



On the effect of temperature on the insertion of zinc into hydroxyapatite

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ARTICLE INFO

Article history:

Received 12 September 2011

Received in revised form 3 December 2011

Accepted 5 December 2011

Available online 13 December 2011

Keywords:

Bioceramics

Zinc doping

Calcium phosphates

Rietveld refinement

Thermal treatment

ABSTRACT

Rietveld analysis of X-ray powder diffraction patterns recorded from 28 hydroxyapatite (HAp) samples containing various amounts of zinc (0, 1.6, 3.2 and 6.1 wt.% Zn) and heat treated at various temperatures (between 500 °C and 1100 °C) has enabled the Zn insertion mechanism into the HAp crystal structure to be finely characterized. The formation of Zn-doped HAp was achieved above 900 °C only. Zn-doped HAp has the $\text{Ca}_{10}\text{Zn}_x(\text{PO}_4)_6(\text{OH})_{2-2x}\text{O}_{2x}$ ($0 < x \leq 0.25$) chemical composition with a constant Ca/P ratio of 1.67 due to the insertion mechanism into the hexagonal channel (partial occupancy of the 2b Wyckoff site with the formation of linear O–Zn–O entities). Samples heat treated at 500 °C were almost single phase, HAp did not incorporate Zn and about half of the Zn atoms incorporated during the synthesis are not observable by X-ray powder diffraction (contained in an amorphous compound or physisorbed at the HAp surface). The reversible formation of Zn-doped β -TCP phase was observed at 600 °C, reached its maximum content at 900 °C and had almost vanished at 1100 °C. The results presented here strengthen the recently described mechanism of Zn insertion in the interstitial 2b Wyckoff position of the HAp structure, and explain the origin of the contradictory reports in the corresponding literature.

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1. Introduction

Apatites, $\text{Ca}_{10}(\text{PO}_4)_6(\text{F,Cl,OH})_2$, are a complex and diverse class of materials [1] which have gained increasing importance due to their biological role. One of the main constituents of bone and hard tissue in mammals is a calcium phosphate mineral whose structure closely resembles hydroxyapatite (HAp), $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. The so-called biological apatite refers to poorly crystallized non-stoichiometric carbonate-containing HAp. The inorganic content varies from 65% in bone to 90% in dental enamel [2].

Because biological apatites are formed in biological conditions, they usually contain a large variety of doping elements (F, Si, Sr, Mg, etc.) that can also have some specific biological properties. The important role of zinc has been put forward in the recent literature [3–6]. In effect, uptake and release of Zn in the body are strongly mediated by the bone reservoir, where the Zn content ranges from 125 to 250 ppm (against 28–33 ppm for the whole body) [6]. It has been demonstrated that zinc has a stimulatory effect on bone formation and mineralization in vivo and in vitro [7,8], and that Zn incorporation into implants promotes bone formation around the material [9–11], improves biological properties [9,12] decreases the inflammatory response [13,14], and has an antibacterial effect [15].

In order to understand the mechanisms of incorporation of doping elements in HAp, and to correctly characterize natural and/or pathological nanocrystalline multi-substituted apatite materials, it is of great importance to perform detailed structural characterizations of substituted synthetic HAp. Our previous study has established the Zn location into the HAp structure [16]. For high synthesis temperatures (1100 °C), Zn^{2+} cations are inserted along the hexagonal channel of the HAp structure at the 2b Wyckoff site forming O–Zn–O linear entities. Zn^{2+} leads to an insertion solid solution with general chemical formula $\text{Ca}_{10}\text{Zn}_x(\text{PO}_4)_6(\text{OH})_{2-2x}\text{O}_{2x}$, contrary to β -tricalcium phosphate (β -TCP, β - $\text{Ca}_3(\text{PO}_4)_2$) that realizes a substitution solid solution with chemical formula $\text{Ca}_{3-x}\text{Zn}_x(\text{PO}_4)_2$. The present study aims to enlarge the investigation of the Zn^{2+} incorporation in HAp vs. the temperature (heat treatment from 500 °C to 1100 °C). This study was motivated by the contradictory reports in the literature on the Zn^{2+} incorporation in HAp; namely about its solubility, ranging from a few percent to 15 mol.% [17–19], about the Zn atoms' location, sorbed on the HAp surface (either sixfold or fourfold coordinated), or incorporated in one of the two crystallographic Ca sites (the ninefold coordinated Ca1 and the sevenfold coordinated Ca2 sites) of the HAp structure [17,20–28].

2. Materials and methods

2.1. Sol–gel elaboration

The sol–gel route was used to synthesize undoped and Zn-doped HAp samples [16]. Briefly, to produce 2 g of pure HAp

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powder, 4.7 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Aldrich) and 0.84 g of P_2O_5 (Avo-cadoResearch chemicals) were dissolved in anhydrous ethanol under stirring and refluxed at 85 °C for 24 h. Then, this solution was kept at 55 °C for 24 h, to obtain a consistent gel and further heated at 80 °C for 10 h to form powder. Seven samples were prepared from this powder heat treated at 500 °C, 600 °C, 700 °C, 800 °C, 900 °C, 1000 °C and 1100 °C during 15 h. To prepare Zn-substituted samples, the required amounts of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Acros Organics) were added to the solution, simultaneously with $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. Nominal compositions have been calculated, assuming the previously described interstitial insertion mechanism for zinc into hydroxyapatite: composition $\text{Ca}_{10}\text{Zn}_x(\text{PO}_4)_6\text{O}_{2x}(\text{OH})_{2-2x}$ with a constant Ca/P ratio of 1.67 whatever the Zn content. Four series of samples have been synthesized with $x = 0.00, 0.25, 0.50, 1.00$ (corresponding to nominal ZnO of 0.0, 2.0, 3.9 and 7.6 wt.% respectively). In the following, samples are labelled $\text{Zn}_x\text{-}y$ with x the amount of Zn^{2+} doping and y the heat treatment temperature. A total of 28 samples were prepared and analysed.

2.2. X-ray powder diffraction (XRPD)

XRPD patterns were recorded on an X'Pert Pro PANalytical (Al-melo, the Netherlands) diffractometer, with θ - θ geometry, equipped with a solid detector X-Celerator, and using Cu K_α radiation ($\lambda = 1.54184 \text{ \AA}$). XRPD patterns were recorded at room temperature in the interval $3^\circ < 2\theta < 120^\circ$, with a step size of $\Delta 2\theta = 0.0167^\circ$ and a counting time of 200 s for each data value. A total counting time of ~ 200 min was used for each sample. Fig. 1 shows XRPD patterns recorded for the $\text{Zn}_{0.25}$ series. An XRPD pattern was collected from a pure LaB_6 NIST standard (SRM 660b) by using the same experimental conditions in order to extract the instrumental resolution function to improve the peak profile fitting and to extract intrinsic microstructural parameters.

2.3. Rietveld analyses

Rietveld refinements of X-ray powder patterns were performed for each sample with the program FullProf.2k [29]. The procedure used (both data collection and refinement strategy) corresponds to the general guidelines for structure refinement using the Rietveld (whole-profile) method formulated by the International Union of Crystallography Commission on Powder Diffraction [30–32]. The initial structural parameters of hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, were taken from Ref. [33]: space group $P6_3/m$, $Z = 1$, $a = 9.4218 \text{ \AA}$

and $c = 6.8813 \text{ \AA}$, seven independent atomic positions: two Ca positions in sites $4f$ ($z = 0.0007$) and $6h$ ($x = 0.2465, y = 0.9933$), one P position in site $6h$ ($x = 0.3968, y = 0.3693$), and four O positions in sites $6h$ ($x = 0.331, y = 0.480$ and $x = 0.579, y = 0.455$), $12i$ ($x = 0.3394, y = 0.2569, z = 0.0694$) and $4e$ ($z = 0.192$ with a half occupancy). Zn atoms were placed in the $2b$ Wyckoff site at $(0, 0, 0)$ [16], after systematic verification of their absence in the Ca1 and Ca2 calcium sites. The initial structural parameters of β -TCP, $\text{Ca}_3(\text{PO}_4)_2$, were taken from [34]: space group $R3c$, $Z = 21$, $a = 10.4352 \text{ \AA}$ and $c = 37.4029 \text{ \AA}$, 18 independent atomic positions: five Ca positions (three in site $18b$ and two in site $6a$ at one-half occupancy), three P positions (two in site $18b$ and one in site $6a$), and ten O positions (nine in site $18b$ and one in site $6a$). Zincite (ZnO with structural parameters taken from Ref. [35]), lime (CaO with structural parameters taken from Ref. [36]), and α -TCP ($\text{Ca}_3(\text{PO}_4)_2$ with structural parameters taken from Ref. [37]) were observed as minor and temperature-dependent phases. The following parameters were first refined: scale factors, zero shift, line profile parameters, lattice parameters, preferential orientations and asymmetry parameters. In a second step, atomic displacement factors were refined (only three thermal displacement values were considered – one for divalent cations, one for P and one for O – in order to avoid strong correlation between site occupancies and atomic displacement factors [30–32]), as well as atomic coordinates from the HAp structure. Anisotropic average apparent crystal size parameters were refined in a third step for the HAp phase (refinements were performed with spherical harmonics by using the corresponding $6/m$ Laue class of symmetry). Site occupancies of cations, phosphate and hydroxyl anions were systematically checked in the last runs. Scholzite, $\text{Zn}_2\text{Ca}(\text{PO}_4)_2(\text{H}_2\text{O})_2$, and dehydrated scholzite, $\text{CaZn}_2(\text{PO}_4)_2$, were never observed in any of the 28 samples.

2.4. Micro-Raman spectroscopy

Micro-Raman spectra were recorded at room temperature using a Jobin-Yvon T64000 device. The spectral resolution obtained with an excitation source at 514.5 nm (argon ion laser line, Spectra Physics 2017) is $\sim 1 \text{ cm}^{-1}$. The Raman detector was a charge coupled device (CCD) multichannel detector cooled by liquid nitrogen to 140 K. The laser beam was focused onto the sample through an Olympus confocal microscope with $100\times$ magnification. Measured power at the sample level was kept low (less than 10 mW) in order to avoid any damage of the material. The Raman scattered light was collected with the microscope objective at 180° from the excitation and filtered with a holographic Notch filter before being dispersed by a single grating (1800 grooves per mm). Spectra were recorded in the frequency ranges $100\text{--}1500 \text{ cm}^{-1}$ and $3000\text{--}3800 \text{ cm}^{-1}$ in order to investigate respectively the vibration modes of phosphate and hydroxyl stretching. Spectra were analysed by a profile fitting procedure using a Lorentzian function.

3. Results

Elemental analysis of the samples by ICP-AES confirms the global nominal compositions as usually observed with this synthesis procedure [38] (Table 1).

3.1. Mineralogical composition

Quantitative phase analyses were extracted from Rietveld refinements. Refined mineralogical compositions of the samples are listed in Table 2. Fig. 2 shows the thermal evolution of the HAp, β -TCP, ZnO and CaO weight percents. HAp was constantly the major phase. The HAp minimal content is $\sim 65 \text{ wt.}\%$ observed

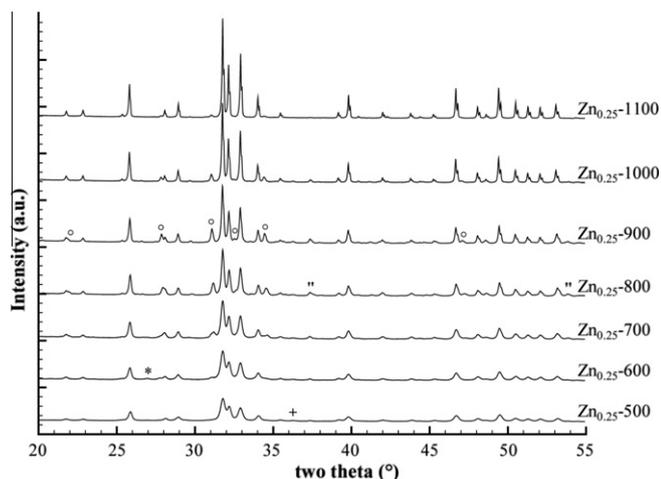


Fig. 1. PXRD patterns for the $\text{Zn}_{0.25}$ series ($\lambda = 1.54184 \text{ \AA}$). Major phase is HAp for all patterns, minor phases are ZnO, α -TCP, CaO and β -TCP (for which main diffraction peaks are respectively marked by +, *, and \circ).

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