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Sol–gel synthesis and characterization of Sr/Mg, Mg/Zn and Sr/Zn co-doped hydroxyapatites

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ABSTRACT

In the present work, a series of hydroxyapatite (HAp) samples co-doped with Sr/Mg, Mg/Zn, and Sr/Zn were synthesized using sol–gel method. The formation of the HAp phase was found to be in the range of 93.0–97.4%. Compared to the undoped HAp, with increasing amount of the co-dopants, a gradual decrease in the values of the crystallinity percent, lattice parameters and volume of the unit cell decrease were observed. B-type carbonate substitution was detected for all the samples. All the samples had the morphology consisting of the nanoparticles.

1. Introduction

Hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$), which is a well-known member of calcium phosphate ceramics, has been widely used for biomedical applications because of its non-toxicity, chemically stability, high bioactivity and biocompatibility. HAp has a very similar chemical composition to the inorganic part of human hard tissues such as bones and teeth [1–7].

Several techniques such as sol–gel, hydrothermal, solid state reactions, microwave irradiation and spray pyrolysis have been used to synthesize HAp. Among these techniques, sol–gel is one of the most-preferred methods to synthesize nanosized HAp having high purity and crystallinity [5–7].

Mg, Zn and Sr are trace elements in the human body, and have been used for medical purposes due to their useful properties (e.g., accelerating bone formation) [8–11]. For this reason, in the present study, a series of HAp samples co-doped with Sr/Mg, Mg/Zn and Sr/Zn were prepared using sol–gel technique to investigate the effects of the binary combinations of these dopants, and their characterizations were carried out using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy techniques.

2. Materials and method

The synthesis process of HAp samples was done using sol–gel route, and all the chemicals used in the synthesis were purchased from Sigma-Aldrich. Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$, CN), diammonium hydrogen phosphate ($(NH_4)_2HPO_4$, DAP), magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$, MN), zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, ZN) and strontium nitrate ($Sr(NO_3)_2$, SN) were used as starting reagents. The molar ratios of the above-mentioned chemicals used in the synthesis of HAp samples are given in Table 1. For all the samples, (Ca + dopants)/P molar ratio was adjusted to the value of 1.67.

To prepare the pure HAp sample, CN and DAP were dissolved in distilled water in different beakers. The DAP solution was added drop wisely to the CN solution. 10 ml of 0.5 M citric acid ($C_6H_8O_7$) solution was added and the new solution was mixed at 90 °C for 6 h. After observing the gel formation, this gel was dried in an oven at 120 °C for 15 h and heated in an electric furnace at 700 °C for 1.5 h. Then HAp powders were observed. To synthesize the HAp samples doped with Sr/Mg, Mg/Zn and Sr/Zn, the appropriate amounts of the SN, MZ and SM were dissolved in the same beaker containing CN solution.

XRD analyses were carried out using a Rigaku Rad-B diffractometer. The XRD data were evaluated using the XPowder software [12]. The crystallite size (D) was calculated for both raw and corrected (using a correction for instrumental broadening) data by the Scherrer method [13]. The lattice parameters of a and c and volume of the unit cell (V) were estimated using the relations belonging to the hexagonal crystal system [13]. The crystallinity degree (X_C) was calculated according to Landi et al. [14]. The functional groups were determined by FTIR (PerkinElmer Spectrum One Spectrometer) using the KBr pellet method. The morphological observations were performed using a JEOL JSM 7001F scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) analyzer (Oxford Instruments Inca 350).

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3. Results and discussion

The formation of the HAp phase (JCPDS PDF no: 09-0432) with high crystallinity is observed from the XRD patterns shown in Fig. 1, and the secondary phase of the β-tricalcium phosphate (β-TCP, JCPDS PDF no: 09-0169) is also detected. The formation of the β-TCP is an expected result and is in agreement with the literature [15]. The values of the *D* calculated for (0 0 2) and (3 0 0) planes, phase composition percents, *a*, *c* and *V* are given in Table 2. The HAp phase formation for all the samples is higher than the value of 93.0%. In other words, the percent of the secondary phase of the β-TCP does not exceed 7.0%. All of the as-used co-dopants affect significantly the phase composition. Furthermore, the higher amounts of these dopants inhibit the HAp formation. The crystallinities of the samples are higher than that of the value of 71.6%. Like the HAp formation, the crystallinity decreases with increasing amount of the co-dopants. This decrease is in a good agreement with the earlier reports [16–20]. The *D* values of the co-doped HAps are smaller than that of the pure HAp. The values of the *a*, *c* and *V* are also affected by the

Table 1
The elemental compositions of the HAp samples.

Sample	CN (mol)	DAP (mol)	MN (mol)	ZN (mol)	SN (mol)
HAp	0.0500	0.0300	–	–	–
MZHAp1	0.0490	0.0300	0.0005	0.0005	–
MZHAp2	0.0480	0.0300	0.0010	0.0010	–
SZHAp1	0.0490	0.0300	–	0.0005	0.0005
SZHAp2	0.0480	0.0300	–	0.0010	0.0010
SMHAp1	0.0490	0.0300	0.0005	–	0.0005
SMHAp2	0.0480	0.0300	0.0010	–	0.0010

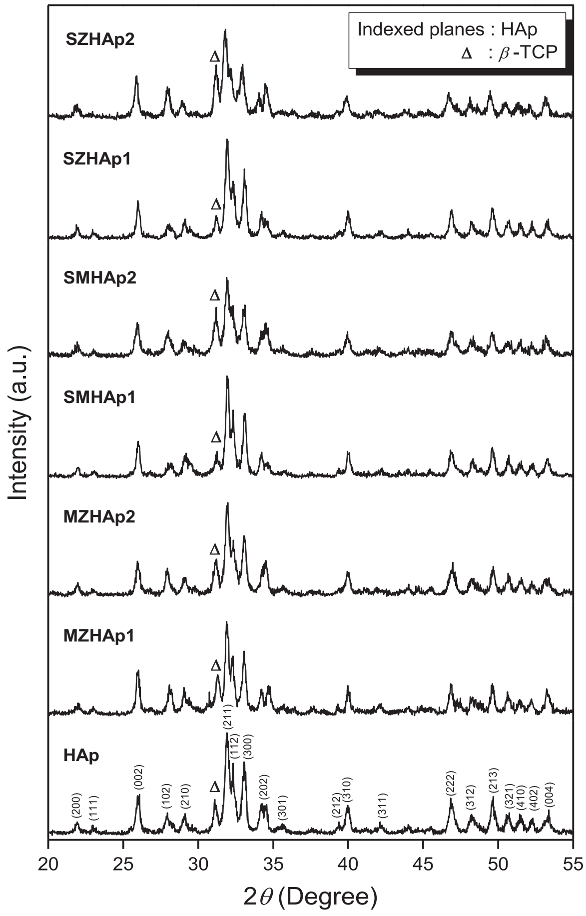

Fig. 1. XRD patterns of the as-synthesized samples.

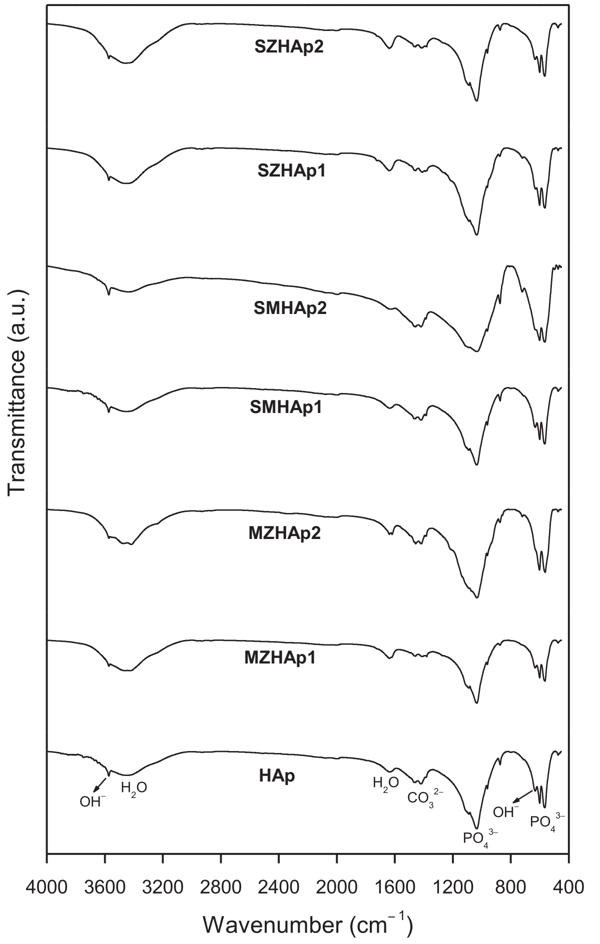

Fig. 2. FTIR spectra of the HAp samples.

Table 2
The detailed XRD analysis result for each sample.

Sample	Phase composition (%)		X_C (%)	D_{002} (nm)		D_{300} (nm)		*a* (nm)	*c* (nm)	*V* (nm^3)
	HAp	β-TCP		For raw data	For corrected data	For raw data	For corrected data			
HAp	96.7	3.3	81.9	33	42	30	38	0.9412	0.6875	0.5274
MZHAp1	95.9	4.1	79.4	29	38	27	35	0.9375	0.6853	0.5216
MZHAp2	94.9	5.1	72.2	25	30	25	32	0.9369	0.6849	0.5206
SZHAp1	97.4	2.6	81.0	31	39	27	36	0.9379	0.6859	0.5225
SZHAp2	94.3	5.7	73.7	30	38	25	32	0.9373	0.6854	0.5215
SMHAp1	97.1	2.9	78.6	30	38	29	37	0.9366	0.6848	0.5202
SMHAp2	93.0	7.0	71.6	26	32	26	34	0.9351	0.6838	0.5178