

# Characterization of Hydroxyapatite Synthesized by Wet Chemical Precipitation

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**Abstract:** In the present work HA powder is synthesized by wet chemical precipitation method using calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ) and ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) as precursors. The synthesized samples are further characterized by X-Ray Diffraction, and Scanning Electron microscopy techniques.

**Key Words:** Hydroxyapatite(Hap), XRD, SEM

## 1. INTRODUCTION:

Hydroxyapatite (HA) is an important component of bone tissues. It helps to form a direct bond with the neighbouring bone. Hydroxyapatite powder (HAp) has an excellent compatibility with living organisms and is capable of interacting biologically with the bone tissues.[1][2] HA belongs to the family of apatite whose general formula can be written as  $\text{M}_{10}(\text{XO}_4)_6\text{Z}_2$ . where,  $\text{M}=\text{Ca}^{+2}$ ,  $\text{Sr}^{+2}$ ,  $\text{Ba}^{+2}$ ,  $\text{Na}^+$ ,  $\text{Pb}^{+2}$ ,  $\text{La}^{+3}$ , and many rare earth elements;  $\text{XO}_4= \text{PO}_4^{-3}$ ,  $\text{VO}_4^{-3}$ ,  $\text{SiO}_4^{-4}$ ,  $\text{AsO}_4^{-3}$ ,  $\text{CO}_3^{2-}$ ;  $\text{Z}= \text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{CO}_3^{2-}$  [3]. The chemical coprecipitation from water solutions containing  $\text{Ca}^{+2}$ ,  $\text{PO}_4^{-3}$  and  $\text{OH}^-$  is a popular method. The pH value of the solution should be kept greater than 7 in order to form primary crystals of insoluble Hydroxyapatite.[4] In the present work, Hydroxyapatite is synthesized using the wet chemical precipitation technique.

XRD is a unique method in determination of crystallinity of a compound. In the present work, samples of HAp heat treated at three different temperatures are characterized using XRD in order to identify the face composition and crystallinity of the calcium phosphate compound.

The morphology of the synthesized HAp is studied using SEM images.

## 2. METHOD:

Chemical precipitation is done by preparing a suspension consisting 75 g calcium hydroxide,  $\text{Ca}(\text{OH})_2$ , in 510 ml distilled water and a solution of 40 ml orthophosphoric acid  $\text{H}_3\text{PO}_4$ , in 200 ml distilled water, in order to obtain a hydroxyapatite slurry.  $\text{H}_3\text{PO}_4$  suspension is added drop wise to the alkaline solution based on  $\text{Ca}(\text{OH})_2$ , at constant  $75^\circ\text{C}$  for three hours under the condition of constant stirring. The pH was maintained 9.5 - 10 during the addition of suspension, using concentrated aqueous ammonia solution  $\text{NH}_4\text{OH}$ , yielding a hydroxyapatite having stoichiometric ratio  $\text{Ca}/\text{P} = 1.67$ . The reaction mixture is then kept aside for 46 hours for aging.

The precipitate is separated from the suspension by vacuum filtration, washed with distilled water and ethanol, in order to remove any impurities. The filtered cake is then dried in an oven at  $130^\circ\text{C}$  for 24 hours and then grounded to a fine powder using a mortar and pestle. Three samples of the obtained hydroxyapatite powder were prepared by heat treating each sample at  $200^\circ\text{C}$ ,  $600^\circ\text{C}$  and  $1200^\circ\text{C}$  for two hours.



FIGURE 1. Sample being calcinated at  $1200^\circ\text{C}$  in a furnace

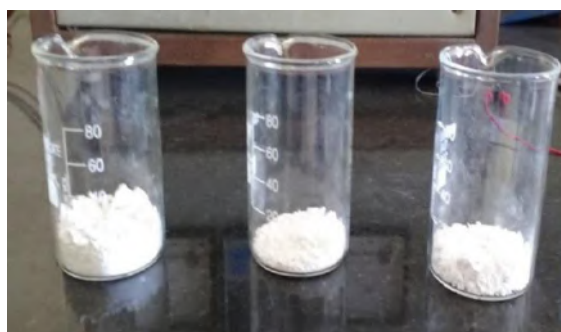


FIGURE 2. Samples after being calcinated at  $200^\circ\text{C}$ ,  $600^\circ\text{C}$  and  $1200^\circ\text{C}$

## 3. CHEMICAL REACTION:



#### 4. CHARACTERIZATION TECHNIQUES:

The structural characterization of the different heat treated samples is done by XRD. The wavelength used was  $\text{Cu}_{k\alpha} = 1.5405 \text{ \AA}$  and the data collected in the  $2\theta$  range  $10\text{-}80^\circ$ . The phases present, the degree of crystallinity and dimension of crystallites of the synthesized samples is assessed by XRD patterns as shown in figure 3, 4 and 5.

Crystalline phase is identified by comparing the pattern of diffraction of HAp with standard JCPDC card no. – 09432. The XRD patterns of HAp is discussed in detail in the result part. The SEM pattern for the HA sample calcinated at  $1200^\circ\text{C}$  shows uniform grain size with a narrow distribution showing crystalline structure.

#### 5. RESULTS AND DISCUSSION:

Figure 3 shows the presence of an amorphous phase in the HA powder calcinated at  $200^\circ\text{C}$ . The amorphous phase decreases as temperature increases as shown in the Figure 3 and Figure 4. According to Scherrer's formula, the crystal size for HAp increases from  $30.83 \text{ nm}$  to  $53.94 \text{ nm}$  with increase in the temperature from  $200^\circ\text{C}$  to  $1200^\circ\text{C}$ . [5]

From the XRD pattern of the sample heat treated at  $1200^\circ\text{C}$ , The diffraction peaks at  $2\theta$  values of  $22.88$ ,  $25.88$ ,  $31.74$ ,  $32.88$ ,  $34.06$ ,  $39.26$ ,  $43.82$ ,  $49.44$ ,  $51.22$ ,  $53.16$ ,  $57.10$ ,  $65.04$  and  $73.98$  were identified to originate from (111), (002), (211), (300), (202), (212), (113), (213), (410), (004), (313), (511) and (423) planes respectively.

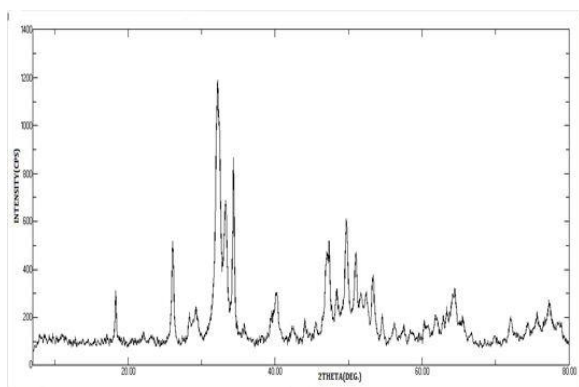


FIGURE 3. XRD pattern for sample heat treated at  $200^\circ\text{C}$

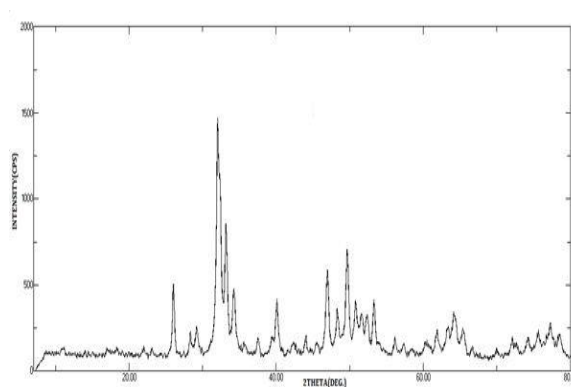


FIGURE 4. XRD pattern for sample heat treated at  $600^\circ\text{C}$

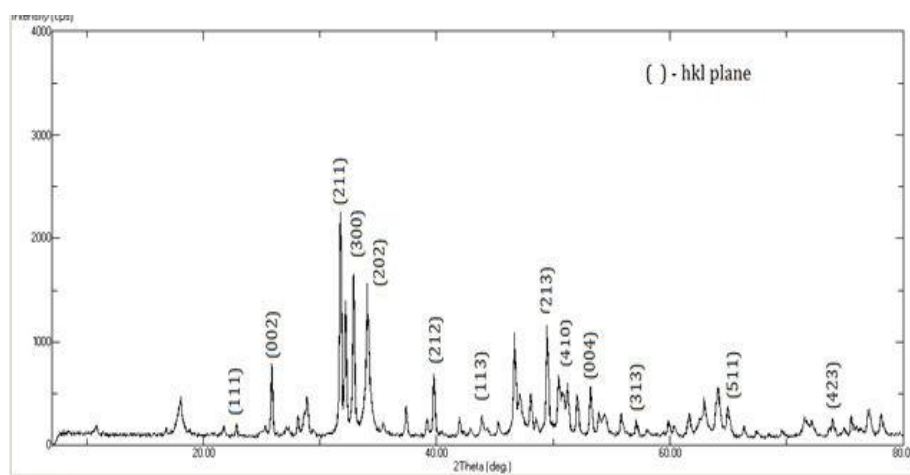


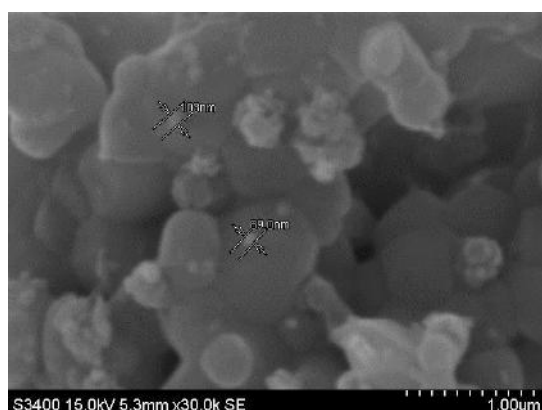
FIGURE 5. XRD pattern for sample heat treated at  $1200^\circ\text{C}$

TABLE-1 Size of HAp nanoparticles using Scherrer's Equation. (for sample calcinated at  $1200^\circ\text{C}$ )

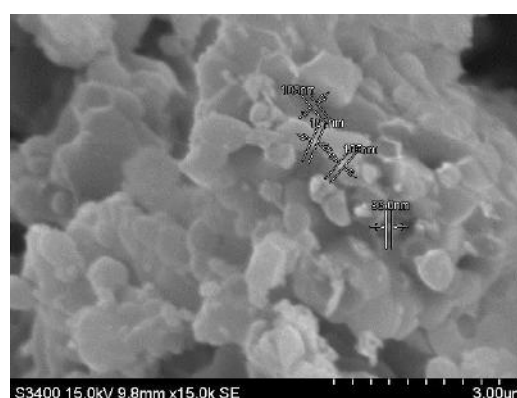
Peak no.	$2\theta$	d-value	FWHM (W) (in degree)	(h k l)	$D = \frac{k \lambda}{W \cos \theta}$ (nm)
10	22.88	3.8866	0.09	(111)	94.0592
12	25.88	3.4420	0.12	(002)	70.9447

22	31.74	2.8135	0.16	(211)	53.9120
25	32.88	2.7187	0.14	(300)	61.7916
29	34.06	2.6303	0.07	(202)	123.9665
37	39.26	2.2963	0.05	(212)	176.8134
44	43.82	2.0627	0.07	(113)	127.7586
60	49.44	1.8407	0.16	(213)	57.0888
65	51.22	1.7798	0.09	(410)	102.2344
71	53.16	1.7210	0.14	(004)	66.2693
84	57.10	1.6109	0.07	(313)	134.9393
102	65.04	1.4328	0.07	(511)	140.5719
116	73.98	1.2795	0.07	(423)	148.3900

The SEM pattern of the HA powder heat treated at 1200° C is shown in following Fig 6 and 7. The figures show the morphology and particle size of the synthesized HA powder examined under SEM. These SEM patterns give insight into the HA structure with respect to particle size and shape. When it is heat treated gradually from 200 - 1200° C, the microscopic changes occur which include re-crystallization of the HA powder as well as removal impurity at high temperature (1200° C). [6] The above SEM images of the HA powder heat treated at 1200° C shows the predominant size of the grain in the range of 90-100 nm. [7]



**FIGURE 6.** SEM pattern for sample heat treated at 1200° C (1µm scale)



**FIGURE 7.** SEM pattern for sample heat treated at 1200° C (3µm scale)

## 6. CONCLUSION:

The macroscopic and microscopic characterisation of synthesized HA powder is done by XRD and SEM respectively. The XRD pattern shows that the synthesized HA powder is nearly pure. Broad peaks are obtained in the XRD pattern which indicates the formation of crystalline phase in sample calcinated at 200° C and 600° C which increases with increase of temperature. As the temperature is increased to 1200° C, width of some XRD peaks of HA powder become narrower, clear and separate indicating the increase in crystallinity.

SEM shows that the synthesized HA powder constitutes spherical particles with fine grain in nano range. The nano sized HA powder can be extremely useful as a bone replacement material.

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