Synthesis and Characterisation of Pure and Doped Hydroxyapatite Nano Powders by Sol Gel Method

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Abstract

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is the main inorganic component of human bones and teeth, showing a very good biocompatibility, bioactivity and osteoconductivity due to its nontoxic, and noninflammatory properties. Nanostructured Hydroxyapatite is extensively employed in orthopedics and dentistry the world over. Biological and physicochemical properties of HA can be improved by the substitution with ions usually present in natural apatites of bone. Most natural apatites are non-stoichiometric because of the presence of minor constituents such as cations (Mg^{2+}, Mn^{2+},Zn^{2+}, Na^{+}, Sr^{2+}) or anions (HPO_4^{2-} or CO_3^{2-}). Hence the present work deals with the preparation of pure, Zn doped and Mn doped Hydroxyapatite nano powders by sol gel method. Structural characterisation was analysed through XRD. Experimental results and the crystallographic parameters matched well with the literature values. The presence of functional groups in the sample was analysed using FTIR analysis. Optical properties were studied using UV-VIS spectrophotometer. Optical band gap value was estimated using Tauc's plot. Surface morphology and chemical compositions were analyzed using Scanning Electron Microscope (SEM) and Energy Dispersive X-ray analysis (EDX) respectively.

1.Introduction

In the last few years nanotechnology and engineered nanoparticles has become an emerging field in the area of materials science. Nanotechnology manipulates matter at an atomic scale creating new nano products with novel properties [1, 2]. The scientific research takes a lot of effort in order to provide new and improved biomaterials with specific applications in medicine[3, 4]. Nowadays, the scientists are looking towards developing new bioactive compounds. Among the

various biocompatible materials, hydroxyapatite is particularly an ideal material with excellent biocompatibility due to the similar chemical properties to the inorganic component in calcified tissues[5]. Hydroxyapatite bio ceramics are frequently used materials in bone implant surgery. However, one of the most important disadvantages of hydroxyapatite biomaterials is their brittleness and low load bearing mechanical property[6]. Thus development of biocompatible hydroxyapatite with enhanced mechanical properties is of great importance.The load bearing disadvantage is usually rectified by synthesizing hydroxyapatite nanopowders through hot processing techniques. An alternative economical way to obtain highly dense hydroxyapatite nanopowders at low temperature is by incorporating additives or dopants during powder processing[7].

2. Experimental

In the present study, calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$), (H_3PO_4) and ammonia (NH_3) were used as starting precursors. The schematic representation of the procedure is given in fig-1. Firstly, 0·25 M phosphoric acid was prepared in double distilled water. Ammonia was added in to this solution, and stirred till a constant pH = 10 was obtained. 1 M calcium nitrate tetrahydrate was prepared by completely dissolving it in double distilled water. This calcium nitrate tetrahydrate solution was slowly added to the above phosphoric acid – ammonia solution, maintaining a Ca/P ratio of 1·67. The solution was kept constant at pH = 10 by further adding small amounts of ammonia. The solution was rigorously stirred for 1 h and kept for ageing for 24 h at room temperature. The gel obtained after ageing was dried at 65 °C for 24 h in a dry oven to get the pure hydroxyapatite nano powder (s1). Then zinc doped hydroxyapatite nano powders were synthesized using mixed aqueous solutions of prepared pure nano hydroxyapatite powder and varying amounts of zinc oxide. The dopants were used in the amount of 50 and 100 wt. % to obtain 50 % Zn (s2), 100 % Zn (s3) , 50 % Mn (s4) and 100% Mn (s5) doped hydroxyapatite nanopowders. The obtained suspensions were filtered and dried in a hot air oven at 373 ^oC for 5 hours.

3. Results and Discussion

3.1. Powder X-Ray Diffraction Studies

The prepared nanopowders were characterized by employing XPERT PRO powder X-ray diffractometer. Fig - 2 shows the recorded powder X-ray diffraction patterns of pure and doped (50 % Zn, 100 %, 50 % Mn & 100 % Mn) hydroxyapatite nanopowders. It shows that the pure sample consists of less crystalline hydroxyapatite nanoparticles (JCPDS card No: 74-0566) compared to that of zinc doped hydroxyapatite nanoparticles (JCPDS card No: 71-0889) and manganese doped hydroxyapatite nanoparticles (JCPDS card No: 75-1112). The crystallite size were calculated according to Debye-Scherrer formula and the average crystallite size of hydroxyapatite nanoparticles is 31.3 nm, 68.9 nm, 69.3 nm 40.9 nm and 52.2 nm for the pure, zinc doped (50 % and 100 % Zn) and manganese doped (50 % and 100 % Mn) hydroxyapatite samples respectively.

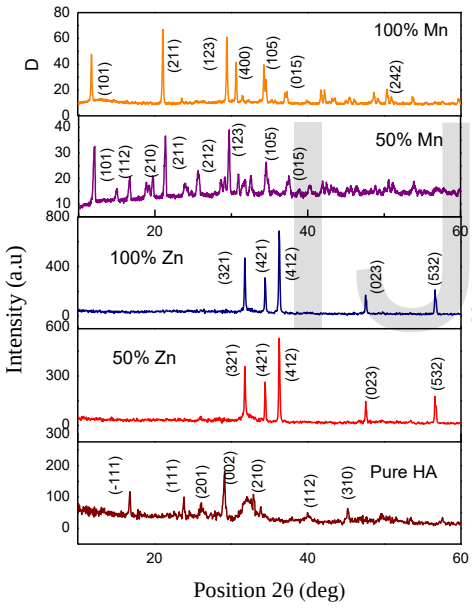

Fig 2: Powder XRD Spectra

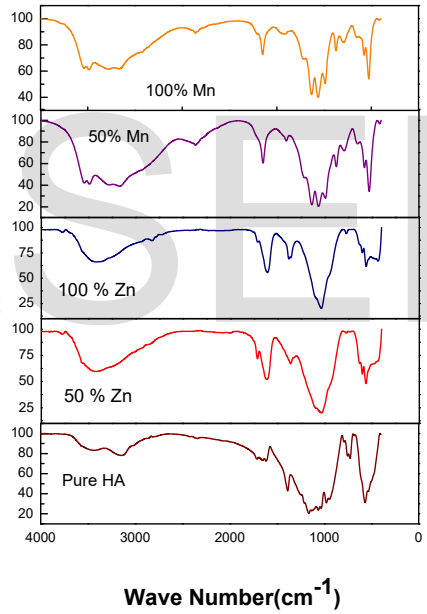

Fig 3: FTIR Spectra

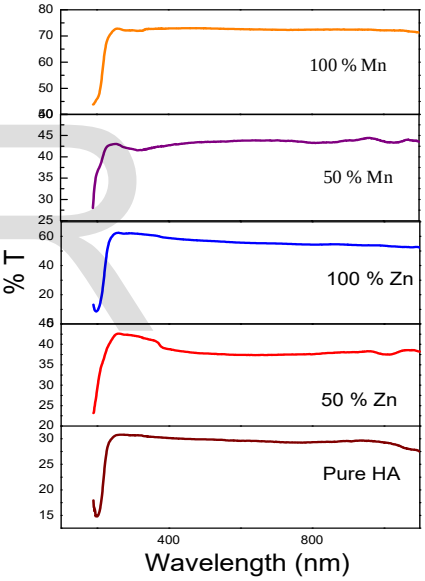

Fig 4: UV-Vis Spectra

3.2. FTIR Spectral Analysis:

Fig 3 shows the FTIR spectrum recorded in the range 400 – 4000 cm^{-1} to identify the functional groups present in the pure and doped hydroxyapatite samples.The observed band positions and their respective assignments are presented in Table-1. It is evident from the Table-1 that the corresponding band positions for H-P-O, P-O , C-O and O-H groups are well-defined

and are in excellent agreement with the characteristic FTIR data for crystalline hydroxyapatite phase. Also the band positions for Zn-O (564, 562 cm^{-1}) and Mn-O (416, 418 cm^{-1})are present in the zinc doped and manganese doped hydroxyapatite samples.

3.3. UV-Vis Spectrophotometer Studies:

The optical transission spectrum of the prepared nanopowders were recorded in the wavelength range 200 - 1100 nm using a Perkin Elmer Lamda 35 UV-VIS spectrophotometer. The obtained transmission spectrum of the pure and doped hydroxyapatite samples is shown in Fig.4. It shows the presence of a wide transparency window lying between 300-1100 nm for the 100 % Zn and 100 % Mn doped hydroxyapatite sample. It was also clear that the percentage of transmittance increases with increase in dopant concentration. The band gap energy was calculated using Tauc's plot and the estimated values are 4.95, 4.8, 4.6, 5.2 and 5.0 eV for the pure, zinc doped (50 % and 100 % Zn) and maganese doped (50 % and 100 % Mn) hydroxyapatite samples respectively.

3.4. EDAX Analysis:

For detailed elemental analysis, the electron microscope was equipped with an energy dispersive X- ray attachment (EDAX).

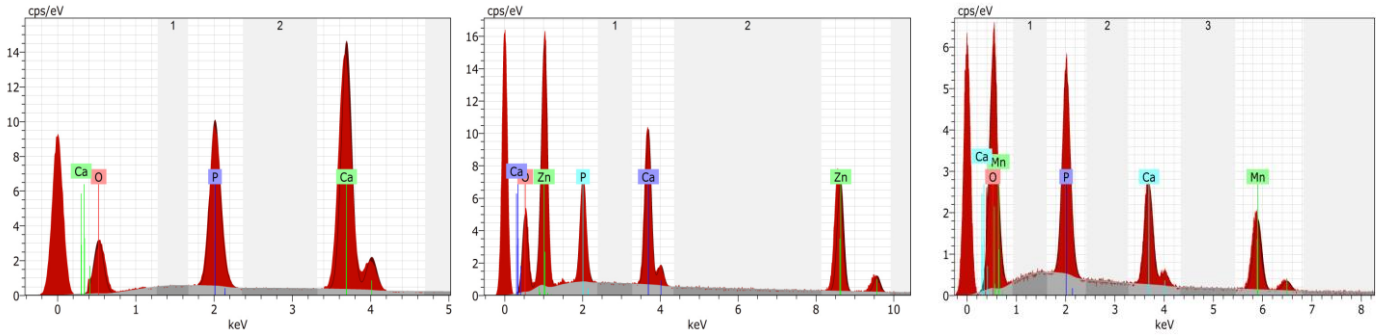

Fig 5a: Pure HA **Fig 5b: 100% Zn** **Fig 5c: 100% Mn**

Fig 5: EDAX Spectra of Pure and Doped Hydroxyapatite Nanopowders

Fig 5 shows the EDAX spectra of pure and doped hydroxyapatite samples. The spectrum confirms the presence of Zn and Mn on hydroxyapatite samples. From fig 5 it was clear that the pure hydroxyapatite sample consists of calcium [Ca], phosphor [P] and oxygen [O] and the Zn

and Mn doped hydroxyapatite sample consists of calcium [Ca], phosphor [P], oxygen [O] along with zinc [Zn] and manganese [Mn] respectively.

4. Conclusion

Hydroxyapatite zinc doped and manganese doped hydroxyapatite nanopowders have been successfully synthesized through sol-gel method. XRD, FTIR, UV-Vis characterizations studies have been done for the synthesized nanoparticles. XRD spectrum reveals the various peaks corresponding to hydroxyapatite, zinc doped hydroxyapatite and manganese doped hydroxyapatite according to standard JCPDS card values.The average particle size was calculated using Debye Scherrer formula. The FTIR spectrum confirms the presence of hydroxyapatite nanoparticles. Optical studies shows that the optical transparency increases with increase in zinc concentration. EDAX studies confirmed the presence of elements in all the samples.

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