



Development and Characterization of Fumed Silica Filled Hydroxyapatite Composites

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ABSTRACT

In this study, preparation of fumed silica reinforced Hydroxyapatite (HAp) composites having different concentration of fumed silica from 1 to 4wt% has been prepared. XRD studies on HAp calcined at two temperatures have been done and analysed. XRD analysis indicates the structural modification with the addition of fumed silica. X ray analysis of fumed silica filled Hydroxyapatite (HAp) composites dried and calcined showed additional X ray peaks at 46.4 and 28.8 ° in case of 4 wt% fumed silica composite. Diameter of HAp particles changed on changing the calcination temperature.

Key words: Bras, Metal removal rate, Response Surface methodology, EDM

INTRODUCTION

Hydroxyapatite (HAp) is a bio ceramics generally used as replacement material for bones and teeth substitution. Apatite [Ca₁₀(PO₄)₆X₂] family is biocompatible in nature among all phosphate compounds. In this structure, X represents fluoride (F⁻) group for fluorapatite, hydroxyl (OH⁻) group for hydroxyapatite (HAp), and chloride (Cl⁻) groups for chloroapatite. It is well established that for orthopedic use need Ca/P ratio to be 1.52±2.0. (1-12).

Porous HAp has low mechanical strength as compared to pure HAp, which has limited its use. Both mechanical strength and bioactivity of HAp is controlled by grain size, distribution, porosity and crystallinity. HAp powder has been synthesized using several methods such as a) wet chemical method in aq solutions, b) hydro thermal method, c) sol-gel method, d) thermal deposition e) precipitation. However, the low fracture strength has restricted the use of HAp for load-bearing body applications (1-11). The inert ceramic were used in past for physiological system through mechanical interlocking. Among the ceramic reinforcement, alumina (Al₂O₃) was used in orthopedic application due to its excellent wear resistance. But when this oxide was used the decomposition of HAp to β-TCP was reported earlier. Fully densified HAp – Al₂O₃ composites showed a much faster bone-like layer growth than pure HAp, except for 10 wt.% alumina content. There is no study on development of fumed silica filled HAp composite, drying at 85°C followed by calcining at 1050°C and characterization of N20 grade fumed silica filled HAp composite.

In this study, N20 grade fumed silica filled HAp-composites have been prepared by using wet chemical precipitation method and Calcium hydroxide Ca(OH)₂ and Ortho phosphoric acid H₃PO₄ precursors in a muffle furnace and characterized.

MATERIALS AND METHODS

Calcium Hydroxide Ca(OH)₂ (Sigma Aldrich) and Ortho Phosphoric Acid H₃PO₄ (Sigma Aldrich), Ammonia solution 25% (Rankem). All reagents used were of AR grade. Fumed Silica was obtained from Wacker Chemical Fumed Silica Co Ltd. Commercial grade of this fumed silica was N20.

Firstly HAp powder was prepared by Calcium Hydroxide and Ortho Phosphoric acid chemical precipitation route and then fumed silica dispersed in ethanol was mixed with the help of magnetic stirrer and ultrasonicator. After thoroughly mixing, the powders were dried calcined at different temperatures uniformly. In this way, fumed SiO₂-added HAp powders containing 1.0, 2.0, 3.0 and 4wt. % fumed SiO₂, respectively, were prepared. Disk-shaped pellets of HAp containing different amounts of fumed SiO₂ were made by pressing the processed powders in 10 mm diameter circular steel die.

Preparation of HAp by Calcium Hydroxide and Ortho Phosphoric acid By Chemical Precipitation Route

In order to prepare Hydroxyapatite (Hap), Ca (OH)₂ and H₃PO₄ were used as precursors. Solutions of these two materials were prepared with a specific concentration and subsequently, ammonia solution was mixed for maintaining pH. To achieve the good yield the solution was kept for 24 hrs, HAp powder was precipitated and then washed several times to remove NH₃. Precipitate was dried and then calcined.

Deionized water was used in all synthesis steps. 0.5M aqueous solution of Ca (OH)₂ and 0.3M aqueous solution of H₃PO₄ was precipitated. The H₃PO₄ solution was added drop wise into Ca (OH)₂ solution. Addition rate was kept 1 ml min⁻¹. During the process, the pH value of the solution was adjusted to 10.5 by using 25% NH₄OH solution. The reaction was conducted under a stirring rate of 800 rpm at the room temperatures for 10 hrs. The obtained precipitate was aged for 5 h followed by settling for 24 h. It was then washed and filtered in a filter glass with application of mild suction. It was then dried at 85°C for 24 h, calcined at, 850 °C for 4.30 hrs and at 1050°C for 3.30 hrs in a muffle furnace. This was then grounded with an agate mortar (5 g per 60 min) to obtain white HAp powder. Following schematic Fig. 1 shows the flow diagram of preparation of HAp powder from Calcium Hydroxide and Ortho Phosphoric acid by precipitation route (8). Powder samples were calcined at different temperatures. Calcined powder was used for optical photograph. X-ray diffraction studies of all samples were carried at the powder samples calcined at different temperatures.

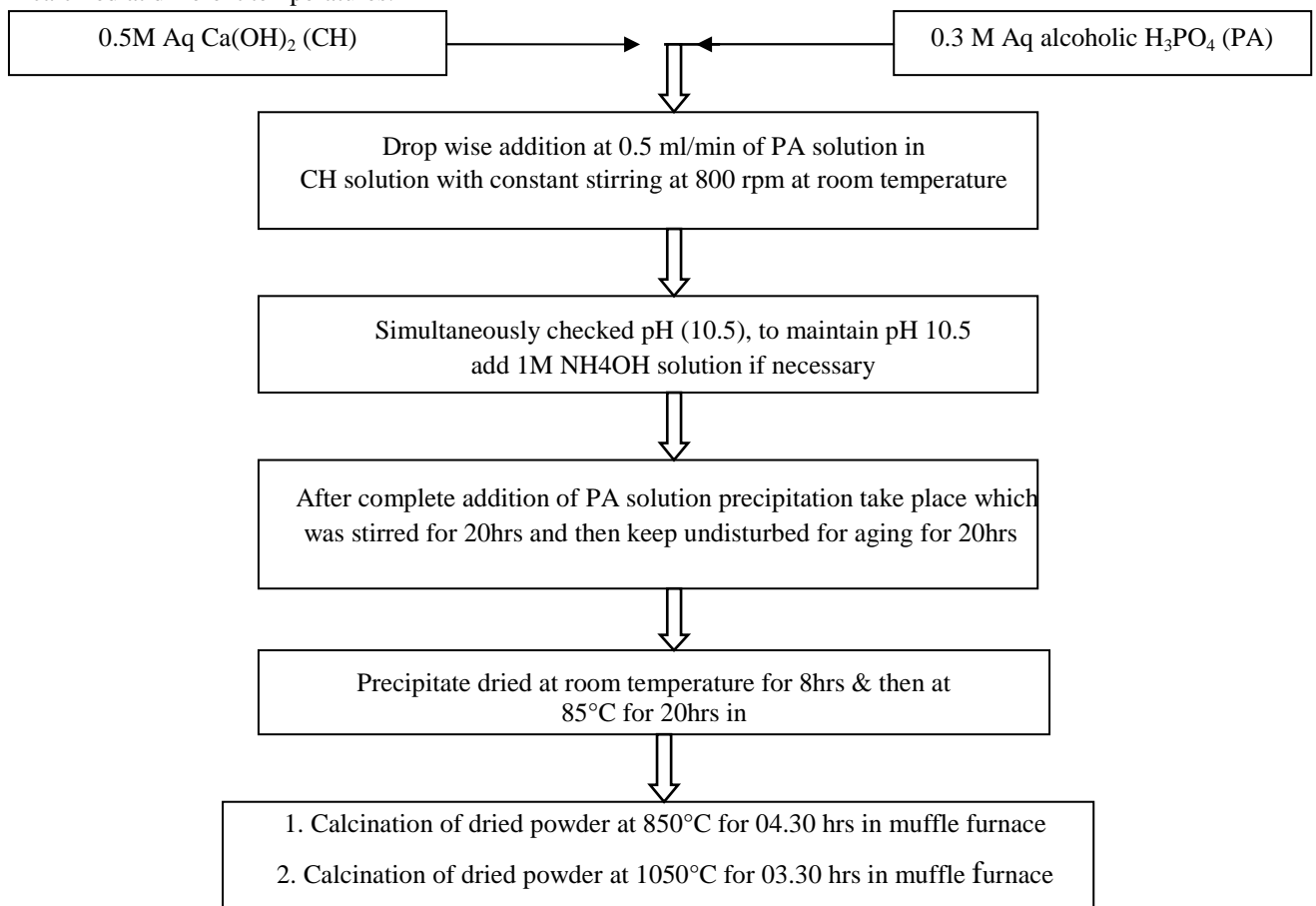


Fig. 1 Flow chart for Preparation of HAp powder

X ray Measurements

X-ray diffraction studies on the powder samples were carried out using a high resolution RIGAKUMINIFLEX DESKTOP VERSION XRD Diffractometer, with a CuK α monochromatic beam ($\lambda = 0.15406\text{\AA}$) produced at 40kV and 40mA. The scanning range (2θ) was performed from 0° to 80° with a step size of 0.02° 2 theta/s (ref)

1. The crystallite size of the sample: Scherrer's Equation
$$X_s = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

2. The fraction of crystallinity (X_c) of the HAP nanoparticle calculated from the equation:
$$X_s = \left[\frac{0.24}{\beta} \right] \quad (2)$$

3. Specific surface area of the HAP determined by the formula:
$$S = \frac{6 \times 10^3}{d\rho} \quad (3)$$

Where β = flex width, ρ = the crystallite size (nm), d = theoretical density of HAP (3.16 g/cm³),
 θ = angle of diffraction (°)

RESULTS AND DISCUSSION

Fig. 2 shows the HAp powder obtained by using Calcium Hydroxide and Ortho Phosphoric Acid by precipitation Route. This powder of pure HAp is of white colour. Table -1 list the Particle Size Analysis Of different temperature calcined HAp powders using a Laser Scattering Particle Size Distribution Analyzer Partica LA-9. In this table it can be seen that the diameter of HAp increased from 1.1128 μm to 2.1090 on calcining the sample at higher temperature 1050° C for low time.

Fig.3. shows the photo of pellets of HAp powders which were made by compacting the powders in a circular compaction die in a hydraulic press.

Fig.4 shows the photos of fumed silica HAp composites compacted in a compaction press by setting the powder in a circular die having different composition of fumed silica filled – HAp Composite powders. Disk-shaped pellets of HAp containing different amounts of fumed SiO_2 (0, 1.0, 2.0, 3.0 and 4wt. % fumed SiO_2 , from left to right).

Fig. 5 shows XRD plots of fumed SiO_2 . This XRD pattern shows a hump and a broad peak due to fumed silica.

Fig. 6 Shows the XRD plot of HAp calcined at 1050°C 3.30 hrs - having 0% fumed SiO_2 . This is mainly the diffraction pattern of HAp. This has the diffraction peaks at 31.65 and 32.8 2θ positions.

Table -1

	Particle Size Analysis of Sample Calcined at 850°C for 04:30hrs	Particle Size Analysis of Sample Calcined at 1050°C for 03:30hrs
Mean Size	7.40021 μm	10.72633 μm
Diameter.	1.1128 μm	2.1090 μm



Fig. 2 HAp powder obtained by Calcium Hydroxide and Ortho Phosphoric Acid by precipitation Route



Fig.3 Pellets of HAp powder



Fig. 4 Pellets of HAp powder

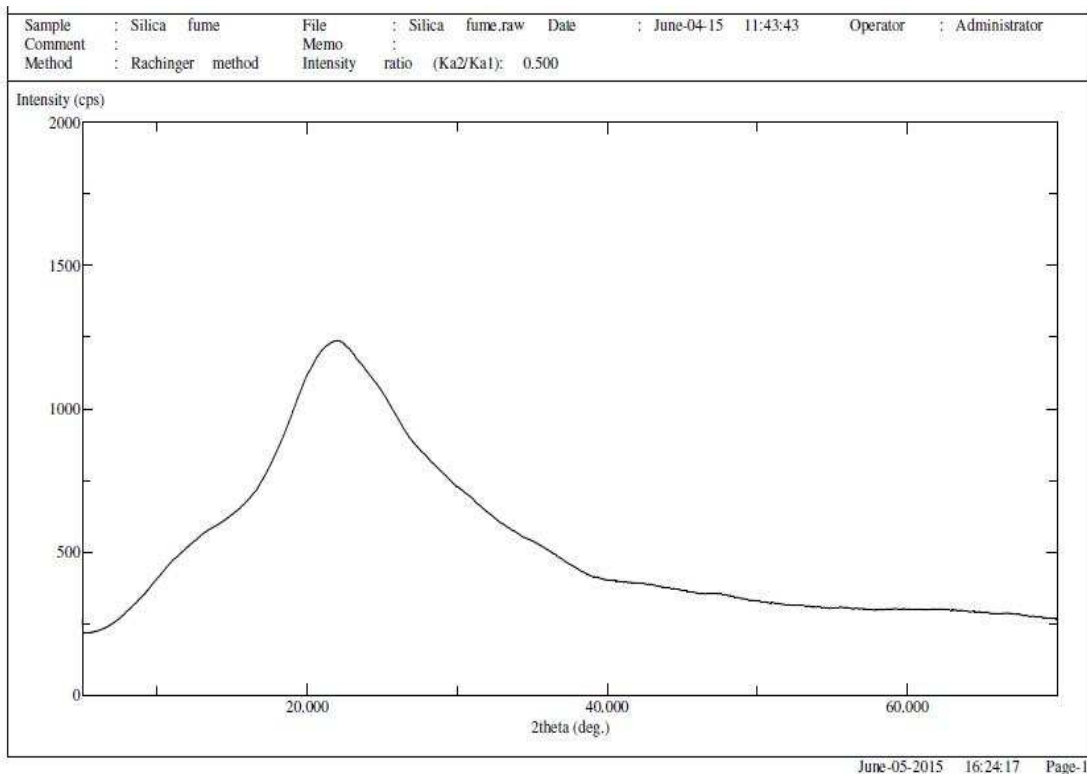


Fig. 5 XRD plots of fumed SiO₂

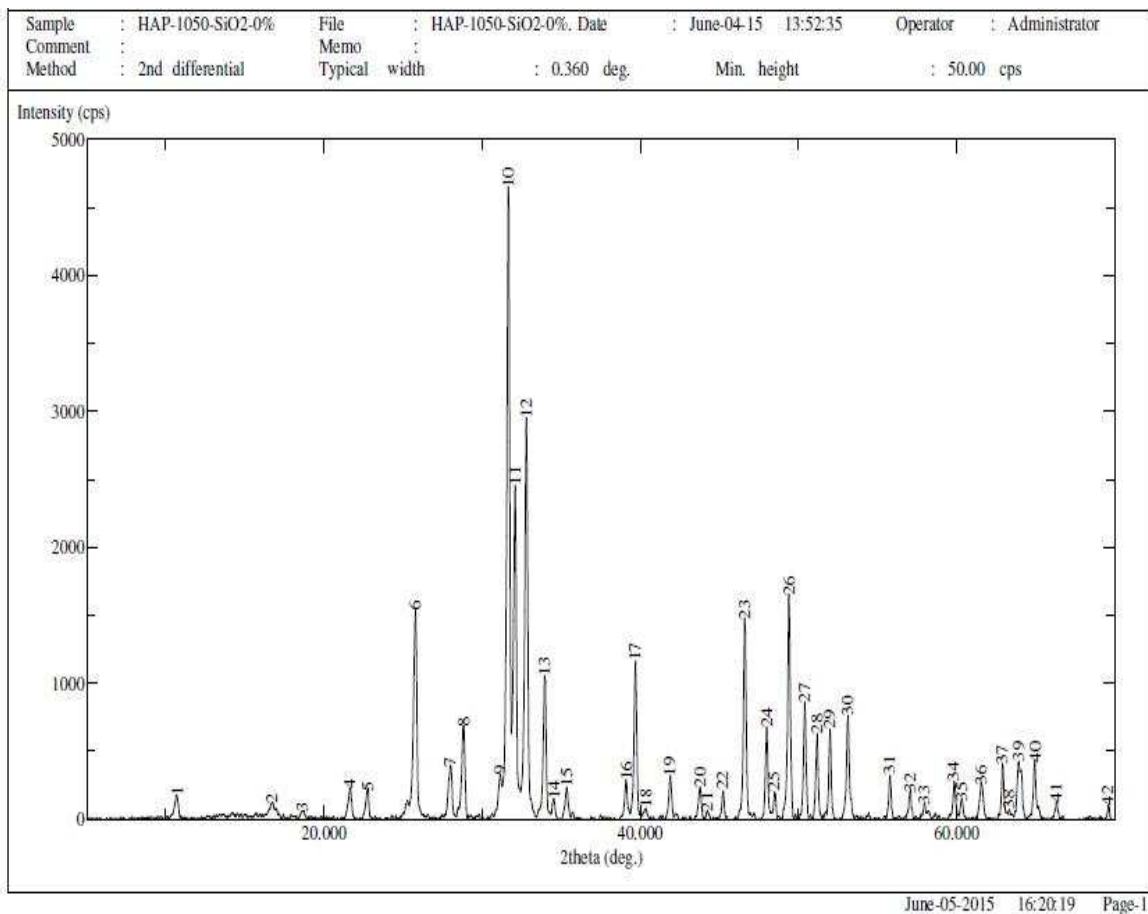


Fig. 6 XRD analysis of HAP -1050 -having 0% fumed SiO₂

Table -2 Lists the XRD Data of HAp Calcined at 1050°C for 3.30 hrs and having 0%SiO₂ Composite

I/O	d value	2 theta	Flex Width
100	2.8246	31.650	0.235
64	2.7282	32.800	0.299
53	2.7861	32.100	0.235
36	1.8434	49.400	0.235
34	3.4503	25.800	0.235
32	1.9474	46.600	0.235
25	2.2685	40.350	0.294
23	2.6384	33.550	0.294

Table -3 lists the XRD Data obtained from HAp Calcined at 1050°C for 3.30 hrs 1%SiO₂ Composite

I/O	d value	2 theta	Flex Width
100	2.8290	31.600	0.235
64	2.7322	32.750	0.235
51	2.7945	32.000	0.235
34	3.4635	25.700	0.294
33	1.9494	46.550	0.294
24	2.6421	39.00	0.235
23	2.2712	39.650	0.235
16	3.1026	28.750	0.294

Fig. 7 shows XRD of HAp- 1% fumed SiO₂ composite whereas Fig. 8 shows the plot of XRD of HAp calcined at 1050°C for 3.30 hrs composite having 2% fumed SiO₂. Fig .9 shows the XRD plot of HAp calcined at 1050°C for 3.30hrs composite having 3% fumed SiO₂.

Fig. 10 shows the XRD plot of HAp calcined at 1050°C for 3.30hrs composite having 4%fumed SiO₂. An XRD peak at 31.7, 32.75, 25.7, 49.35, 33.9, 46.6, 39.1, and 21.1 corresponds to phase transformation in HAp. XRD patterns of as prepared sample calcined at temperature of 1050°C respectively. These powders exhibited shift in HAp peak position 4% fumed SiO₂ filled Hap composite exhibited 2 theta peaks at 31.65, 32.8, 32.05, 25.2, 46.6, 46.6 ,46.4 and at 28.8°.On adding 4 wt% fumed silica in composite 32.75 peak shifted to 32.05. Two new X ray peak appeared at 46.4 and at 28.8° in case of 4 wt% fumed silica composite.

Several investigators have developed different patterned structures by using different routes and analysis methods [13-14]. These all new 46.4 and at 28.8 ° peaks form different structures as compared to Hap on adding 4%fumed SiO Crystallite size of HAp synthesized by this route and calcined at 1050 °C had 42 nm size.

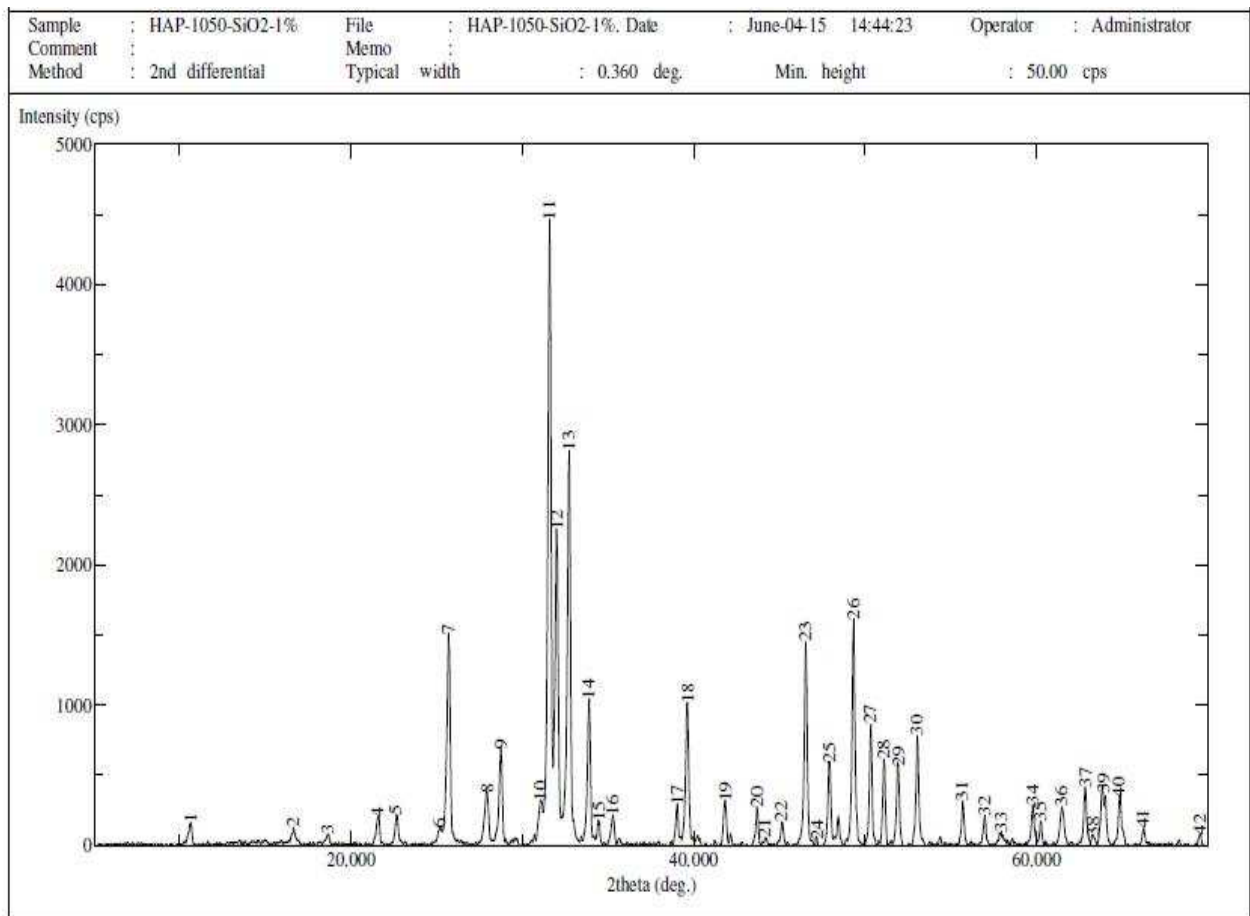


Fig. 7 XRD of HAp- 1% fumed SiO₂ composite

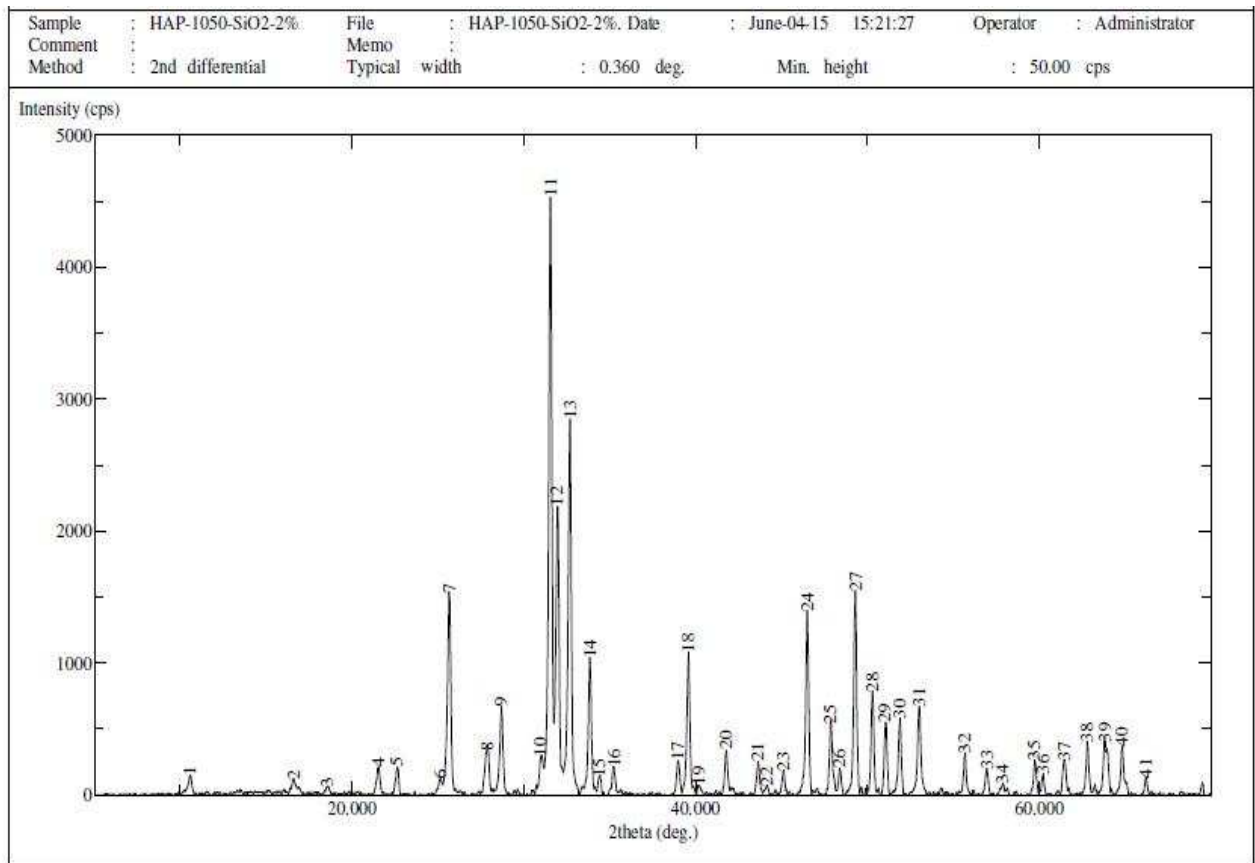


Fig. 8 XRD of HAP- 2% fumed SiO2 composite

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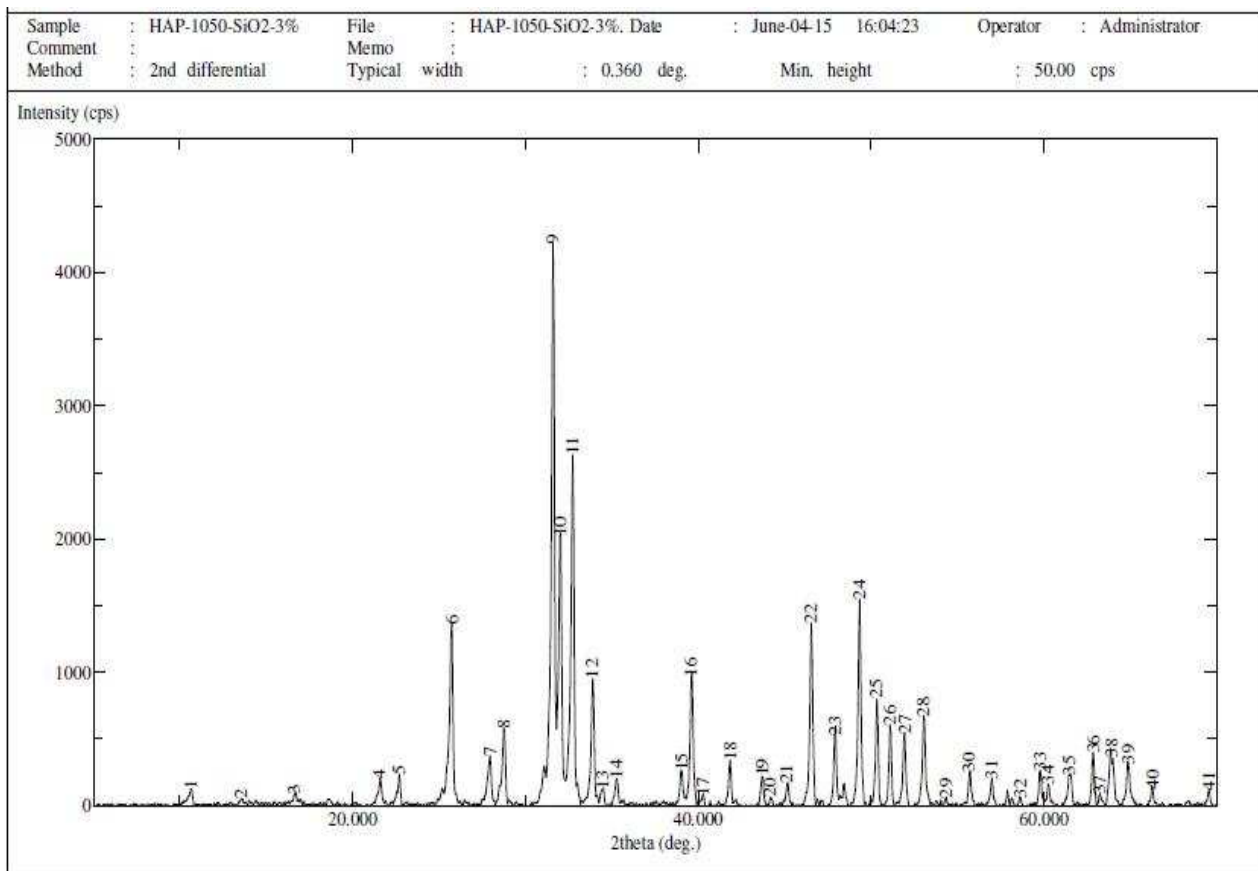


Fig. 9 XRD plot of Hap- 3% fumed SiO2 composite

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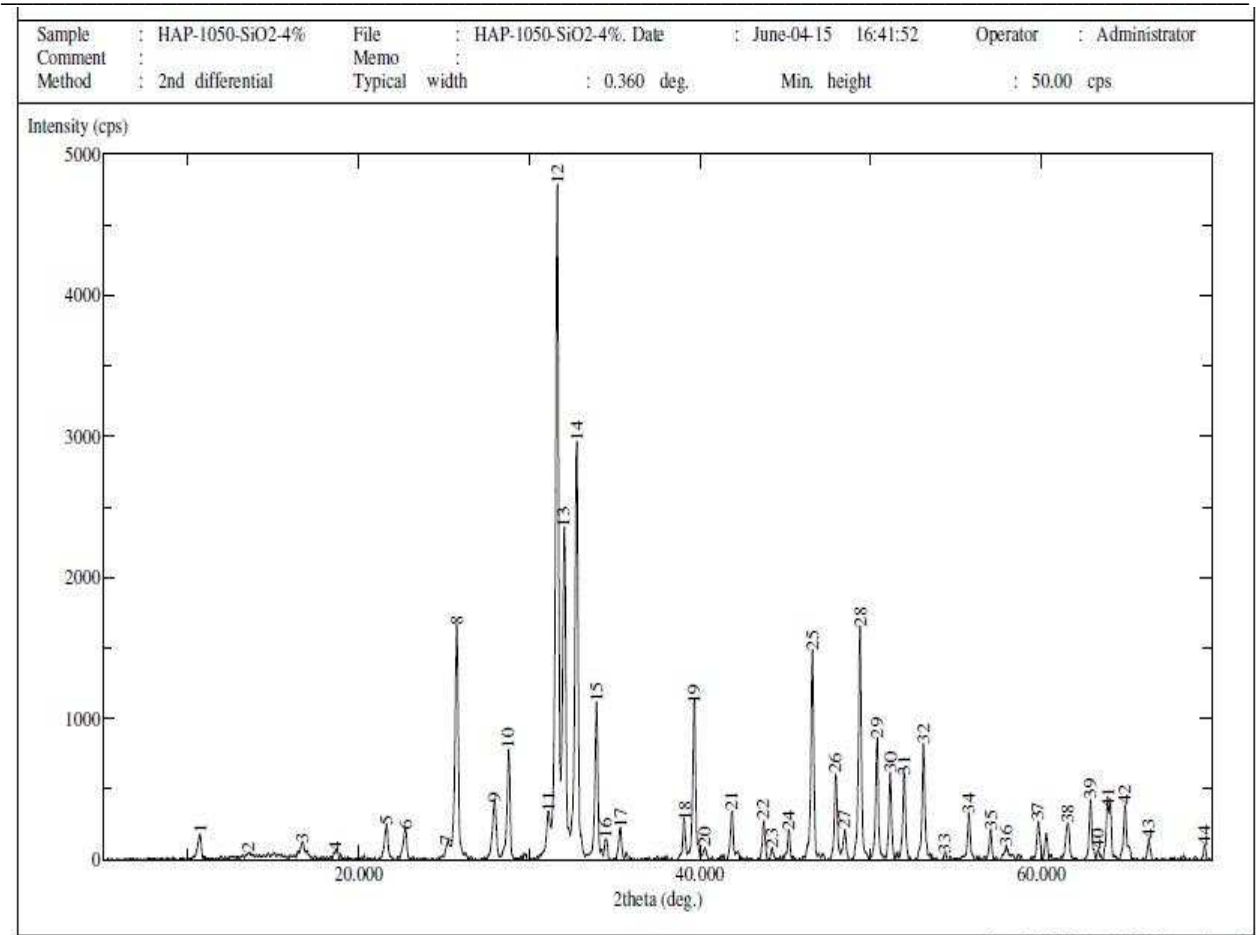


Fig. 10 XRD plot of HAP- 4%SiO₂ composite

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Table -4 Lists the XRD Data of Hap Calcined at 1050°C for 3.30 hrs Composite having 2% Fumed SiO₂

I/I ₀	d value	2 theta	Flex Width
100	2.8334	31.550	0.294
63	2.7363	32.700	0.235
49	2.7988	31.950	0.235
31	1.9513	46.500	0.235
24	2.2740	39.600	0.235
23	2.6459	33.850	0.23

Table -5 Lists the XRD Parameter of Hap Calcined at 1050°C for 3.30hrs 3%SiO₂ Composite

I/I ₀	d value	2 theta	Flex Width
100	2.8290	31.600	0.235
63	2.7322	32.1750	0.235
48	2.7945	32.000	0.235
33	3.4569	25.750	0.235
23	2.6421	33.900	0.235
19	1.8108	50.350	0.294
17	1.7248	53.050	0.235
17	1.1248	21.100	0.412

Table-6 Lists the XRD Parameters of HAP Composite having - 4% fumed SiO₂

I/I ₀	d value	2 theta	Flex Width
100	2.8246	31.650	0.235
62	2.7282	32.800	0.235
50	2.7903	32.050	0.235
35	3.4569	25.200	0.235
32	1.9474	46.600	0.235
22	1.9474	46.600	0.588
19	1.8091	49.400	0.235
17	3.0974	28.800	0.294

CONCLUSION

- Fumed silica filled Hydroxyapatite was successfully prepared by wet chemical precipitation method.
- Two new X ray peaks appeared at 49.4 and at 28.8 ° in case of 4 wt% fumed silica composite.

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