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Lithium-doped hydroxyapatite nano-composites: Synthesis, characterization, gamma attenuation coefficient and dielectric properties

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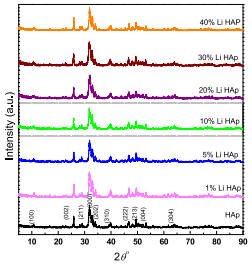
HIGHLIGHTS

- Lithium-hydroxyapatite nano-composites were synthesized by sol-gel technique/microwave-hydrothermal treatment.
- All the studied nano-composites were analyzed by XRD to calculate all lattice parameters.
- FE-SEM/EDS, FTIR and Raman were used to characterize the nano-composites.
- Dielectric properties/ac conductivity were studied in details and analyzed under different frequencies.
- Li-HAp is a new nano-composite useful for medical applications and could be doped with gamma shield materials.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium-hydroxyapatite (0, 1, 5, 10, 20, 30 and 40 wt% Li-HAp) nano-composites were synthesized by sol-gel technique followed by microwave-hydrothermal treatment. The composites were characterized by X-ray diffraction (XRD), Field emission scanning electron microscope (FE-SEM), energy dispersive spectroscopy (EDS), Fourier transform infrared (FTIR) and Raman techniques. Gamma attenuation coefficient and the dielectric properties for all composites were investigated. The crystallinity degree of Li-doped HAp was higher than that of un-doped HAp. Gamma attenuation coefficient values increased from 0.562 cm^{-1} for 0 wt% Li-HAp to 2.190 cm^{-1} for 40 wt% Li-HAp. The alternating current conductivity increased with increasing frequency. The concentration of Li affect the values of dielectric constant where Li doped HAp of low dielectric constant can have an advantage for healing in bone fractures. The calcium to phosphorus ratio decreased from 1.43 to 1.37 with the addition of lithium indicating the Ca deficiency in the studied composites. Our findings lead to the conclusion that Li-HAp is a new nano-composite useful for medical applications and could be doped with gamma shield materials.

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1. Introduction

Apatite is the name of a large mineral calcium phosphate family characterized by its ionic substitution capability. This capability makes it ideal for medical applications (Evis and Webster, 2011). Hydroxyapatite (HAp), also called hydroxylapatite, is an hydroxyl end member of the apatite group with the formula $Ca_{10}(PO_4)_6(OH)_2$ (Suchanek et al., 1997). HAp contains the main mineral component of human bones and teeth where mature bone consists of 60–70% of HAp (Walters et al., 1990; Bigi et al., 2007). HAp is one of the most attractive materials for human hard tissue implants. The close resemblance of HAp to bones and teeth makes this material useful in the medical fields as an implant material in dental and orthopedic applications (Adzilaa et al., 2013; Seeley et al., 2008; Tkalcec et al., 2001; Zhang et al., 2010; Kitsugi et al., 1993; Hontsu et al., 1997). Hydroxyapatite is widely used as a coating on the surface of implant metals/alloys to connect the implant material and bone to promote osseointegration (Metikos-Hukovic et al., 2003). Beside the biocompatibility of HAp, it is of much interest as a drug-delivery medium. For example, porous hydroxyapatite implants are used for local drug delivery in bone (Schwarz, 1998; Wang et al., 2006).

Nano-crystalline HAp would be more desirable in clinical applications. The greater surface area of nano-sized HAp improves its mechanical properties (Ahn et al., 2001; Pramanik et al., 2007). Because of its brittleness, Significant enhancements in strength and toughness of pure HAp have been achieved by making composite materials, using various types of second phases (Choi et al., 1998). HAp is usually doped with the different elements such as Mg, Y, Cd, Co, Ta, Ni and Zn (Kaygilia et al., 2013a). Lithium could be used as a dopant for HAp. The small lithium ions can pass through biological membranes and reach control sites (Kaygilia et al., 2013b). In the literature, the studies on the properties of apatites in the presence of lithium are limited. Lithium causes a decrease in the solubility of hydroxyapatite. The uptake of traces of Li^+ by hydroxyapatite was reported by Mayer et al. (1986) without any change in the crystal structure of the apatite.

It is well known that, bone is a dielectric material. The dielectric properties of hydroxyapatite are important for various hydroxyapatite applications including sensors and bone substitutes (Kaygilia et al., 2014a). It has been found that the application of electromagnetic fields can accelerate the healing of fractures in bones and enhance the rate of bone osteobonding and bone growth Pickering and Scammell (2002).

In this work, we have prepared seven different lithium-hydroxyapatite composites by sol-gel/microwave-hydrothermal technique. Dielectric properties, Phase composition, crystal structure, microstructure, functional groups and gamma linear attenuation coefficient of the composites were carefully investigated.

2. Experimental details

2.1. Synthesis of Li-doped HAp nano-composites

The x wt% Li-doped HAp ($x=0$, 1, 5, 10, 20, 30 and 40) composite was prepared by sol-gel process followed by microwave radiation treatment. 0.5 M calcium nitrate tetrahydrate ($Ca(NO_3)_2\cdot 4H_2O$) and 0.3 M diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) were dissolved separately in distilled water then the $(NH_4)_2HPO_4$ was added drop by drop to $Ca(NO_3)_2\cdot 4H_2O$. The surfactant cetyltrimethyl ammonium bromide ($(C_{16}H_{33})N(CH_3)_3Br$) was added to the solution and stirred for one hour at 90 °C. Ammonium hydroxide was added to keep the pH = 10. Lithium nitrate ($LiNO_3$) was added to the above solution to prepare a different set of Li-doped HAp nano-composites. The stirring continued for another hour till the formation of gel. To obtain the crystalline phase of HAp, Anton Paar microwave synthesis solutions system was used for 20 min at 145 °C and 700 W, then the obtained powder was dried at 100 °C for 24 h.

2.2. Devices and measurements

The as-prepared Li-HAp nano-composites were characterized by field emission scanning electron microscope (FE-SEM) (JSM-7500 F; JEOL-Japan) equipped with energy dispersive spectroscopy (EDS) microanalysis system. X-ray diffraction (XRD) measurements were carried out with Shimadzu LabX-XRD-6000 diffractometer with CuK_α ($\lambda=1.5406$ Å) radiation and secondary monochromator attached with Shimadzu software with pdf-2 library for the analysis of XRD data. The data collection was carried out at room temperature.

FT-IR spectra of Li-HAp were also recorded using THERMO SCIENTIFIC, DXR FT-IR spectrometer by KBr pellet method in the wavenumber range of 4000–400 cm^{-1}.

Raman spectra were recorded using THERMO SCIENTIFIC DXR FT-Raman spectrometer with laser source emitting at 532 nm and had a power of 2 mW.

Gamma attenuation coefficient measurements were measured using lead shielded NaI(Tl) detector 1.5 PX 1.5/2.0 IV (REXON, components, Inc. USA) attached to a universal computer spectrometer UCS-20. The Li-doped HAp composites were irradiated for 100 s using Cs-137 (662 keV) at room temperature. The initial gamma radiation intensity (before shielding with Li-HAp samples) and the final intensity (after shielding with Li-HAp samples) were measured in all Li-HAp nano-composites. All gamma measurements were carried out with the same thickness ($d=1$ mm) of Li-HAp samples.

The dielectric and alternating current conductivity properties were measured using computer-controlled Keithley 4200-SCS semiconductor characterization system.

3. Results and discussion

3.1. X-ray diffraction of Li-doped HAp nano-composites

XRD spectra of un-doped and Li-doped HAp taken within the 2θ range of 5–90° are shown in Fig. 1. The XRD spectra for all the samples were closely identical with the standard HAP (JCPDS card No: 09-0432). No second phases were observed in all composites. Hexagonal lattice parameters ($a = b$ and c) and the unit cell volume (V) of all samples were calculated from the following relations (Cullity, 1978):

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \quad (1)$$

$$V = \left(\sqrt{3}/2\right) a^2 c \quad (2)$$

where d is the distance for two adjacent planes, and h, k and l are the Miller indices. The crystallinity degree (X_c) of HAP was calculated from the following relation (Landi et al., 2000):