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Synthesis and characterization of Ce-substituted hydroxyapatite by sol–gel method

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ABSTRACT

Both undoped hydroxyapatite (HAp) and three Ce-substituted HAp samples with variable amounts (from 0.5 to 2 at.%) of Ce were synthesized by sol–gel method. The samples were studied by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy to determine the crystallite size, crystallinity degree, phases, functional groups, morphology and elemental composition. In all samples, the amount of HAp exceeded 92%, while the amount of admixture β-TCP was always below 8% and no changes were observed by addition of Ce. The crystallinity degree of the samples was always within 84–89%, while the calculated dimensions of crystallites appeared to be within 26–35 nm. The microstructure and elemental composition of all the samples were found to be affected by the addition of Ce.

1. Introduction

Hydroxyapatite (HAp), with the chemical formula of $Ca_{10}(PO_4)_6(OH)_2$ and Ca/P ratio 1.67, is one of the most popular bioceramic materials [1–3]. Since it resembles the major inorganic constituent of human bones and teeth [4], HAp implants possess the eminent properties such as non-toxicity, biochemical tolerance, bioactivity and biocompatibility. Therefore, HAp bioceramics have been widely used in medicine including dentistry [5] and orthopedic applications [1–3]. Under the physiological temperature and pH conditions, HAp is a sparingly soluble compound [6,7]. In addition, due to the above-mentioned prominent properties, various types of HAp-based composites, coatings and thin films have been extensively developed and used for biomedical applications by many researchers [8–13].

Various techniques such as sol–gel synthesis, solid-state reactions, chemical precipitation, spray pyrolysis, combustion synthesis, mechanochemical route, microemulsion and microwave synthesis have been developed to synthesize HAp [14,15]. Among the available methods, the sol–gel technique is used to prepare nanostructured HAp of high purity and crystallinity [16–18]. Furthermore, HAp and other calcium orthophosphates might be easily doped with various cations and anions to improve their microstructure, biocompatibility and mechanical properties [19–25].

Cerium (Ce) can act similar to calcium in organisms, so it accumulates in bones in small amounts, therefore, Ce-containing compounds can stimulate metabolism in organisms [26,27]. The electronegativity of metallic Ce is 1.06, while the ionic radius of Ce^{3+} is 0.107 nm. Both values are close to those of Ca (1.01 and 0.100 nm for Ca^{2+}, respectively). Therefore, Ce^{3+} may replace Ca^{2+} in the lattice of HAp. In addition, trivalent Ce^{3+} cations possess some antibacterial properties, which are beneficial for biomedical applications [28].

In the present work, we used a sol–gel method to synthesize both undoped HAp and Ce-doped HAp samples with variable amounts of Ce. The effect of Ce on the crystal structure, morphology and elemental composition of the HAp samples was investigated by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy techniques. Thus, we intended to investigate whether the addition of Ce, which was found to affect the solubility of HAp [28], could influence the crystallite dimensions and microstructure, which might become a crucial starting point in further studies for biomedical applications of the Ce-containing calcium orthophosphates.

2. Materials and methods

Samples of both undoped HAp and Ce-doped HAp were prepared by a sol–gel route. The amounts of Ce were 0 (undoped HAp), 0.5, 1.0 and 2.0 at.% and the samples were referred to as H1, H2, H3 and H4,

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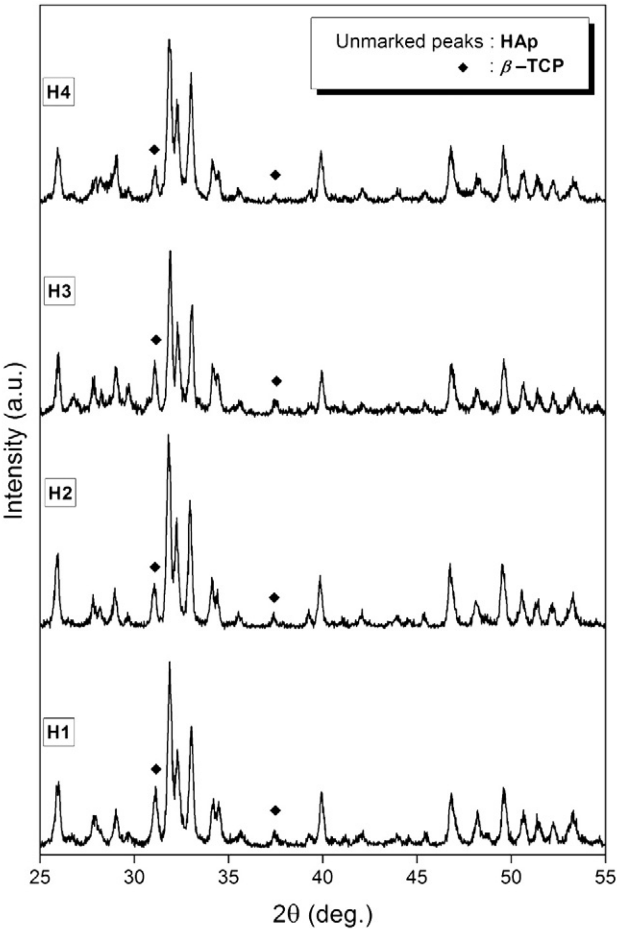

Fig. 1. XRD patterns of pure HAp and Ce-containing HAp samples prepared by sol–gel method.

respectively. To retain the HAp structure and get the comparable results, the Ca/P and (Ca + Ce)/P molar ratios were adjusted to 1.67. The samples were synthesized as follows. Firstly, diammonium hydrogen phosphate (DAP, $(NH_4)_2HPO_4$, Merck) was dissolved in distilled water using a magnetic stirrer. The pH value of the solution was adjusted to 10.5 by addition of NH_4OH (Merck). Secondly, calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$, Merck) and cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, Merck) were also dissolved in one beaker of distilled water using a magnetic stirrer and then the solution was slowly added into the DAP solution. The obtained mixtures were kept stirred for 8 h at 90 °C in closed vessels and white gels were prepared as the result. Then, the gels were dried in an oven for 20 h at 110 °C followed by calcining for 1.5 h at 750 °C. White powders were obtained as the result.

XRD analyses in the range of $2\theta = 25$–$55°$ were performed on a Bruker D8 Advance diffractometer operated at 40 kV and 40 mA. The crystalline phases were identified with reference to the Joint Committee on Powder Diffraction Standards (JCPDS) files. FTIR spectra of the samples were recorded by a PerkinElmer Spectrum One spectrophotometer in the 450–4000 cm^{-1} region. The microstructure of the samples was also investigated using a SEM (JEOL JSM-7001F) operated at 15 kV, coupled with EDX (Oxford Instruments INCA Energy 350).

3. Results and discussion

The XRD data of both Ce-free and Ce-containing HAp samples are shown in Fig. 1. All the diffraction peaks belong to the standard HAp (PDF No: 09-432) except two peaks attributed to β-TCP (PDF No: 09-169). As shown in Fig. 1, no obvious phase changes were noticed in the XRD patterns of the samples with Ce-addition ranging from 0.5 to 2 at.%. For all the samples, the amount of HAp exceeded 92%, while the amount of admixture β-TCP was always below 8% (Table 1). The numerical values of a crystallinity degree (X_C) were calculated according to Landi et al. [29] and appeared to be in the range of 84–89% (Table 1). This finding pointed out to the well crystalline structure of all samples. Furthermore, the crystallinity degrees of all Ce-substituted HAp samples were found to be slightly higher than that of undoped HAp. Thus, addition of small amounts of Ce helped crystallization of HAp. However, since the highest degree of crystallinity was found for sample H2 containing the minimum level (0.5 at.%) of Ce, further increase in the amount of Ce resulted in the decrease in crystallinity degree, which is in a good agreement with the literature data [28]. Probably, this might be due to the charge differences between Ca^{2+} and Ce^{3+} ions. Namely, since HAp easily forms non-stoichiometric Ca-deficient compounds [3], small amounts of Ce^{3+} ions replacing small amounts of Ca^{2+} ions might result in better stoichiometry and, therefore, better crystallinity, while the increased amounts of incorporated Ce^{3+} ions result in decreased crystallinity due to charge imbalances.

The crystallite dimensions (D) were calculated using Debye–Scherrer equation [30]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where λ is the wavelength of the incident X-rays ($\lambda = 0.15406$ nm for CuKα radiation), β is the full width at half maximum (FWHM) in radians and θ is the diffraction angle in degrees. The crystallite sizes were calculated for the perpendicular crystal planes of (002) and (310), and the calculated values of D_{002} and D_{310} were also placed into Table 1. It can be seen that the addition of small amounts of Ce caused some changes in the crystallite sizes. However, except the H3 sample, the D_{002} and D_{310} values of the samples were nearly equal to each other. Nevertheless, the crystallite dimensions of H2, H3 and H4 samples were always bigger than those of undoped HAp (H1). Since the ionic radius of Ce^{3+} ions (0.107 nm) is slightly bigger than that of Ca^{2+} ions (0.100 nm), this effect was attributed to incorporation of Ce into the apatitic structure [31].

Additionally, the calculated values of lattice parameters (a and c) of the samples with the hexagonal crystal structure are put into Table 1 as the last columns. One can see that addition of Ce resulted in changes of lattice parameters. To summarize, the XRD data pointed to incorporation of small amounts of Ce into the crystal structure of HAp. This is not a surprise, since both the radius and the electronegativity of Ce are so close to those of Ca [31,32].

Table 1
The phase and structural data for all samples.

Sample	Phase composition (%)		D_{002} (nm)	D_{310} (nm)	X_C (%)	a (nm)	c (nm)
	HAp	β-TCP					
H1	92.6	7.4	27.46	26.43	84.2	0.9395	0.6854
H2	95.9	4.1	29.76	29.98	89.2	0.9412	0.6880
H3	93.9	6.1	35.01	30.31	86.9	0.9379	0.6854
H4	95.6	4.4	28.42	28.38	85.4	0.9395	0.6864