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EDX, XRD, SEM, FTIR of Hydroxyapatite Synthesized by Wet Chemical Precipitation

Abstract: *In the present work HA powder is synthesized by wet chemical precipitation method using calcium hydroxide ($Ca(OH)_2$), orthophosphoric acid (H_3PO_4) and ammonium hydroxide (NH_4OH) as precursors. The synthesized samples are further characterized by X-Ray Diffraction, Scanning Electron microscopy, Fourier-Transform Infrared Spectroscopy, Energy-Dispersive X Ray Analysis techniques.*

Key Words: *Hydroxyapatite (HAp), XRD, SEM, EDX, FT-IR*

1. INTRODUCTION:

Hydroxyapatite (HAp) 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] HAp belongs to the family of apatite whose general formula can be written as $M_{10}(XO_4)_6Z_2$. where, M=Ca^{+2}, Sr^{+2}, Ba^{+2}, Na^{+}, Pb^{+2}, La^{+3}, and many rare earth elements; XO_4= PO_4^{-3}, VO_4^{-3}, SiO_4^{-4}, AsO_4^{-3}, CO_3^{2-} ; Z= OH^{-}, Cl^{-}, F^{-}, CO_3^{2-} [3]. The chemical coprecipitation from water solutions containing Ca^{+2}, PO_4^{-3} and 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. EDX characterization technique gives the stoichiometric ratio of synthesized material. Presence of functional chemical groups reveals by FT-IR..

2. METHOD:

Chemical precipitation is done by preparing a suspension consisting 75 g calcium hydroxide, $Ca(OH)_2$, in 510 ml distilled water and a solution of 40 ml ortho-phosphoric acid H_3PO_4, in 200 ml distilled water, in order to obtain a hydroxyapatite slurry. H_3PO_4 suspension is added drop wise to the alkaline solution based on $Ca(OH)_2$, at constant 75°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 NH_4OH, yielding a hydroxyapatite having stoichiometric ratio Ca/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°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°C, 600°C and 1200°C for two hours.

FIGURE 1. Sample being calcinated at 1200°C in a furnace

FIGURE 2. Samples after being calcinated at 200°C, 600°C and 1200°C

3. CHEMICAL REACTION:

$$10\ Ca(OH)_2 + 6\ H_3PO_4 \rightarrow\ Ca_{10}(PO_4)_6(OH)_2 + 18\ H_2O$$

4. CHARACTERIZATION TECHNIQUES:

The structural characterization of the different heat treated samples is done by XRD. The wavelength used was Cu_{k_α}= 1.5405 Å and the data collected in the 2θ range 10-80°. 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 HAp sample calcinated at 1200°C shows uniform grain size with a narrow distribution showing crystalline structure. Elemental composition was found by EDX.

The FT-IR spectrum shows the different bonding of functional groups at particular wave number. FT-IR spectra were carried out using the infrared spectrometer (Spectrum GX, Perkin Elmer, U.S.A.) in the range of 4000 cm^{-1} to 400 cm^{-1}

5. RESULTS AND DISCUSSION:

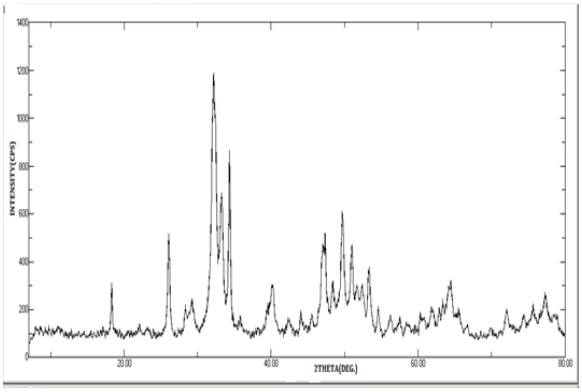

FIGURE 3. XRD pattern for sample heat treated at 200°C

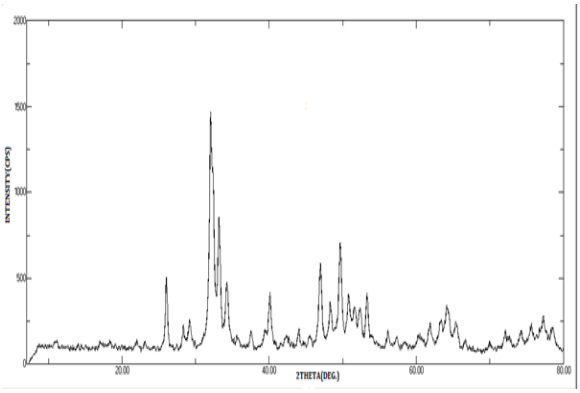

FIGURE 4. XRD pattern for sample heat treated at 600°C

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

From the XRD pattern of the sample heat treated at 1200 °C, The diffraction peaks at 2 θ 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.

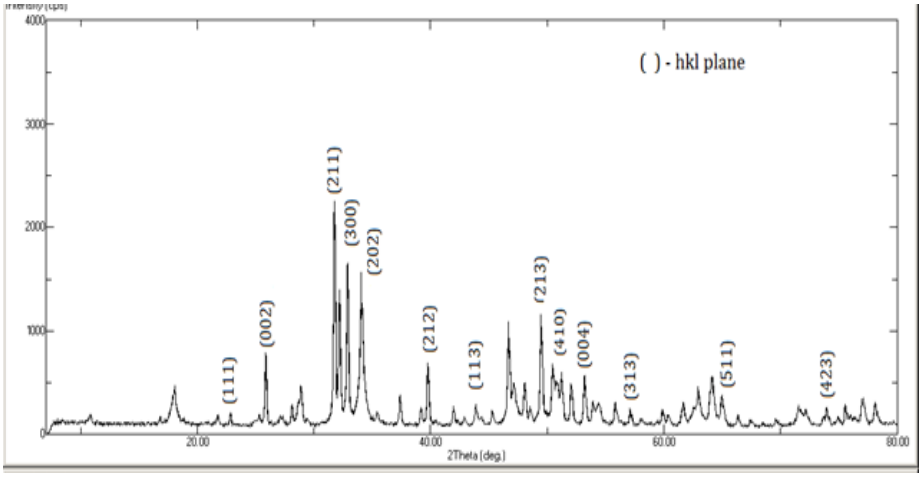

FIGURE 5. XRD pattern for sample heat treated at 1200°C

TABLE 1. Size of HAp nanoparticles using Scherrer's Equation. (For sample calcinated at 1200 ° C)

Peak no.	2θ	d-value	FWHM (W) (in degree)	(h k l)	D = k λ W cos θ (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 HAp 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]

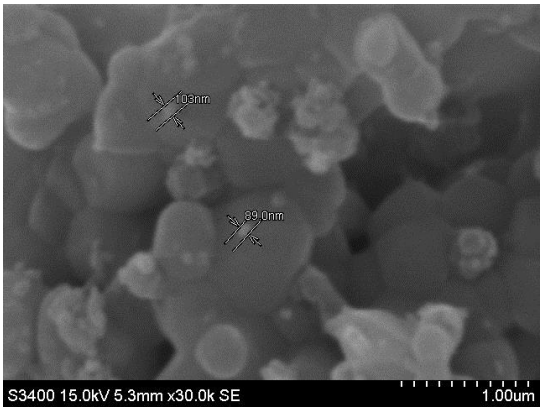

FIGURE 6. SEM pattern for sample heat treated at 1200°C (1µm scale)

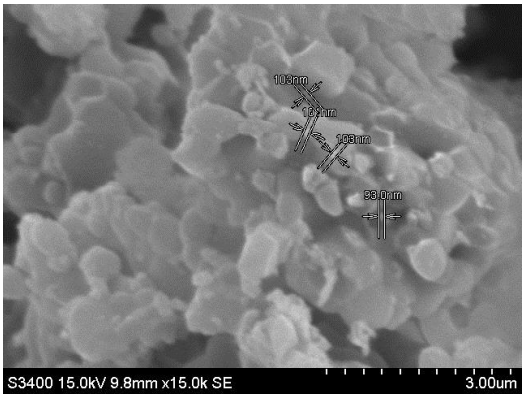

FIGURE 7.SEM pattern for sample heat treated at 1200°C (3µm scale)

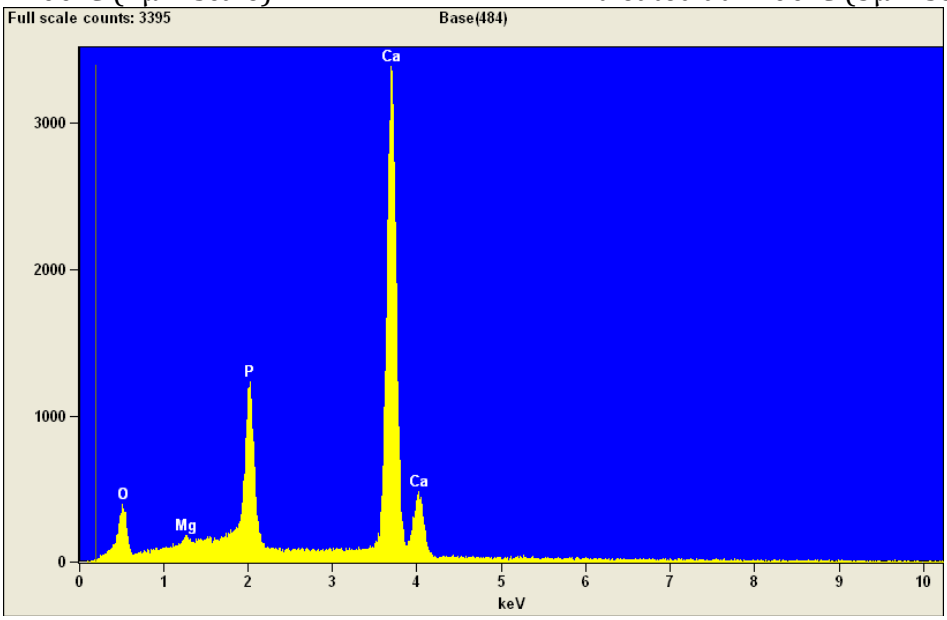

FIGURE 8. EDX spectra of Hydroxyapatite

Standard EDX spectra of nano HAp are shown. Recorded spectrum shows the stoichiometric ratio of Ca/P which is nearly equal to human bone different at different temperature. Ratio near to 1.67 at temperature 600° C and below shows no CaO content while 1.75 and above shows minor amount of CaO for calcined HAp. The more amount of calcium and phosphorus rather than other elements confirms that powder is HAp.[8]

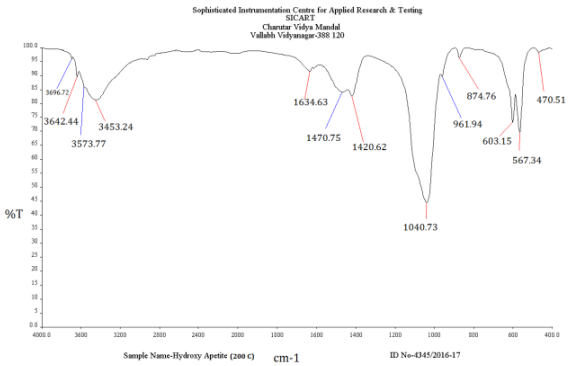

FIGURE 9. FT-IR Spectra of HAp heat treated at 200°C

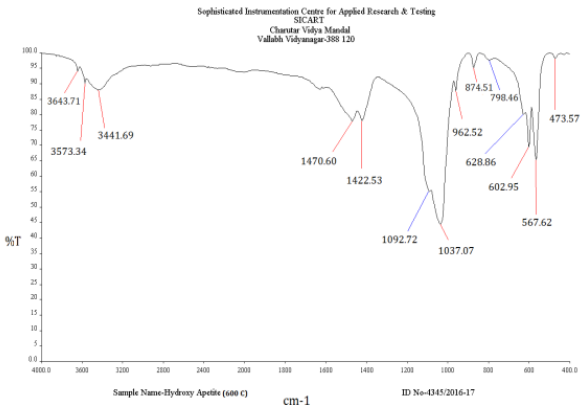

FIGURE 10. FT-IR Spectra of HAp heat treated at 600°C

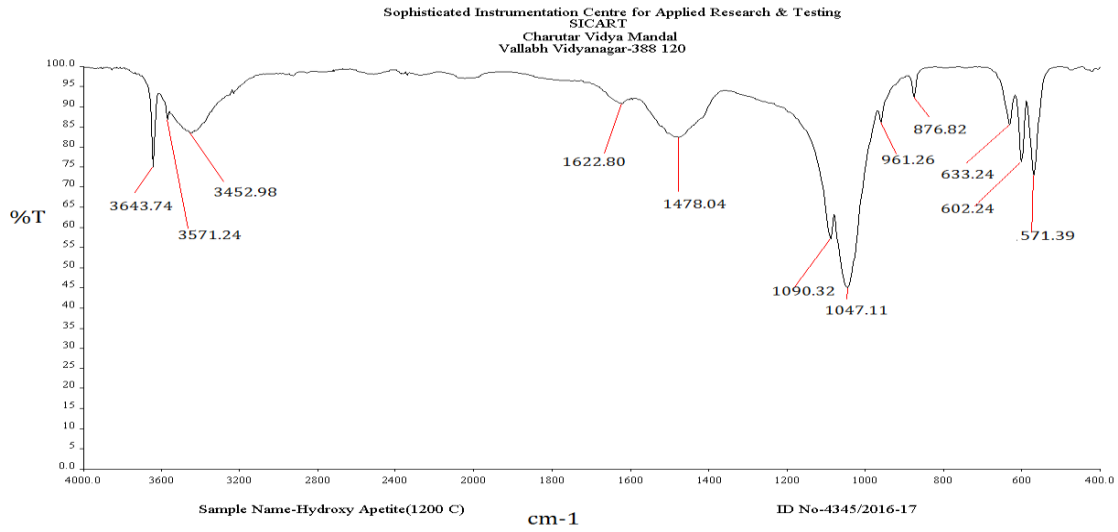

FIGURE 11. FT-IR Spectra of Hydroxyapatite heat treated at 1200°C

FT-IR spectrum shows different peaks for bonding of groups present in synthesized material. The peaks in spectrum at the wave numbers 1047.11 cm^{-1}, 961.26cm^{-1} and 602.24 cm^{-1} are corresponding to asymmetric stretching mode, symmetric stretching mode and bonding mode of vibration indicates the PO_4^{-3} in calcined material at 1200°c temperature[9],[10]. Peaks at wave number 633.24 cm^{-1} and 3571.24 cm^{-1} of stretching and liberation mode confirm the presence of OH^- group[11]. The OH vibration at 3643.74 is due to the decomposition of $CaCO_3$. A weak bond of symmetric stretching mode at 876.82$cm^{-1}$and asymmetric stretching mode at 1420.64 cm^{-1} confirms the minor amount of carbonate in calcined HAp[12],[13]. After the heated at 1200°C, no peak related to CO^{3-} is detected. The broad spectrum at wave number 1622.80 cm^{-1} and 3452.98 cm^{-1} evince the water molecule (adsorbed) entangled in crystalline HAp[14].

TABLE 2. Absorption bands of FT-IR spectra according to chemical groups.

Chemical group	**Mode of vibration**	**Absorption bands (cm-) for 200°C**	**Absorption bands (cm-) for 600°C**	**Absorption bands (cm-) for 1200°C**
1. PO_4^{-3}	Bending	567.34, 602.15	567.62, 602.95	571.39, 602.24
	Sym. Stretching	961.94	962.52	961.26
	Asym . Stretching	1040.73	1037.07, 1090.72	1047.11, 1090.32
2. OH^-	Stretching mode	--	628.86	633.24
	Liberation mode	3573.77	3573.34	3571.24
3. CO_3^{-2}	Sym. Stretching	874.76	874.51	876.82
	Asym. Stretching	1470.75	1470.60	1478.04, 1622.80
4. H_2O (Adsorbed)	Stretching mode	1634.63, 3453.24	1634.63, 3453.24	1622.80, 3452.98

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 HAp 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.

From EDX Calcium-Phosphate ratio to be viewed near to human bone and existence of component in concocted material.

FT-IR analysis and spectra confirms that synthesized material is crystalline HAp.

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