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Crystal structure analysis of selenium-doped hydroxyapatite samples and their thermal stability

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ABSTRACT

The aim of this study is to obtain more information about the fine crystal structure of selenium-doped hydroxyapatite (Se-HA) and investigate the effect of Se doping on the thermal stability of HA. Se-HA samples with different Se/P ratios were synthesized by the chemical precipitation method. The physicochemical properties of the powders were characterized by X-ray fluorescence spectroscopy, X-ray diffraction, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and transmission electron microscopy. The results indicate that selenite and a small amount of carbonate co-incorporate into the well-crystallized samples by substituting for phosphate groups. Rietveld refinement was performed to further analyze the crystal structure and determine the crystal structure model of the Se-HA samples. Se incorporation leads to an increase of the *a* lattice parameter and a decrease of the *c* lattice parameter of the crystal lattice. The thermal stability of the Se-HA powders during sintering is also discussed. Doping the HA structure with a small amount of selenium improves the thermal stability of HA. Compared with HA, the Se-HA samples with Se/P $\leq$ 0.05 doping are more stable after heat treatment without any impurities, which makes these materials promising for bone repair materials.

1. Introduction

Hydroxyapatite (HA) is one of the most used biomaterials for bone grafting in hard tissue implants and other bone tissue engineering applications because of its excellent bioactive, biocompatible, and osteoconductivity properties [1–3]. It is important to note that HA has a non-stoichiometric composition in natural bone and the flexible structure with relatively low crystallinity degree leads to substitution of some cations and anions. For example, calcium cations in the HA structure can be replaced by Mg^{2+}, Cu^{2+}, Zn^{2+}, and Sr^{2+}, hydroxyl groups can be replaced by F^- and CO_3^{2-} (A-type), and phosphate groups (PO_4^{3-}) can be replaced by SiO_4^{4-} and CO_3^{2-} (B-type) [4–8]. Trace amounts of substituted ions can have a significant effect on the physicochemical properties and biological performance of HA, especially the purity, structure, and thermal stability, and this should be considered before studying the effect of substituted ions on the HA bioactivity [9,10].

Selenium (Se) is an essential trace element in the human body that has antitumor effects, and antioxidation and antibacterial actions, which is closely related to human health [11–13]. Some studies have shown that adequate selenium supply enhances bone fracture resistance and delays bone ageing, although both a deficiency and an excess of selenium have a negative effect on bone growth and biomechanical strength [14–16]. Taking into account the positive effect of Se on antitumor activity and bone growth, incorporation of Se into the HA structure can make HA more efficient for preventing the recurrence of cancer while promoting bone growth. Se is expected to have dual functions of bone tissue repair and cancer therapy, such as osteosarcoma and hepatocellular carcinoma treatment [17,18]. Se is also promising as a carrier of anti-cancer drugs to special sites [19–21] and it has antibacterial properties [22].

A few studies have focused on the effect of selenium doping on the structure of HA. It has been suggested that selenium incorporates into the HA structure by replacing carbonate groups with selenite groups (SeO_3^{2-}) [22]. However, more studies have suggested that Se is likely to occupy phosphate positions [23–25]. Ma et al. [23] found that substitution of phosphate by selenite causes lower carbonate involvement and only the *c* lattice parameter decreases. Kolmas et al. [24] compared HAs doped with selenite and selenate. They found that substitution of selenite results in an increase in the *a* lattice parameter, while the *c* lattice parameter remains unchanged. Zhang et al. [25] synthesized selenium-doped HA (Se-HA) by the hydrothermal method and then characterized its structure. Both the *a* and *c* lattice parameters increased with Se substitution. In these previously studies, different doping mechanisms have been proposed and quite different changes in the Se-HA crystal structure have been obtained. Thus, the doping mechanisms and the crystal structure of Se-HA remain unclear, especially

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the detailed structure. No attempt has been made to discuss the change of the Se-HA fine structure and the position of selenite in the structural refinement process. Furthermore, little attention has been paid to the thermal stability of Se-HA during the heat treatment process. Ma et al. [23] found that Se-HA with Se/P = 0.1 is thermally stable at 900 °C for 2 h. However, few other studies have performed a systematic study focusing on the thermal stability of Se-HA. For example, incorporation of some elements into HA, such as magnesium and strontium, can reduce the thermal stability of HA and promote formation of β-tricalcium, α-tricalcium, or biphasic calcium phosphates [7,26]. Whether selenium doping of HA will have the same effect needs to be investigated.

In this study, a series of Se-HA samples with different Se/P ratios were prepared by the chemical precipitation method, and the substitution mechanism was comprehensively investigated. In addition, the fine structure information of the Se-HA samples was analyzed by Rietveld refinement, which can be used to construct the Se-HA structure model. Heat treatment was performed to investigate the effect of Se-doping on the phase stability of Se-HA. Based on their thermal stabilities, the optimum sintering conditions of the Se-HA samples need to be investigated.

2. Materials and methods

2.1. Preparation of HA and Se-HA

HA and a series of Se-HA samples with different Se/P ratios were prepared by the chemical precipitation method using $Ca(NO_3)_2$ (AR), $(NH_4)_3PO_4{\cdot}3H_2O$ (AR), and $Na_2(SeO_3)$ (AR) as the sources of Ca, P, and Se, respectively. The amounts of the reagents were calculated to maintain the Ca/(P + Se) molar ratio at the stoichiometric value (1.67) (Table 1).

In brief, Na_2SeO_3 (0.1 M) was added to $(NH_4)_3PO_4{\cdot}3H_2O$ (0.25 M) solution. The pH value of the mixture was maintained above 10.0 by adding ammonium hydroxide. Similarly, the pH value of $Ca(NO_3)_2$ (0.5 M) was adjusted to 11.0. The mixture was added dropwise to a stirred solution of $Ca(NO_3)_2$ at a rate of 5 mL min^{-1} using a peristaltic pump. To avoid nanoparticle agglomeration, polyethylene glycol (PEG, 0.2 g, M_W = 6000) was added as a dispersant. The temperature of the reaction was set to 60 °C. After 3 h of continuous stirring, the mixture was aged at room temperature for 24 h. Following aging, the resulting precipitate was centrifuged three times with distilled water and alcohol, dried overnight at 60 °C, and then ground and sieved. Finally, to investigate the effect of Se doping on the thermal properties of HA, all of the synthetic samples were calcined in a muffle furnace at different temperatures for 3 h with heating and cooling rates of 5 °C min^{-1}.

The resulting HA and Se-HA samples with different Se/P ratios are denoted Se/P-Se-HA. For example, the sample with Se/P = 0.05 is denoted 0.05-Se-HA.

Table 1
Amounts of the reactants used to synthesize HA and Se-HA with various Se/P ratios.

Samples	$Ca(NO_3)_2$ (mol)	$(NH4)_3PO_4$ (mol)	Na_2SeO_3 (mol)	Se/P	Ca/(P + Se)
HA	0.05	0.0500	–	–	1.67
0.05-Se-HA	0.05	0.0285	0.0014	0.05	1.67
0.08-Se-HA	0.05	0.0277	0.0022	0.08	1.67
0.1-Se-HA	0.05	0.0272	0.0027	0.1	1.67
0.3-Se-HA	0.05	0.0230	0.0069	0.3	1.67
0.5-Se-HA	0.05	0.0200	0.0100	0.5	1.67
1-Se-HA	0.05	0.0150	0.0150	1	1.67
3-Se-HA	0.05	0.0075	0.0225	3	1.67
5-Se-HA	0.05	0.0050	0.0250	5	1.67

2.2. Characterization

X-ray fluorescence (XRF) spectroscopy (Axios PW4400, PANalytical, The Netherlands) was performed to determine the Ca, P, and Se contents in the HA and Se-HA powder samples. Fourier transform infrared (FTIR) spectroscopy (Nicolet 360 spectrometer, USA) was performed to investigate the structural changes of the powder samples. The wavenumber range 400–4000 cm^{-1} was recorded. The surface chemical states of the elements were analyzed by X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Scientific, USA). The thermal behavior of the powder samples was investigated by thermogravimetry–differential thermal analysis (TG–DSC) using a simultaneous thermal analyzer (STA449C, Germany). The test was performed in an alumina crucible with a heating rate of 10 °C min^{-1} up to 1200 °C. Transmission electron microscopy (TEM, JEM-1400Plus, Japan) was performed to observe the morphologies of the powders.

The phase compositions of the as-prepared and heat-treated powders were identified by X-ray diffraction (XRD, X'Pert PRO, PANalytical, The Netherlands). The test data were collected over the 2θ range 10–70° with a step size of 0.02° and a scanning rate of 4° min^{-1} using Cu Kα radiation.

2.3. Rietveld refinement

Rietveld refinement can provide rich structural information hidden in the diffraction data by adjusting various parameters in the fitting process. Rietveld refinement was performed to investigate the effect of Se doping on the HA fine structure. The GSAS and EXPGUI programs were used to refine the structures. The slow-scanning XRD data were collected using a step size of 0.005° and a scanning rate of 0.05° s^{-1} for the refinement. The standard crystallographic data of apatite were used as the starting atomic parameters based on the space group of the HA structure (*P*63/*m*, No. 176) [27]. Because the diffraction peaks are influenced by many factors, we refined the parameters, including the background, lattice parameters, peak parameters, and instrument zero. Some structural parameters were determined, such as the P–O bond length and the O–P–O bond angle in the phosphate tetrahedron. To remove other foreign ions and improve the crystallinity of the samples without changing the microstructure, the samples were pretreated by low-temperature heating. The weighted profile *R* factor (R_{wp}) and the reduced χ^2 value were used to assess the goodness-of-fit of the Rietveld refinement. When $R_{wp} \leq 5\%$ and $\chi^2 \leq 3$, the results were considered to be acceptable.

3. Results

3.1. Elemental analysis by XRF spectroscopy results

The atomic percents of the different elements were determined by XRF spectroscopy. The Se/P and Ca/(P + Se) atomic ratios of the pure HA and Se-HA samples are listed in Table 2. All of the measured Se/P ratios are less than the nominal value, which indicates that some of the Se ions remained in the mother liquor solution after precipitation. Moreover, the Ca/(P + Se) ratio of each sample is less than the stoichiometric Ca/P ratio of HA (1.67), indicating that Ca-deficient HA and

Table 2
Molar ratios of HA and Se-HA with various Se/P ratios determined by XRF spectroscopy.

Samples	*n* (Ca) (mol)	*n* (P) (mol)	*n* (Se) (mol)	Se/P	Ca/(P + Se)
HA	1.0068	0.6129	0	–	1.6425
0.05-Se-HA	0.9902	0.5923	0.0225	0.0380	1.6105
0.1-Se-HA	0.9698	0.5741	0.0444	0.0773	1.5679
0.3-Se-HA	0.9218	0.5002	0.1159	0.2317	1.4962
0.5-Se-HA	0.9014	0.4280	0.102	0.4022	1.5010

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