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Ferroelectric properties of Sr doped hydroxyapatite bioceramics for biotechnological applications

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ABSTRACT

Electrical and dielectrical properties of strontium doped hydroxyapatite ceramics have been investigated by impedance and ferroelectric spectroscopy. SEM, FTIR and EDS techniques were used to analyze the chemical and structural properties of Sr doped HaP ceramics. The structural analysis shows that the particles size of HaP and Sr doped biomaterials are in the range of nanometer, i.e., the biomaterials are nanomaterials. Sr doping changes the particle distribution and particle size of HaP samples. The dielectric constants of the ceramics are significantly changed with Sr doping. The polarization vs electric fields plots indicate that Sr doped HaP samples are ferroelectric materials. It is evaluated that the ferroelectric properties of hydroxyapatite is controlled by Sr doping.

1. Introduction

One of advanced materials is biomaterials which have been extensively investigated for biotechnological applications in recent years. The functional properties of these materials can be improved by nanosize for various applications [1]. The apatites are one group of biomaterials used for biotechnological applications [2–4]. The hydroxyapatite (HAp), $Ca_{10}(PO_4)_6(OH)_2$ is one of calcium phosphate (CaP) ceramics [5,6]. The HaP which has a good a biocompatibility and bioactivity is an important material for bone repairing [7,8]. This material is promising material for biotechnological applications [9–11]. The biological response of HaP is related to electric polarization to manipulate biomedical tissues [12–15]. The electrical polarization is related to dielectric parameters. The dielectric constants of HaP can be improved by various metal ion contents. The improved dielectric and ferroelectric properties of HaP are pertinent to orthopedic and dental applications, etc. [16,17].

In present study, we synthesized nanostructured hydroxyapatite by sol gel method. We have controlled the dielectrical and ferroelectric properties for biotechnological applications. The synthesis and dielectric properties of Sr doped HaP samples were investigated in detail.

2. Materials and method

The strontium (Sr) doped hydroxyapatite (HaP) samples were prepared using the calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) and diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) and strontium acetate. The Sr doped HaP samples were doped for various x ratios (x = 0.1, 0.2, 0.3, 0.4 and 0.5). Firstly, the calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) with nominal value was dissolved in deionized water and stirred for 10 min. Afterwards, the pH of the solution was set to 8 by adding ammonia and the diammonium hydrogen phosphate was added to the solution and stirred for 2 h at 80 °C. Sr doped HaP solutions were prepared with the same procedure. The gel solutions of the samples were dried at 100 °C for 12 h. The obtained powder samples were calcinated at 800 °C for 2 h. the dielectric constants and alternating current conductivity (AC) were measured using a HIOKI LCR meter. The polarization-voltage measurements were performed using a Radiant ferroelectric tester. A Nicolet FTIR spectrophotometer was used to obtain FTIR spectra of the samples. The structural properties of the samples were investigated by JEOL electron microscope.

3. Results and discussion

3.1. Structural properties of Sr doped HaP ceramics

FTIR spectra of Sr doped HaP samples are shown in Fig. 1.As seen in Fig. 1, the observed bands in FTIR spectra corresponds the bands confirming the chemical structure of the samples. The observed

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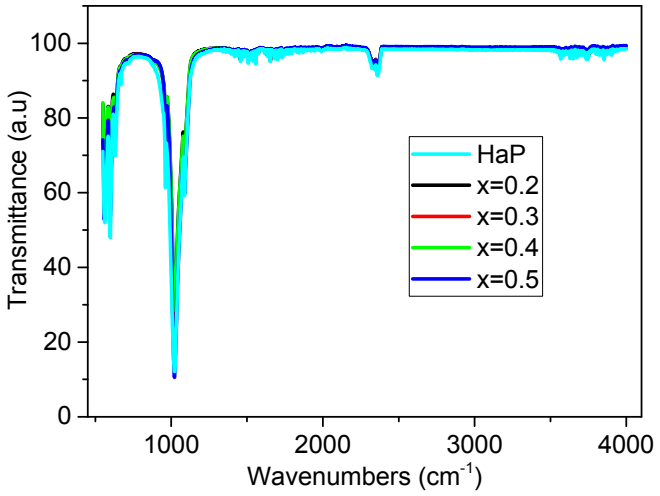

Fig. 1. FTIR spectra of Sr doped HaP ceramics.

bands are the bands of hydroxyl and absorbed water phosphate species. The band observed at 3572 cm^{-1} is related to hydroxyl stretching mode. At 903–962 cm^{-1}, ν_1 stretching mode of PO_4^{3-} group was observed while ν_3 stretching mode was observed at 1032–1092 cm^{-1} [18,19]. For the samples, OH and PO_4 bands was observed at 550 cm^{-1}–650 cm^{-1} and 1091–962 cm^{-1}, respectively. The presence of these bands confirms the formation of HAp and α-TCP structures. The peak intensity of the bands at 560 cm^{-1}–600 cm^{-1} is decreased with Sr doping. This confirms that the substitution of Sr into structure of HaP. The phosphate group was observed with the presence of the bands at 1020 cm^{-1} and 1100 cm^{-1} [16,17]. The chemical structure of HAp samples were confirmed with the observed bands in FTIR spectra confirmed [19].

The scanning electron microscopy images of Sr doped hydroxyapatite samples are shown in Fig. 2. As seen in Fig. 2, the particles size of HaP was found to be in the range of 40–72 nm. This indicates that the particle size of HaP is in the nanosize region. The particle size is changed with Sr doping. The particle size distribution of HaP is controlled by Sr doping. It is evaluated that the Sr doping change both particle size and distribution of particles in HaP. We used X-ray Energy Dispersive spectroscopy (EDS) to confirm the chemical composition of the HaP. For this, we got EDS spectrum of HaP. It is seen in Fig. 3 that the HaP included phosphorus, calcium and oxygen, while Sr doped HaP samples included phosphorus, calcium, and oxygen and strontium elements. The ratio of calcium to phosphorus was found to 1.67 and we gave only one spectra for HaP sample.

In order to determine the crystal structures of the samples, we employed X-ray diffraction technique and XRD patterns of the Sr doped HaP samples are shown in Fig. 4. XRD patterns were analyzed and all patterns confirm the hexagonal phase with the space group of *P*63/*m* and cell constants a = b = 9.4240 Å, and c = 6.8790 Å (JCPDS: 74–0565). In undoped HaP, β-TCP peak was observed and the intensity of this peak is decreased and disappeared. This change indicates the substitution of Sr with Ca ion the hydroxyapatite structure.

3.2. Dielectric properties of Sr doped hydroxyapatite ceramics

We analyzed the dielectric relaxation mechanism of the ceramics using the dielectric spectroscopy. The real and imaginary parts of the complex dielectric constants for the samples are shown in Fig. 5. The dielectric constant and dielectric loss dependence of frequency means that the dielectric parameters of the ceramics are dispersive. As seen in Fig. 5, the dielectric constants of the ceramics are changed with Sr dopant. The change in the dielectric constant is due to the electrical polarization which is controlled by Sr dopant. The doping of Sr into HaP changes the electrical polarization and in turn, the dipole moments in HaP. These moments are oscillated with applied electric field. As seen in Fig. 5, at the lower frequencies, the dielectric constant of the HaP was about 10. After the doping for x = 0.2, it is decreases and after x = 0.3 doping, it increases with Sr content. The obtained ε_r of HaP is close to the dielectric constant obtained by another methods [20,21].

Fig. 6 shows the dielectric loss factor,ε_i, of Sr doped ceramics. The imaginary part of the dielectric constant increases with frequency and exhibited a dielectric relaxation peak and its position is shifted to the higher frequencies with Sr doping. The relaxation mechanism of the Sr doped ceramics was analyzed by Cole-Cole analysis and Cole-Cole plots are shown in Fig. 7. The plots of ε_r vs εi gives two semicircles with the various diameters. It is seen in Fig. 7 that the diameter of Cole-Cole curves is changed with Sr doping. The plotted Cole-Col curves were analyzed by the following relation,

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + (j\omega\tau)^{1-\alpha}} \quad (1)$$

where $\varepsilon^*(\omega)$ is the complex dielectric function, ε_∞ and ε_o are the high and low frequency limiting dielectric constants, respectively, τ is the relaxation time and α is the distribution parameter determining the dielectric relaxation mechanism. The α values for Sr doped ceramics were determined from Cole-Cole curves and the obtained a values indicates that the ceramics exhibited a non-Debye type dielectric relaxation mechanism.

3.3. AC conductivity properties of Sr doped HaP ceramics

The alternating current conductivity (AC) of Sr doped ceramics are shown in Fig. 8. It is seen in Fig. 8 that the AC conductivity increases linearly with frequency and it does not exhibit a direct current conductivity. This confirms that the Sr doped HaP ceramics exhibited an insulator behavior. The insulator conduction mechanism of the ceramics can be analyzed by the following relation [22,23].

$$\sigma(f) = \sigma_o f^n \quad (2)$$

Where *f* is the frequency, σ_o is a constant, and n is an exponent. In order to analyze the conduction mechanism, we should find n value from AC conductivity plot. The n value for the ceramics were found to be about 1.0. The obtained n value indicates that monolinear AC conduction mechanism is taking place in the Sr doped HaP ceramics. Also, we analyzed the DC conduction mechanism with electric resistance measurement. We obtained ~10^{-11} S/cm electrical conductivity of Sr doped ceramics. This also confirms that the Sr doped ceramics are insulator materials and they do not include free electrons.Fig. 8

3.4. Ferroelectric properties of Sr doped HaP ceramics

We analyzed the ferroelectric behavior of the ceramics, because this property is related the electric polarization. The electric polarization behavior is related the polarized surface as biological response for biomedical applications. For this, we measured the polarization versus electric field (P–E) hysteresis curves and are shown in Fig. 9. The polarization plots exhibited the ferroelectric loops and the shape of the loops is changed with Sr content. The