{-1} , 1023.12 cm^{-1} , 1020.89 cm^{-1} and 1002.43 cm^{-1} in 900°C, 1000°C, 1100°C, 1200°C and 1300°C, respectively due to the asymmetric stretching mode of vibration for PO_4^{3-} group.

The presence of CO_3^{2-} bands identified at about 1454.71 cm^{-1} in $900\text{ }^\circ\text{C}$ and 1445.31 cm^{-1} in $1000\text{ }^\circ\text{C}$ correspond to the ν_3 mode of CO_3^{2-} . As the temperature increased from $1100\text{ }^\circ\text{C}$ to $1300\text{ }^\circ\text{C}$, there is no peak of CO_3^{2-} was observed. This can be attributed by the decomposition of carbonate from the lattice at high temperature [14-15]. Bands at 3602.54 cm^{-1} , 3835.94 cm^{-1} and 3843.75 cm^{-1} characterize the OH^- stretching vibration modes for $900\text{ }^\circ\text{C}$ [14], $1000\text{ }^\circ\text{C}$, $1100\text{ }^\circ\text{C}$ respectively. As can be seen in the FTIR spectrum, the OH^- peaks disappeared as sintering temperature increased at $1200\text{ }^\circ\text{C}$ and $1300\text{ }^\circ\text{C}$. This might due to the releases of OH^- at high temperatures. Barinov *et al.*, (2006) [16] have investigated the effect of sintering temperature on carbonated hydroxyapatite and reported that FTIR spectrum of OH^- group was just disappeared after sintering the hydroxyapatite at $1100\text{ }^\circ\text{C}$ and $1500\text{ }^\circ\text{C}$.

3.3 Surface Morphology analysis by SEM

Representative SEM micrographs (5000x magnification) of samples for non-sintered and sintered at various temperatures from $900\text{ }^\circ\text{C}$ to $1300\text{ }^\circ\text{C}$ are respectively presented in Figure 3.0. Morphology of non-sintered sample do not reveals the homogenous grains due to the existence of organic material in bone. As sintered at $900\text{ }^\circ\text{C}$ to $1100\text{ }^\circ\text{C}$ the surface exhibit a homogenous small grain. The grains look to be interconnected as sintering temperature up to $1200\text{ }^\circ\text{C}$ same images results found by (Ooi *et al.*, 2007) [4].

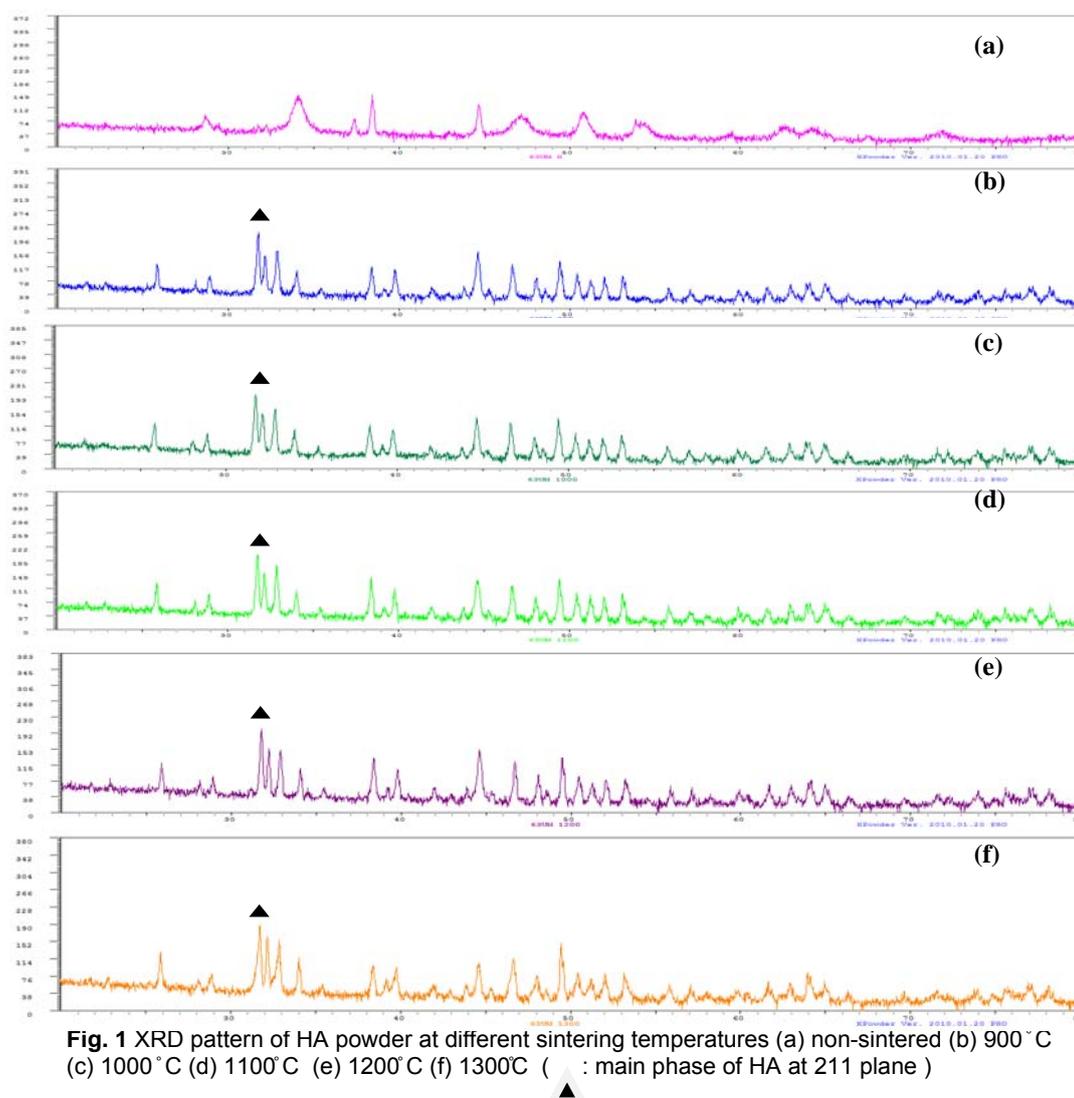


Fig. 1 XRD pattern of HA powder at different sintering temperatures (a) non-sintered (b) $900\text{ }^\circ\text{C}$ (c) $1000\text{ }^\circ\text{C}$ (d) $1100\text{ }^\circ\text{C}$ (e) $1200\text{ }^\circ\text{C}$ (f) $1300\text{ }^\circ\text{C}$ (▲ : main phase of HA at 211 plane)

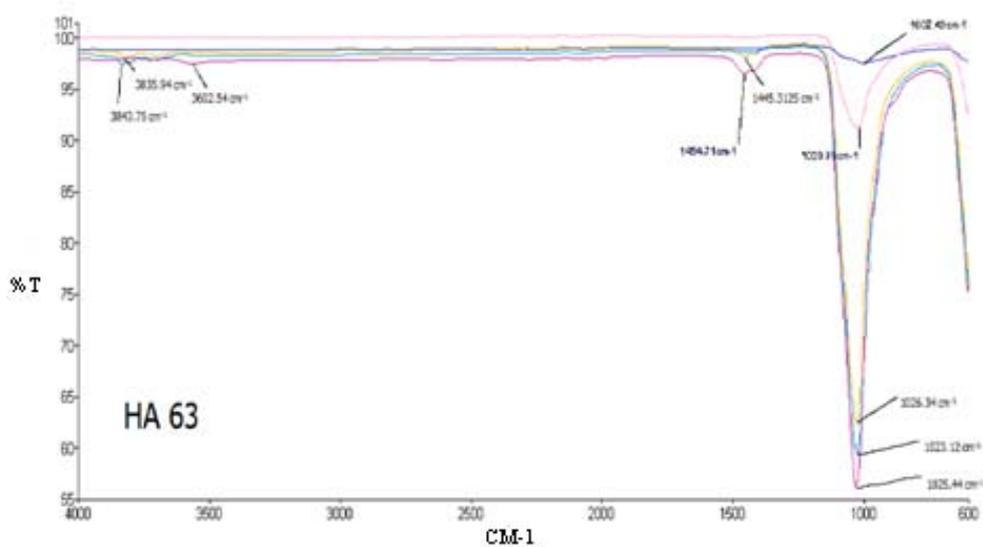


Fig. 2 FTIR spectrum of HA powders sintered from 900 °C to 1300 °C

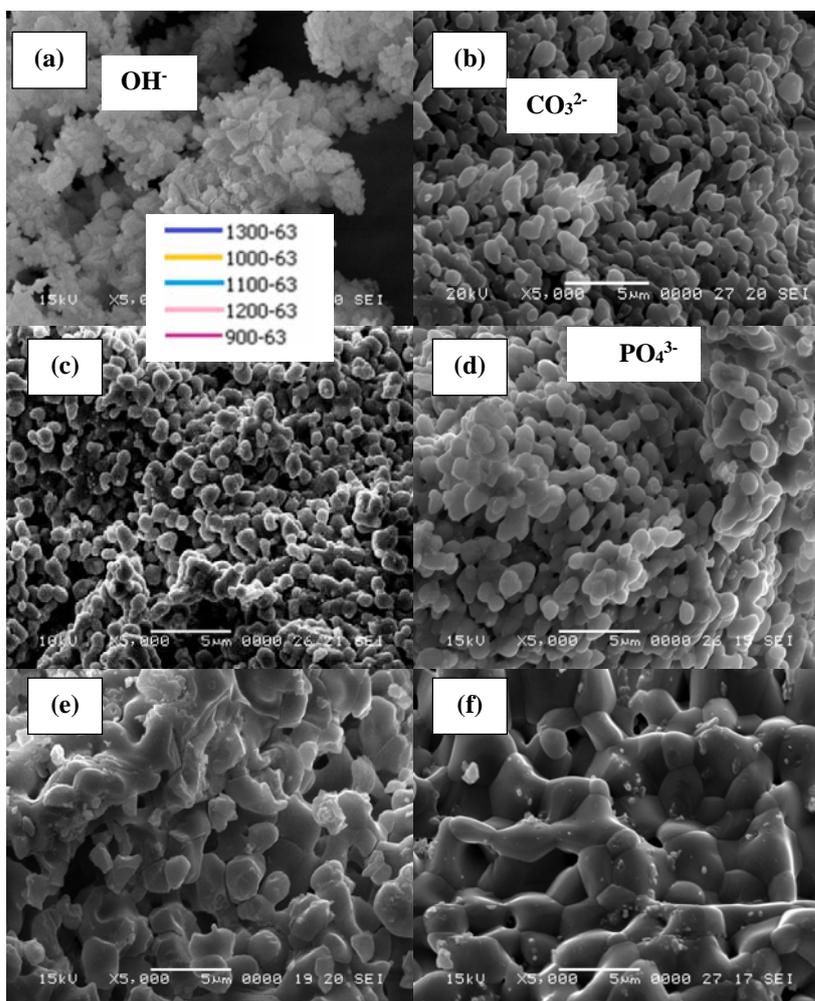


Fig. 3 SEM micrograph of : (a) sample non-sintered (b) 900 °C (c) 1000 °C (d) 1100 °C (e) 1200 °C and (f) 1300 °C with 5000x magnification.

4. CONCLUSION

Natural HA from femur cow bone has been successfully extracted and sintered at different temperatures. The structural, composition as well as surface morphology have been characterized. Its powder mainly composed of HA as confirmed by the XRD analysis. The main HA phases were detected in the range of 31.72° - 31.82° (2θ) corresponding to 211 planes. The crystallite size of HA increases with sintering temperature from 900°C to 1100°C . Spectrums of FTIR revealed the existences of functional groups of carbonate (CO_3^{2-}), phosphate (PO_4^{3-}) and hydroxyl (OH^-) peaks. Homogenous grains of HA were obtained at 900°C to 1100°C and grains look interconnected as temperatures increased. From this study, sintering process was found to be an easy and low cost method to produce natural HA from femur cow bones.

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