Metal Ion Doped Nano-Bio-Ceramic Thick Films for Dielectric Properties

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Abstract : Fe ion exchanged hydroxyapatite (HAp) thick films have been utilized to improve its dielectric properties. HAp nano powder is synthesized by chemical precipitation process and ion exchange route is employed for exchange of Ca ions with Fe ions in HAp matrix. The structural and functional group identification of pure and metal ion doped HAp thick film is examined by means of X-ray diffraction and FTIR spectroscopy. Moreover, surface morphology is visualized by means of SEM analysis. Dielectric properties such as dielectric constant (K) and dielectric loss (tan δ) of pure as well as Fe modified HAp thick films are carried out as a function of frequency (10 Hz-1 MHz). It is observed that, Fe doped HAp thick film improves the dielectric characteristics as compared to pure HAp.

IndexTerms - Nano-Bio-Ceramic Thick film, Dielectric spectroscopy, hydroxyapatite, chemical precipitation

1. Introduction

Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$, abbreviated as HAp], is of considerable interest owing to its potential usefulness as biomaterials, adsorbents, ion-exchangers and gas sensors [1-3]. Synthetic HAp, is analogous to natural apatite, the major inorganic component of bone and teeth [4]. HAp has extensively been studied as filler for bulk bone regeneration and for improving oesteointegration of biomedical implants due to its bioactive and osteoconductive properties.[5]. Recently, HAp has found interesting applications in other areas such as a support for adsorption of bacteria or viruses, for ammonia catalysis, as a catalyst support material, support bone ingrowth and osseointegration when used in orthopaedic, dental and maxillofacial applications.[6-8]. An investigation of the dielectric properties is of interest for biomedical applications. This has several causes. First, the application of electrical fields can accelerate the healing of fractures in bones [9-11]. Furthermore, an electrical stimulation enhances the rate of bone growth for bone grafts in spinal fusion [12-13] and is also used to treat osteoarthritis and osteonecrosis [14]. Finally, the electric poling of HAp enhances its bioactivity [15]. For all these reasons and because bone is a composite of fluids, collagen and the HAp matrix, especially the electric and dielectric properties of HAp are very important.

Accordingly, the present study focuses on the structural, morphological properties of Fe doped HAp thick films and to examine doping effect of Fe ion in HAp matrix for its dielectric properties.

2. Experimental details

2.1 Material synthesis:

Nano-ceramic HAp, used in the present study, is synthesized by wet chemical process. Calcium nitrates ($Ca(NO_3)_2.4H_2O$), and di-ammonium hydrogen phosphate ($(NH_4)_2.HPO_4$) are used as starting precursors as a source of calcium and phosphate. The detail synthesis process of HAp is reported in our earlier work [16]. The ion exchange process is carried out by the addition of known amount of the synthesized nano-HAp powder in variable molar concentrations (0.008, 0.01 and 0.05M) of $Fe(NO_3).6H_2O$ batch solution. All the samples are thoroughly shaken for 5 hours and are allowed to settle for 12 hrs. After the ion-exchange treatment, the particles are filtered off, washed with double distilled water and finally dried in air oven at 100 °C for 10 hours. Thick films are prepared by screen printing technique using ion exchanged Fe-HAp powders as reported earlier [16-20].

2.2 Dielectric measurements:

In the present study, the dielectric measurements are carried out for pure and Fe doped HAp thick films. For dielectric measurements, the films are prepared in the form of sandwich type structure (Ag-HAp-Ag). The bottom electrode (Ag) is screen printed on glass substrate and dried at 100 ^oC for 20 min under IR lamp and further fired at 500 ^oC for 1 h. On the fired electrode a layer of dielectric material (HAp) is deposited by using screen printing and dried at 100 ^oC for 20 min under IR lamp and further fired at 750 ^oC for 1 hour. After firing the dielectric layer, the upper electrode (Ag) is deposited, and after that for drying and firing, same temperature-time regime is carried out as used for the bottom electrode. Dielectric loss, capacitance and resistance are obtained directly from LCR meter. The parameters such as dielectric constant, ac electrical conductivity are calculated by

using the values of capacitance and resistance for pure and modified samples of HAp at room temperature in the frequency range of 10 Hz to 1 MHz.

2.3 Characterization

The structural and surface characterization is carried out using XRD, SEM analysis. X-ray diffraction pattern is recorded with a Bruker AXS Germany (Model D8 Advanced) having CuKα (λ= 1.5405 Å) incident radiation. The XRD peaks are recorded in the 2θ range of 20°–60°. The surface morphology and microstructure, before and after ion irradiation, is visualized by means of Scanning Electron Microscope (FE-SEM Hitachi S-4800).

3. Results and Discussion

3.1. X-ray Analysis

X-ray diffraction profiles of pure & Fe doped HAp thick films as a function of variable molar concentration (0.008, 0.01 and 0.05M) is as shown in Fig. 3.1 (A-D). The XRD phase identification is performed by using JCPDS standard XRD card (09-432), (33-664) for pure HAp and Fe-HAp respectively. All the diffraction peaks present in X-ray spectrum are well matched with their corresponding planes and thus the study confirms the formation of HAp hexagonal phase with highly crystalline nature. The peaks present at 2θ value 33.39°, 41.09 ° and 49.82 ° are due to Fe ions which are pointed out by (#) in Fig. 3.1(B-D). Hence, the study concludes that Fe ion has effectively replaced by Ca ion via ion exchange reaction. Moreover, it is remarkable to observe that addition of Fe ions increases intensities of all XRD peaks with increase in molar concentration up to 0.05 M. The crystallite size for pure and Fe-HAp is calculated by using Debye Scherer's equation. The crystallite size associated to pure HAp thick film is found to be around 37 nm and that calculated for Fe doped HAp with a molar concentration 0.008, 0.01, 0.05 M are found to be 45 nm, 42 nm, 30 nm, respectively.

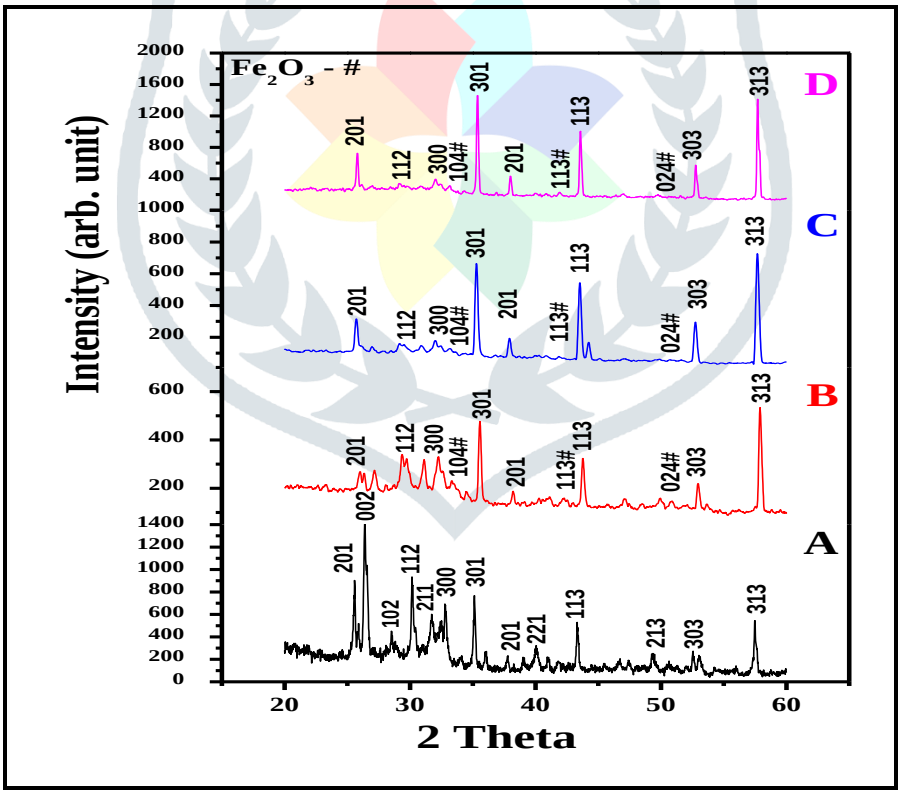

Fig. 3.1(A-D) XRD patterns of Fe-HAp thick films with variable molar concentration; (A) Pure HAp, (B) Fe-HAp (0.008 M) (C) Fe-HAp (0.01 M), (D) Fe-HAp (0.05 M).

3.2 SEM Analysis

Fig. 3.2 (A-C) shows the surface morphology of Fe doped HAp thick films with variable concentration (0.008, 0.01 and 0.05 M) by means of Scanning Electron Microscopy. Fig. 3.2(A) depicts the micrograph of Fe-HAp (0.008 M) which shows the formation of plate like structure due to agglomeration of grains. Similar type of structure with large size plates are observed (Fig. 3.2 (B)) for increased concentrations of Fe-HAp (0.01 M). However, at higher concentration of Fe-HAp (0.05 M), small separated grains are observed with a variable size and shape covering whole surface along with presence of large micropores (Fig. 3.2(C)). It is

well known that large surface area with presence of micropores improves the gas diffusion and removal process thus there is possibility that the sensor performance should be improved [21].

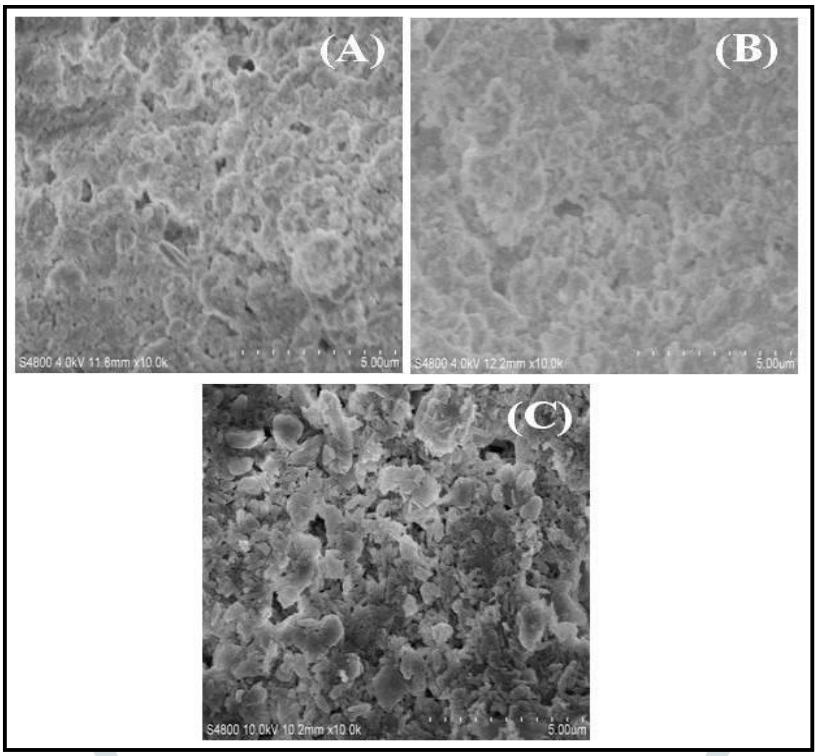

Fig.3.2(A-C) SEM images of Fe-HAp thick films with molar concentrations (A) Fe-HAp (0.008 M) (B) Fe-HAp (0.01 M), (C) Fe-HAp (0.05 M).

3.3 Dielectric Study

The representative dielectric constant (K) profile, for pure and ion exchanged Fe-HAp thick film with molar concentration as a function of frequency is shown in Fig. 3.3(A). It is observed that the dielectric constant decreases continuously at higher frequencies for all the samples and it is found to be in the range of 15–65. At low frequency (10 Hz) the dielectric constant for pure HAp is found to be (K= 15). Furthermore, it can be evidenced from the Fig. 3.4(A) that dielectric constant is found to be increases with increase in Fe ion concentration in HAp matrix and higher dielectric constant is found for Fe-HAp (0.05) thick film (K= 62 @ 10 Hz). These values of dielectric constant are quite higher and comparable with the values reported in the literature for HAp film prepared by screen printing, pulsed laser deposition and sol gel methods [22-25]. Dielectric loss (δ) for pure HAp and Fe-HAp with different molar concentration also shows the dielectric dispersion with increase in frequency as presented in Fig. 3.3 (B). The values of dielectric loss are increases with increase in Fe molar concentrations in HAp.

The qualitative discussion for dielectric properties of HAp is understood as the HAp structure contains several ionic species such as Ca^{2+}, $(PO_4)^{3-}$ and especially OH^- which are present along c-axis in the form of channel. The major dielectric contribution in HAp is due to the dipole moment of hydroxyl ions (ionic) along with small electronic contribution, since HAp bioceramic is an ionic in nature [26]. Variation of dielectric constant is occurred with frequency due to the polarization of the material. Beyond certain frequency of the electric field, the ionic displacement cannot follow the electric field due to their high mass and low mobility. If the frequency of the alternating field increases, a point is reached when the ionic dipole moment cannot keep up with field and the alteration of their direction lags behind the field. As the frequency of the field continues to increase, further at some stage the ionic dipole moment will hardly have started to move before the field reverses and make almost no contribution to the polarization of the dielectric. As a result, the dielectric constant and dielectric loss of a material may decrease substantially as the frequency is increased with applied ac field [27].

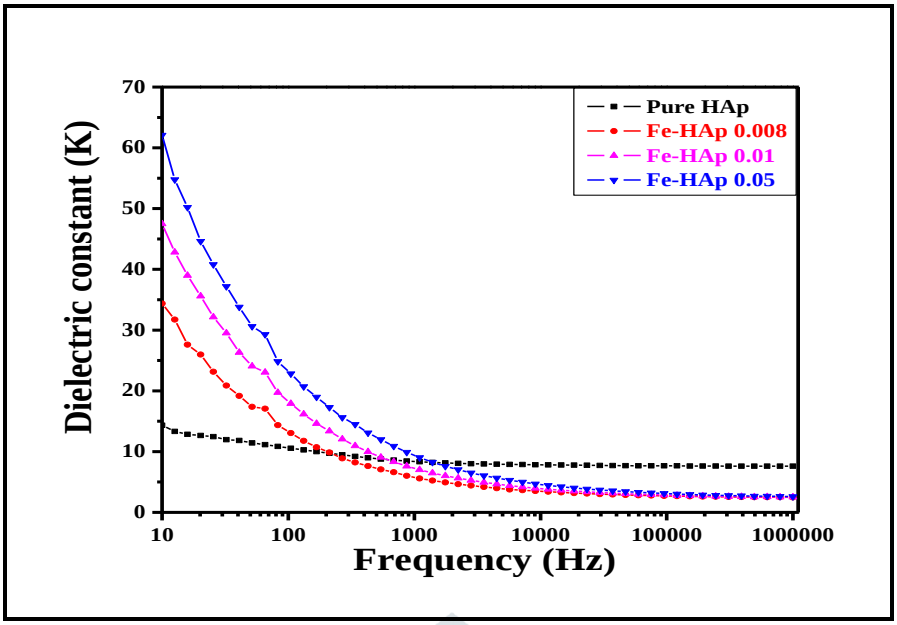

Fig. 3.3(A). Variation of dielectric constant as a function of frequency for pure HAp and Fe doped HAp with molar concentration 0.008, 0.01, and 0.05 M.

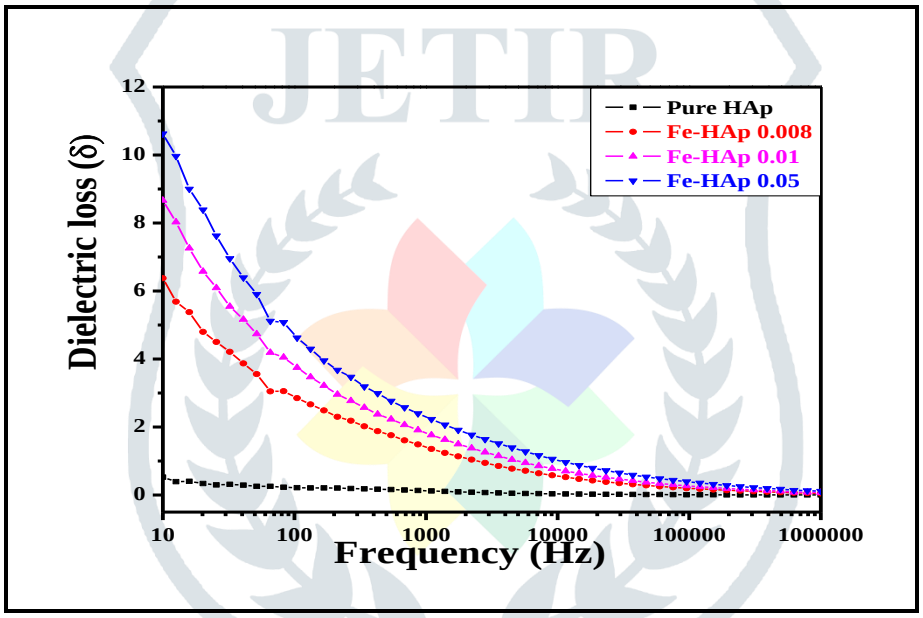

Fig. 3.3(B). Variation of dielectric loss as a function of frequency for pure HAp and Fe doped HAp with variable molar concentration (0.008, 0.01, and 0.05 M).

Conclusions

The Fe doped hydroxyapatite thick films has been synthesized by ion exchange process and utilized to improve the structural, gas sensing and dielectric properties of HAp thick film. The formation of hexagonal HAp phase is identified by X-ray analysis. The surface morphological evolution of pure and Fe-HAp films are visualized by means of SEM analysis. Moreover, in separate study Fe-HAp films exhibit remarkable improvement in dielectric properties such as dielectric constant and dielectric loss. The study concludes that Fe doped HAp thick films show significant improvement in dielectric properties.

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