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Synthesis and characterization of lithium calcium phosphate ceramics

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Abstract

The crystal structure, thermal, dielectrical, alternating current conductivity and microstructure properties of lithium calcium phosphate ceramics synthesized by the sol–gel method were investigated. The average crystallite size, crystallinity, activation energy and enthalpy of crystallization of $Ca_{10}Li(PO_4)_7$ ceramics were determined. The X-ray diffraction (XRD) results indicated that the apatitic structure belonging to HAp was transformed fully to $Ca_{10}Li(PO_4)_7$ phase with the addition of Li. The Avrami exponents of the samples suggest that the crystallization mechanism is based on the surface nucleation and one-dimensional growth. It was found that the alternating current conductivity mechanism of the ceramics is controlled by the hopping motion involving a translational motion with a sudden hopping. The dielectric constant of the samples shows a small increase with increasing amount of Li.

Keywords: Sol–gel method; Calcium phosphates; Activation energy; Crystal structure

1. Introduction

Ceramics used in biomedical applications are named as bioceramics and, they have been extremely used in the treatment of bones, joints and teeth as implant materials since they possess a lot of desirable properties such as chemical stability and non-toxicity [1–3]. Hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$), with a composition similar to that of the mineral phase of bone and teeth, is one of the most known bioceramics, and its crystal system is hexagonal [4–9]. HAp is both biocompatible and bioactive, as well as osteoconductive [10–13]. Sol–gel, which is one of the most preferred methods, has been used to synthesize HAp with high product purity and low synthesis temperature [14–16]. Additionally, HAp is a dielectric material and can be used in the electrical systems. The electrical and dielectrical properties of HAp are an important scientific issue due to the possible applications of HAp material in the fabrication of biological sensors. Furthermore, the electromagnetic fields have been shown to accelerate healing in bone fractures [17]. For this reason, electrical properties of HAp are very important research topic to determine physical properties, especially microstructures, because these measurements are both non-destructive and rapid [18,19].

The chemical, physical, microstructure and dielectrical properties of HAp have been improved with the addition of specific elements such as Mg, Zn, and Sr. Although Mg and Zn are most preferred and used elements as dopants for HAp, Li^+ ions are smaller than Mg^{2+} and Zn^{2+} and can pass through biological membranes and reach control sites. It is well known that lithium (Li), which is present in the human body in trace amounts, is an alkali metal and is known to be a bioelectric material [18,19]. Li, which is an inexpensive drug, has been used in hematology and psychiatry for the treatment of bipolar disorder. Moreover, the stimulating effects of Li (as lithium chloride and lithium carbonate) on proliferation of the human cells, such as thyroid and pancreatic beta cells, have been reported [20–25].

This work mainly focuses on the synthesis, structural characterization and measurements of calorimetric and physical properties of Li-containing calcium phosphate ceramic samples. The experimental results were compared with hydroxyapatite, since all the ceramic samples were synthesized using HAp (chemical formulae).

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2. Experimental

Lithium calcium phosphate ceramics, having the molar ratio (Ca+Li)/P equal to 1.67, were prepared with two various atomic ratios of lithium (10 and 20 at%) using the sol–gel method. The synthesis of lithium calcium phosphate ceramics was performed using $Ca(NO_3)_2{\bullet}4H_2O$, P_2O_5 and $LiNO_3$ reagents dissolved in anhydrous ethanol. The chemicals were dissolved in ethanol for about 1 h. The prepared solutions with Ca and P were poured into a beaker, and were mixed for about 15 min. Then, Li-containing solution was dropped slowly into this mixture, and vigorously stirred for about 30 min. The obtained gel was shaken into a hot-water bath at 60 °C for 2 h, and was then dried in an oven at 120 °C for 15 h. The dried samples were sintered in an electric furnace at 900 °C for 1.5 h.

X-ray diffraction (XRD) data of the samples were collected on a Bruker D8 Advance Diffractometer using Ni-filtered Cu Kα radiation produced at 40 kV and 40 mA. Differential thermal analysis (DTA) measurements of the samples were performed by a Perkin-Elmer equipment at the heating rates of 5, 10, 15 and 20 °C min^{-1} from ambient temperature to 1000 °C. The possible functional groups were detected by a Perkin-Elmer spectrophotometer in the mid-infrared region (4000–400 cm^{-1}) using the KBr pellets. A 3532-50 LCR HiTESTER was used to measure the values of impedance and capacitance in the range of 10 kHz–1 MHz frequency regions. The microstructure of the samples was studied by a scanning electron microscope (LEO EVO 40VXT) operated at 20 kV acceleration voltage.

3. Results and discussion

The crystal structure of the Li including HAp samples was characterized by X-ray diffraction spectra and XRD results of the samples are given together with those of pure HAp published in previous work [17] in Fig. 1. The average crystallite size was calculated using the Debye–Scherrer equation [26]

$$D = \frac{0.9\lambda}{\beta_{1/2} cos\theta} \quad (1)$$

where λ is the wavelength of X-rays (λ=0.15406 nm for CuKα radiation), $\beta_{1/2}$ is the full width at half maximum (FWHM) in radian and θ is the diffraction angle.

The effective crystallite size (D_{WH}) and micro-strain (ε) values were determined by the following Williamson–Hall equation [27]:

$$\frac{\beta_{1/2} cos\theta}{\lambda} = \frac{1}{D_{WH}} + \frac{\varepsilon sin\theta}{\lambda} \quad (2)$$

Furthermore, the crystalline phases in the XRD patterns of the samples were identified by means of JCPDS (Joint Committee on Powder Diffraction Standards) cards. The presence of crystalline lithium calcium phosphate ($Ca_{10}Li(PO_4)_7$, PDF No. 45-0550) phase, with trigonal crystal structure, was obtained in both samples. XRD results of the samples are in perfect harmony with those of Song et al. [28].

XRD patterns of the samples changed with different Li contents. The magnitude of crystalline peaks in the XRD spectra of the samples decreased significantly with the increase of Li content from 10 at% to 20 at%. With the incorporation of Li into HAp, β-TCP and hydroxyapatite phases disappeared and a lithium calcium phosphate ($Ca_{10}Li(PO_4)_7$ phase was formed with Li content.

The average crystallite size (D_{DS}) was found to be 34 nm for 10 at% Li and 59 nm for 20 at% Li. Also, the effective crystallite size (D_{WH}) was found to be 37 nm for 10 at% Li and 55 nm for 20 at% Li. Both Debye–Scherrer and Williamson–Hall analyses are in accordance with each other. The micro-strain (ε) values were found to be 0.041 for 10 at% Li and 0.096 nm for 20 at% Li, and this parameter was increased about two times with the addition of Li. However, this considerable micro-strain has not been found in other works.

The crystallinity (X_C) can be estimated by the following relation [18]:

$$X_C = \frac{\sum A_C}{\sum A_C + \sum A_A} \quad (3)$$

where $\sum A_C$ is the total area under crystal peaks, and $\sum A_A$ is the total area under amorphous peaks. The $\sum A_C$ and $\sum A_A$ values were determined from total area under crystal and amorphous peaks, respectively, of XRD pattern. It was found that the crystallinity (X_C) for the samples is increased from 85.3% to 94.4%, while the amorphous ratio (X_A) is decreased from 14.7% to 5.6%. The lattice parameters of the samples with trigonal system were calculated to be a=10.693 Å and c=36.569 Å for 10 at% Li, and a=10.340 Å and c=39.103 Å for 20 at% Li. With the addition of Li, a is decreased by about 3%, and c is increased distinctly about 7%. The lattice parameters were changed with the lithium content. Additionally, these values are close to both literature standard values of $Ca_{10}Li(PO_4)_7$ (a=10.421 Å and c=37.388 Å) and values reported by Song et al. (a=10.403 Å and c=37.307 Å) [28].

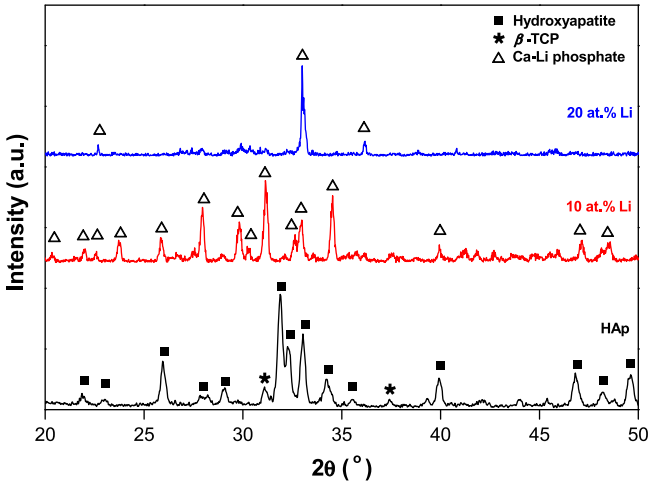

Fig. 1. XRD patterns of Ca–Li phosphate samples and hydroxyapatite.