



Effects of strontium substitution on the phase transformation and crystal structure of calcium phosphate derived by chemical precipitation

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ABSTRACT

This study focused on the effects of strontium substitution on the phase transformation and crystal structure of calcium phosphate. Chemical precipitation was used to prepare Sr-doped hydroxyapatite (HA) precursor powders. The phase transformation of the as-prepared samples during sintering was analyzed. The powders were characterized by X-ray diffraction, X-ray fluorescence spectroscopy, Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. Quantitative analysis of the phase content and fine structure was performed by Rietveld refinement. Sr doping was found to facilitate the phase transformation from HA to beta-tricalcium phosphate (β -TCP) at 1000 °C. The β -TCP content increased with increasing Sr content, causing a decline in the ratio of HA to β -TCP. With Sr contents of ≤ 5 mol%, HA remained the major phase in the biphasic mixtures; in contrast, with Sr contents of ≥ 15 mol%, the mass fraction of β -TCP exceeded 50%. The incorporation of Sr^{2+} into HA and β -TCP caused the lattice parameters of both phases to increase. Additionally, Sr incorporation slightly enhanced the binding energy of Ca. The study confirmed that Sr doping could be used to modulate the phase fractions of HA and β -TCP. The effective partial substitution of Sr in both HA and β -TCP makes these materials promising for bone repair.

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1. Introduction

Calcium phosphate is an important biomedical material, particularly in the form of biphasic calcium phosphate (BCP), which is composed of stable hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) and resorbable beta-tricalcium phosphate (β -TCP, $\beta\text{-Ca}_3(\text{PO}_4)_2$). They are widely used for bone repair because of their similarity to the mineral composition of bone tissue and good biological activity and biocompatibility [1,2]. In hard tissue, biological apatite contains substituted trace elements such as F^- , Mg^{2+} and Si^{4+} . Although only present in trace amounts, these elements are crucial for apatite's biological activity. To mimic the chemical composition and structure of the mineral phase in bone, ion doping is commonly used to modify and enhance the biological properties of BCP material.

It has been reported that ion doping has an impact on the phase composition [3], crystal structure [4] and solubility [5] of calcium phosphate, and also the ratio of HA to β -TCP in BCP [6].

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Changing the phase ratio of HA/ β -TCP can alter the degradability, mechanical properties and biological activity of BCP-based ceramics [7,8]. Strontium (Sr), an essential trace element in humans, has been found not only to increase bone formation but also to decrease bone resorption and reduce the risk of fractures [9,10]. Previous research into the substitution of cations in biphasic mixtures has been limited, and hence the present study focused on Sr-substituted BCP.

To date, less attention has been paid to Sr-doped BCP because of the difficulty of controlling the phase content accurately in synthesized BCP ceramics. There exist different views about the effect of strontium on the phase transformation of BCP. Kumar et al. [11] reported that the β -TCP phase fraction in BCP decreased with increasing Sr content, while Renaudin et al. [12] revealed that doping with Sr^{2+} ions increased the phase content of β -TCP in biphasic mixtures. These contradictory findings may be due to the different synthetic procedures and ion-doping contents. The effect of Sr on the phase transformation of calcium phosphate still remains incompletely understood. It is therefore necessary to investigate how Sr affects the thermal stability and crystal structure of calcium phosphate.

In this work, we synthesize Sr-substituted calcium phosphates with various phase ratios of HA to β -TCP by adjusting the Sr content. Chemical precipitation is used to prepare the Ca-deficient HA precursors and further heat treatment is used to obtain the ultimate Sr-doped calcium phosphates. The effect of the Sr content on the phase transformation of Ca-deficient apatite to a biphasic mixture during sintering is investigated. Furthermore, the crystal structural changes of calcium phosphate and the quantitative HA and β -TCP phase content are analyzed by Rietveld refinement.

2. Materials and methods

2.1. Fabrication of Sr-containing calcium phosphate powders

The Sr-containing calcium phosphate powders were synthesized by chemical precipitation. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{Sr}(\text{NO}_3)_2$ were used as sources of Ca, P and Sr, respectively. The reagents were analytical grade. The Sr content (mol%) in the samples was calculated according to the $(\text{Ca} + \text{Sr})/\text{P}$ molar ratio of 1.67. The amounts of the reactants employed for fabrication are listed in Table 1.

The reaction was carried out at 30 °C. The solutions of $\text{Ca}(\text{NO}_3)_2$ (0.5 M) and $\text{Sr}(\text{NO}_3)_2$ (0.5 M) were mixed and the pH was maintained above 11 by adding ammonium hydroxide. Likewise, $(\text{NH}_4)_3\text{PO}_4$ (0.25 M) solution was prepared at a pH maintained above 10. To avoid nanoparticle agglomeration, polyethylene glycol (0.2 g, Mw 6000) was added as a dispersant to the $(\text{Ca} + \text{Sr})$ solution and stirred vigorously for 0.5 h. Then, the solution of $(\text{NH}_4)_3\text{PO}_4$ was added dropwise to the $(\text{Ca} + \text{Sr})$ mixed solution at a rate of 4 mL min⁻¹ using a peristaltic pump. Following addition, the resulting mixture was stirred continuously for 3 h and then aged for 24 h at room temperature. The resulting suspension was centrifuged three times (twice with distilled water and then once with alcohol), then dried at 50 °C overnight and ground. Finally, to remove the nitrates and obtain various Sr-substituted calcium phosphates, all the precursor powders were calcined in a muffle furnace at 1000 °C for 3 h in air atmospheres, with both heating and cooling rates of 5 °C min⁻¹.

The resulting Sr-containing calcium phosphate specimens, with Sr contents of 0, 5, 15, and 21 mol% relative to Ca, were designated CP, 5Sr-CP, 15Sr-CP and 21Sr-CP, respectively.

2.2. Characterization

The atomic concentrations of the elements Ca, Sr and P in the samples were evaluated by X-ray fluorescence (XRF) spectroscopy (Axios PW4400, PANalytical, Netherlands). The phase composition of the samples was determined by X-ray diffraction (XRD; X'Pert PRO, PANalytical, Netherlands). Data were collected over a 2θ range of 10–70° with a step size of 0.005° and a scanning rate of 0.05° s⁻¹. Fourier transform infrared (FT-IR) spectra was recorded to study the vibrational modes of the powders in the infrared region (Nicolet 360 spectrometer, USA) within the range of 4000–400 cm⁻¹. X-ray photoelectron spectroscopy (XPS) was conducted

to analyze the surface composition and chemical state of the elements (Escalab 250Xi, Thermo Scientific, USA).

2.3. Quantitative analysis by Rietveld refinement

To determine the structures and phase contents of the powders, Rietveld refinement was performed using the GSAS [13] and EXPGUI [14] software. The slow-scanning XRD data were collected with a step size of 0.005° and a scanning rate of 0.05° s⁻¹. The standard crystallographic data for the refinement of HA and β -TCP were as previously published [15–17], using the space groups of the HA structure (P63/m, No.176, $a=9.424$ Å, $c=6.879$ Å, $V=529.086$ Å³) and the β -TCP structure (R3c, No.161, $a=10.439$ Å, $c=37.375$ Å, $V=3527.2$ Å³), respectively.

3. Results

3.1. Elemental analysis

The results of the XRF elemental analysis of the synthesized Sr-containing calcium phosphate powders are shown in Table 2. All the measured $(\text{Ca} + \text{Sr})/\text{P}$ and $\text{Sr}/(\text{Ca} + \text{Sr})$ ratios were lower than the stoichiometric ratio and decreased with increasing amounts of Sr dopant. Furthermore, the amount of Sr dopant was below the theoretical value, suggesting that some Sr ions had remained in the mother liquor during the preparation.

3.2. XRD analysis

3.2.1. Qualitative analysis of phase composition

The XRD patterns of the as-prepared (prior to sintering at 1000 °C) calcium phosphate powders with varying Sr contents are presented in Fig. 1(a). All the diffraction peaks were indexed to HA (PDF Card no. 00-009-0432). However, with increasing Sr content, the diffraction peaks of HA became weaker and the crystallinity decreased. Fig. 1(b) shows the XRD patterns of the samples sintered at 1000 °C for 3 h. As observed, the sintered un-doped calcium phosphate showed sharp and narrow HA peaks. However, with the Sr-doped calcium phosphate samples, additional β -TCP peaks (PDF Card no. 00-001-0941) appeared. The intensity of the β -TCP peaks increased with the Sr content. Sr ions evidently stabilized the β -TCP phase and inhibited the formation of HA during sintering. In addition, Sr²⁺ ions were found to substitute in both HA and β -TCP lattices to form Sr-doped HA (Sr-HA) and Sr-doped β -TCP (Sr- β -TCP).

3.2.2. Quantitative analysis by Rietveld refinement

To investigate the phase content of the samples, the fine structures of the HA and β -TCP phases were analyzed by Rietveld refinement. The structural data for refinement obtained from the powder diffraction patterns of all specimens sintered at 1000 °C are displayed in Table 3. The phase fraction of β -TCP increased sharply when the Sr content was raised from 5 to 15 mol%. HA remained the major phase in the biphasic mixtures when the Sr content ≤ 5 mol%, while the mass percentage of β -TCP was greater

Table 1

Amount of reactants used to synthesize calcium phosphates with various strontium contents.

Samples	$\text{Ca}(\text{NO}_3)_2$ (mol)	$(\text{NH}_4)_3\text{PO}_4$ (mol)	$\text{Sr}(\text{NO}_3)_2$ (mol)	$\text{Sr}/(\text{Ca} + \text{Sr})$	$(\text{Ca} + \text{Sr})/\text{P}$
CP	0.0500	0.03	–	–	1.67
5Sr-CP	0.0475	0.03	0.0050	0.05	1.67
15Sr-CP	0.0425	0.03	0.0075	0.15	1.67
21Sr-CP	0.0395	0.03	0.0105	0.21	1.67

Table 2

Molar ratios of the as-prepared calcium phosphates with various strontium contents assessed by XRF.

Samples	$n(\text{Ca})$ (mol)	$n(\text{P})$ (mol)	$n(\text{Sr})$ (mol)	$\text{Sr}/(\text{Ca} + \text{Sr})$	$(\text{Ca} + \text{Sr})/\text{P}$
CP	0.987	0.630	–	–	1.567
5Sr-CP	0.928	0.624	0.036	0.037	1.545
15Sr-CP	0.793	0.629	0.105	0.117	1.428
21Sr-CP	0.728	0.619	0.148	0.169	1.415

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