International Journal of Latest Trends in Engineering and Technology
Special Issue - International Conference on Nanotechnology: The Fruition of Science-2017, *pp.169-173*
e-ISSN:2278-621X, p-ISSN: 2319-3778

CHARACTERIZATION OF NI DOPED HYDROXYAPATITE NANOPOWDERS SYNTHESIZED BY SOL GEL METHOD

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Abstract-Hydroxyapatite (HAp) having chemical formula Ca10 (PO4)6(OH)2 is the main chemical component of human bone tissue (70%), to cope up with the bone response as a bio active material. In this study Ni doped HAp powder with triclinic phase was synthesized by sol-gel method, by doping Ni of different concentrations (0.02, 0.04, 0.06, and 0.08). The various properties due to different concentration of Ni in HAp were characterized by X-ray diffraction analysis (XRD), Energy dispersive x-ray spectroscopy (EDX) and Fourier transform spectroscopy (FT-IR). The thermal gravimetric analysis (TGA-DTA) was also carried out to evaluate the stability of the synthesized HAP powder.
Key words: X-ray diffraction, Hydroxyapatite, Crystallite size, Thermal gravimetric analysis.

INTRODUCTION:

Hydroxyapatite $(Ca)_{10}$ $(PO4)_6(OH)_2$ (HAp) is an important inorganic biomaterial which has attracted the attention of researchers related to biomaterials field in recent years. Due to its chemical and structural similarity with the mineral phase of bone and teeth, HAp is widely used for hard tissues repair. As a result, this inorganic phosphate has been studied extensively for medical applications in the form of powders. Hydroxyapatite is the dominant inorganic phase in natural bone. Synthetic hydroxyapatite particles, films, coatings, fibers are used extensively in various biomedical applications [1-2]. This bioceramic, Ca10 (PO4)6(OH)2, can be synthesized by sol-gel method is becoming a unique low-temperature technique to produce pure ceramic powders. Recently, hydroxyapatite powders and coatings have been successfully synthesized by the sol gel method. [3-4]. Nickel has good mechanical strength and is anti corrosion. Substitution of Nickel ions for calcium in apatite compounds will increase the mechanical strength and will be a suitable biomaterial for biomedical applications [5].

2. EXPERIMENTAL PROCEDURE:

In this method two different chemical reactants were used. At first phosphoric pentoxide P2O5 (Merck) was dissolved in absolute ethanol to form a solution and secondly calcium nitrate tetra hydrate Ca_{10} $(NO3)_2.6H_2O$ was also dissolved in ethanol to form 1.67 mol/l solution. After this both the solutions were mixed to obtain the desired Ca/P molar ratio of 1.67. But rapid addition of any one reagent to another reactant can cause precipitation. Hence the solution was stirred slowly for 45 minutes until the formation of a gel. Further the gel was dried in an electric oven with temperature of 110°C in air for 30 minutes. The samples are heated at 600°C for 4 h.

3. RESULT AND DISSCUSSION:

3.1. Powder XRD studies:

The crystallographic phases of HA powder was determined by X-ray diffractometer (XRD) using a diffractometer in reflection mode with Cu Kα (λ=1.54056 Å) radiation. The powder X-ray data set was collected in the 2θ range from 10° to 120° with step size 0.02° at SAIF, Cochin, with a monochromatic incident beam of wavelength 1.54056 Å offering pure Cu-Kα radiations. The obtained data was compared with JCPDS and the crystal structure was confirmed as triclinic, with space group of P-1 from the data (JCPDS No. 44-0778). The obtained XRD profile is shown in figure 1. The peaks indicate the formation of crystalline phase, several peaks of XRD pattern which belongs to the HA powder become more distinct and, also the widths of the peaks become more narrow, which suggests that there is an increase in the crystallinity of powder. The grain size of the prepared samples was determined as 24 nm by Debye-Scherer formula, $D=0.9\lambda/\beta \cos\theta$, where λ is the wavelength of x-rays, β is the full width half maximum of the XRD peak, θ is the Bragg reflection angle. The calculated values of crystallite size for pure and Ni doped hydroxyapatite is given in table 1.

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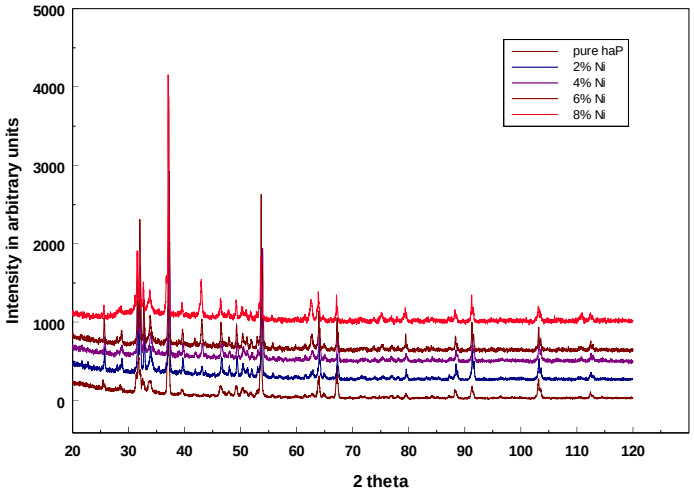


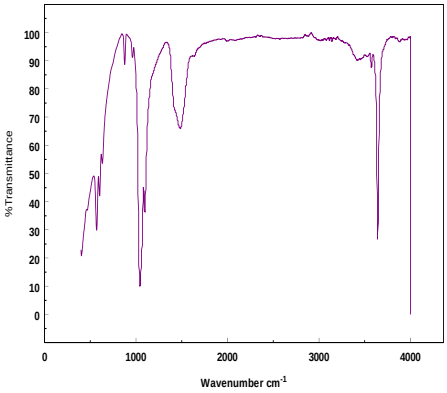
Fig.1. XRD patterns of the pure and Ni doped HAp powder

Table.1. Crystallite size of Hap and Ni-Hap Nanoparticles

Samples	Crystallite Size (nm)
Pure HAp	**15.19**
2% Ni	**23.25**
4% Ni	**25.79**
6% Ni	**28.22**
8% Ni	**28.31**

3.2 FT-IR Analysis:

The presence of functional groups was confirmed using Fourier transform infrared spectroscopy. The spectrum was recorded in the range of 4000–400 cm^{-1} using KBr pellet technique. The resolution of spectrometer was 4 cm^{-1}. The representative FTIR spectrum shows all characteristic absorption peaks of HAp. The FT-IR spectra were obtained over the region 570cm^{-1}–3642 cm^{-1}. The FT-IR spectra are shown in figures 2a-2e. The transmittance data is given in table 2. The first indication for formation of HAp is in the form of a strong complex broad FTIR band centered at about 1000-1100 cm^{-1} due to symmetric stretching mode of vibration for PO_4 group [6]. The crystalline powder generates two characteristic stretching modes of O-H bands at about 3642 cm^{-1} and 3572cm^{-1}. Also there is a O-P-O bending mode in the HAp at 603.48 cm^{-1}.



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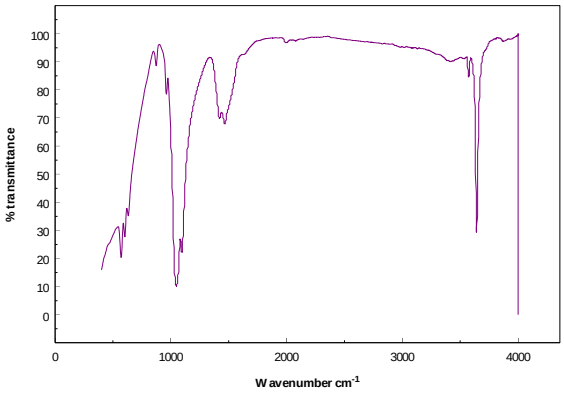
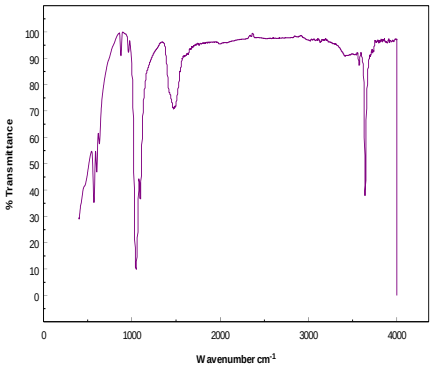


2 (b)



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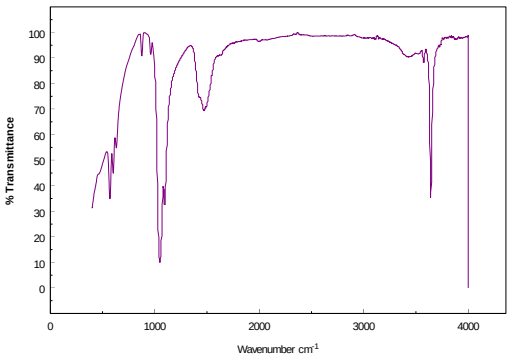

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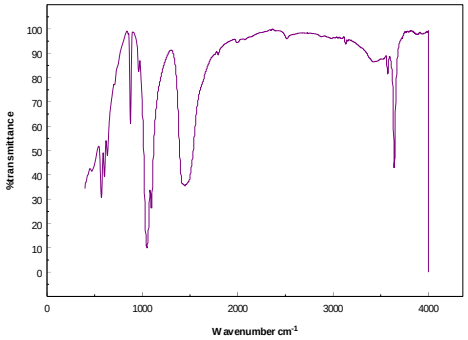


2(e)

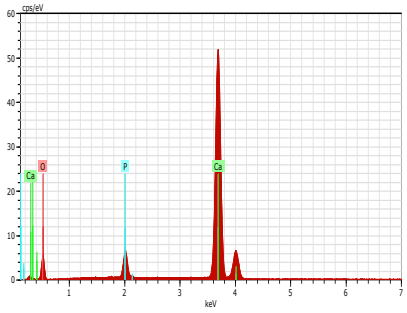
Fig.2. FTIR Spectrum of Ni doped HAp samples (a) Pure HAp (b) 2% of Ni (c) 4% of Ni (d) 6% of Ni (e) 8% of Ni

Table 2.Transmittance data of synthesized Hap samples

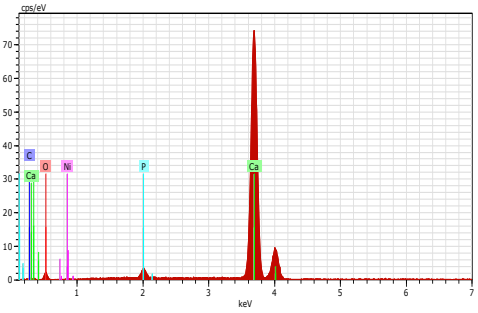
Samples	**Bands(cm)$^{-3}$**	**Groups**	**Modes**
Pure HAp	3642.48	Hydroxyl(OH)	Stretching
2% of Ni	3572.71	Hydroxyl(OH)	Stretching
4% of Ni	1094.72	Phosphate$(PO)_4$	Symmetric
6% of Ni	1471.27	Carbonate$(CO)_3^{2-}$	Asymmetric
8% of Ni	602.91	O-P-O	Bending

3.3 Energy Dispersive X –Ray Spectroscopy:(EDX)

The surface morphology and micro structural features of the synthesized HA powder with elemental composition was studied and evaluated by energy dispersive X-ray analysis (EDAX). EDS makes use of the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis [7]. Qualitative analysis involves the identification of the lines in the spectrum and is fairly straight forward owing to the simplicity of X-ray spectra. Quantitative analysis (determination of the concentrations of the elements present) entails measuring line intensities for each element in the sample and for the same elements in calibration Standards of known composition [8]. The obtained EDS spectrum is shown in figures 3 (a) – 3 (e). The composition of elements is given in table 3.



3(a)



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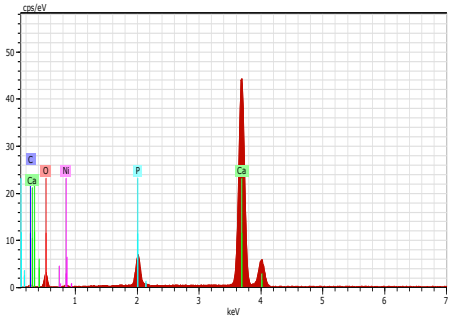

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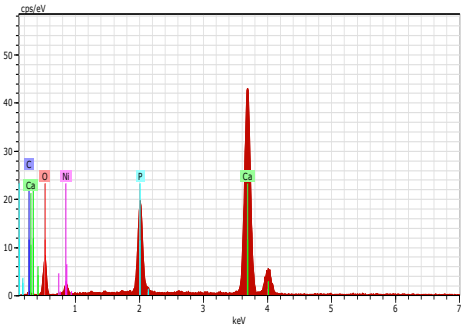

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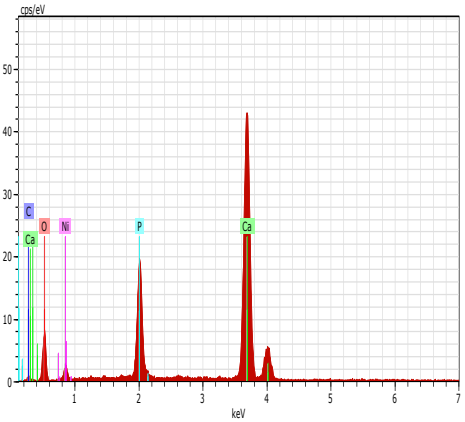


3(e)

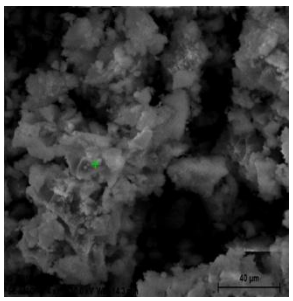
Fig.3.EDS Spectrum of Ni doped HAp samples (a) Pure HAp (b) 2% of Ni (c) 4% of Ni (d) of Ni (e) 8% of Ni

Table: 3 Elemental composition of Hap and Ni-Hap nanoparticles

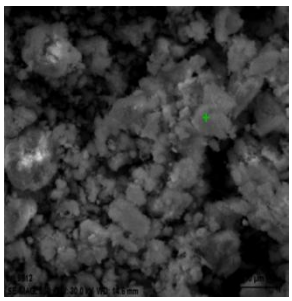
Samples	**Ca**	**P**	**O**	**H**	**Ni**
Pure Hap	71.99	25.32	2.69	-	-
0.02% Of Ni	48.84	45.78	3.28	1.63	0.47
0.04% Of Ni	58.33	29.41	7.08	3.90	1.29
0.06% Of Ni	65.14	17.06	8.09	6.99	2.71
0.08% Of Ni	57.50	22.04	15.31	2.42	2.74

3.4. SEM Analysis(Scanning electron microscope)

SEM data was collected at Gandhigram university, Dindugal. SEM can achieve resolution better than 1 nanometer [9]. The SEM images are shown in figures 4(a) – 4(e). Structural variations are observed for the undoped and Ni doped hydroxyapatite nanostructures.



4(a)



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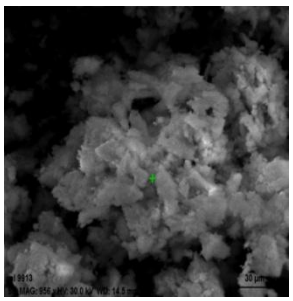

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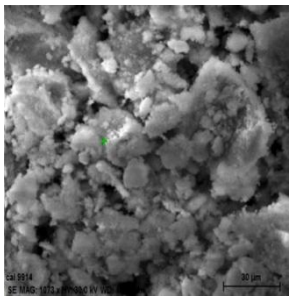
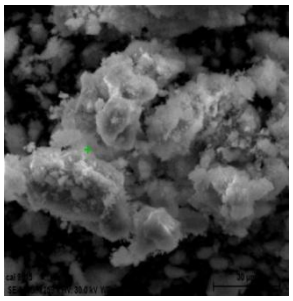


4(d)



4(e)

Fig.4. Surface Morphology of (a) (a) Pure HAp (b) 2% of Ni (c) 4% of Ni (d) 6% of Ni (e) 8% of Ni

4. CONCLUSION:

The present study reveals that HAp powder can be synthesized by sol-gel method. X- ray diffraction and EDX analysis indicates the phase purity and crystallinity of the HAp powder. Sol-gel method is very useful to synthesize the Ni doped bioceramics derived from hydroxyapatite. From XRD data the crystalline size increases with the addition of Ni to hydroxyapatite. The FTIR spectra proved formation of Hap due to the present of OH Structural, PO4 symmetric stretching mode of phosphate functional groups. From EDX spectra the doped and undoped element composition is confirmed.

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