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Finely Dispersed Powders of Silicon-substituted Hydroxyapatite Obtained from Solutions

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Bioactive powders of silicon substituted hydroxyapatites containing 1.4-4.3 wt % Si were synthesized by precipitation from aqueous solutions of calcium nitrate and ammonium (sodium) hydrophospate. Tetraethoxysilane and sodium silicate in basic media were used as a source of silicon. Using scanning electron microscopy, surface morphology of the obtained products was studied. It has been found that procedure using sodium silicate allows obtaining of materials with 100-200 nm particle size. Procedure that utilizes tetraethoxysilane leads to 40-100 nm particles. Chemical, X-ray phase analysis and infrared spectroscopy of samples annealed at 900 °C indicate the formation of monophase crystalline products possessing apatite structure.

Keywords: Hydroxyapatite, Biomaterials, Synthesis from solution, Surface morphology, Nanoparticles, Powder

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1. INTRODUCTION

In the last two decades, novel technologies in bone surgery are based on the utilization of synthetic hydroxyapatite (HA) $Ca_{10}(PO_4)_6(OH)_2$ in a nanodisperse state [1, 2]. Most attention is gained by a regeneration approach where hydroxyapatite based biomaterial is gradually substituted by a native bone, and material serves as an active source of elements needed to build bone tissue [3]. One of those elements is silicon that is a key component required by the body to produce collagen. Partial substitution of phosphate by silicate in HA provides the source of silicon as well as decreases the size of the particles and influences their surface morphology, thus accelerating the bone remodeling process [4, 5]. Several studies describe obtaining of thin silicon substituted HA (Si-HA) films on titanium plates, prepared by magnetron sputtering [6, 7] and electrolytic sedimentation [8]. Granulated HA implants have been used to treat hip joint defects [9]. Biological activity of such implants was investigated on two Si-HA compositions (0.8 and 1.5 wt % Si) obtained by precipitation from aqueous solutions of $Ca(OH)_2$, H_3PO_4 and $Si(CH_3CO_2)_4$, with Ca : P ratio of 1.667. Precipitations were granulated to the size of 1.0-2.0 mm and then annealed at 1200 °C. Biomedical results showed that regeneration process of the bone tissue proceeds two times faster on Si–HA compared to HA [9]. Bakunova et al. [10] obtained Si-HA powders with 0.14-1.4 wt % Si from the solutions of $(NH_4)_2HPO_4$, $Si(C_2H_5O)_4$ and $Ca(NO_3)_2$, and physic-chemical analyses indicated the formation of the apatite phase at 700-1200 °C. Notably, the stability of the phase improves with increase of Si content. Therefore, the scope of this work is to investigate the formation of Si-HA with higher silicon content, i.e. 1.4-4.3 wt % Si.

2. EXPERIMENTAL

2.1 Synthesis

Powders of Si-HA were synthesized by precipitation from aqueous solutions at heating according to scheme:

$$10\,Ca^{2+} + (6-x)\,PO_4^{3-} + x\,SiO_4^{4-} + (2-x)\,OH^{-} \rightarrow$$
$$\rightarrow Ca_{10}(PO_4)_{6-x}(SiO_4)_x(OH)_{2-x} \quad (x = 0.5,\ 1.0,\ 1.5)$$

Si-HA powders were prepared via two routes that differ by initial components, mixing sequence, pH, reaction and work-up temperature, as schematized in Fig. 1.

Route 1 was conducted using aqueous solutions of $Ca(NO_3)_2$ (0.22 mol/L), Na_2HPO_4 (0.33 mol/L), Na_2SiO_3 (0.25 mol/L), NaOH (1.16 mol/L) at 100 °C and pH = 13.5.

Solution of Na_2SiO_3 was added at stirring to the calculated amount of Na_2HPO_4 solution until the phases $Ca_{10}(PO_4)_{6-x}(SiO_4)_x(OH)_{2-x}$, where $x = 0.5$ [0.5 Si-HA(I)] or $x = 1.0$ [1.0 Si-HA(I)], were obtained. To convert SiO_3^{2-} into SiO_4^{4-}, that is needed to form Si-HA, NaOH solution was added until pH = 13.5, which corresponds to the maximum concentration of SiO_4^{4-} [11]. Then the temperature was increased to 100 °C and the solution of $Ca(NO_3)_2$ was added at rigorous stirring until Ca/(P + Si) = 1.67. The obtained precipitation was aged at room temperature for 20 h and then filtered off, washed by NH_4NO_3 solution (3 wt % in water), predried in the air and, finally, annealed at 900 °C for 6 h.

Route 2 was conducted using aqueous solutions of $Ca(NO_3)_2$ (0.22 mol/L), $(NH_4)_2HPO_4$ (0.24 mol/L), NH_4OH (30 wt % in water) and the solution of $Si(C_2H_5O)_4$ in ethanol (0.1 mol/L), at 70 °C and pH = 11.0.

First, NH_4OH solution was added to $(NH_4)_2HPO_4$ solution to reach pH = 11.0, that is needed to obtain HA in ammonia media [12]. Then the temperature was

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increased to 70 °C and solutions of $Ca(NO_3)_2$ and $Si(C_2H_5O)_4$ were added successively to reach $Ca/(P + Si) = 1.67$ in order to obtain the phases $Ca_{10}(PO_4)_{6-x}(SiO_4)_x(OH)_{2-x}$, where $x = 0.5$ [0.5 Si-HA(II)], $x = 1.0$ [1.0 Si-HA(II)] and $x = 1.5$ [1.5 Si-HA(II)]. The obtained precipitations were collected by filtration and annealed at gradually increased temperature (400-900 °C, step 100 °C each 5 h, total 25 h).

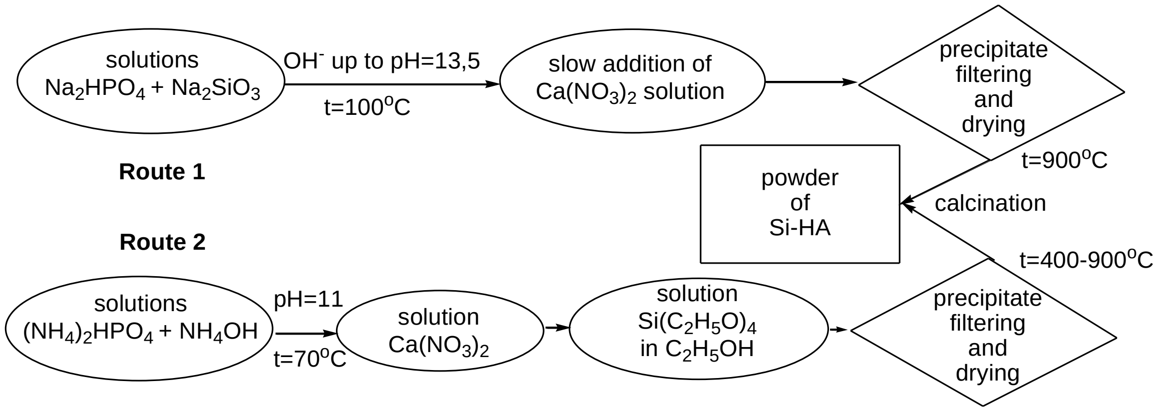

Fig. 1 - Flow chart of synthetic routes towards Si-HA with 1.4-4.3 wt % Si

2.2 Analysis

Concentration of Ca^{2+} was determined by complexonometric titration using Eriochrome Black T as an indicator. Total phosphorous content was determined measuring optical densities of heteropoly molymbdovanadatophosphate acid ($H_4PVMo_{11}O_{40}$) by photometry. Silicon content was determined as SiO_2, obtained by annealing of preliminary isolated (meta)silicic acid at 1100 °C. All pH measurements were done on I-160 ionomer (Belarus). X-ray phase analysis was conducted on DRON-3 diffractometer (Russia) (CuK_α radiation, Ni filter) in the 2θ range of 10-70°. FTIR spectra were acquired using Spectrum BXII (Perkin-Elmer) in the range of 400-4000 cm^{-1}. SEM was imaged on JSM-6490LV scanning electron microscope (Jeol) with lanthanum hexaboride cathode and accelerating voltage of 10-20 kV. Phase elemental analysis was carried out in backscattered electron imaging (BEI) regime, and surface analysis was done in secondary electron imaging (SEI) regime. Elemental analysis during SEM was enabled by energy-dispersion X-ray (EDX) spectrometer INCA Energy-350.

3. RESULTS AND DISCUSSION

Chemical analyses of the obtained precipitations (Routes 1 and 2) are summarized in Table 1. Notably, atomic ratio $Ca / (P + Si) = 1.67$ in 0.5-1.5 Si-HA is in excellent agreement with stoichiometry and corresponds to the formulas, given in Table 2.

Table 1 – EDX analysis data

Code	Element						Ca / (P + Si)
	Ca		P		Si		
	wt %	at. %	wt %	at. %	wt %	at. %	
0,5 Si-HA (I)	41,55	23,44	17,80	12,87	1,39	1,17	1,67
1,0 Si-HA (I)	40,48	24,06	15,80	12,05	2,84	2,39	1,67
0,5 Si-HA (II)	41,03	23,60	17,45	12.98	1,43	1,15	1,67
1,0 Si-HA (II)	40,89	23,88	15,79	11,95	2,87	2,42	1,66
1,5 Si-HA (II)	41,47	24,54	14,44	11,05	4,36	3,68	1,67

Table 2 – Calculated data of Ca, P and Si contents.

Formula	Ca		P		Si		Ca / (P + Si)
	wt %	at. %	wt %	at. %	wt %	at. %	
$Ca_{10}(PO_4)_6(OH)_2$	39,91	22,73	18,50	13,64	-	-	-
$Ca_{10}[(PO_4)_{5,5}(SiO_4)_{0,5}](OH)_{1,5}$, $x = 0,5$	40,24	23,26	17,15	12.79	1,41	1,16	1,67
$Ca_{10}[(PO_4)_5(SiO_4)]OH$, $x = 1,0$	40,65	23,81	15,75	11,90	2,85	2,38	1,67
$Ca_{10}[(PO_4)_{4,5}(SiO_4)_{1,5}](OH)_{0,5}$, $x = 1,5$	41,07	24,39	14,32	10,98	4,31	3,66	1,67

Morphology studies of the obtained powders revealed similarities of their surfaces. Particularly, micrographs of 0.5 Si-HA(I) show 5-50 µm conglomerates consisting of squeezed spheres with the size 100-200 nm (Fig. 2).

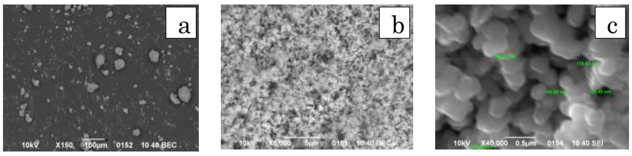

Fig. 2 – SEM images of surface morphology of 0.5 Si-HA(I). Magnification: a) × 150, b) × 5000, c) × 40000

Uniform contrast of the surface of 0.5 Si-HA(I) in SEM images indicates single phase (see Fig. 3a). Absence of segregations and liquations as well as the uniform elements (P, Ca, Si, O) distribution on the surface in the micrographs obtained under characteristic X-ray irradiation, also support that the sample is monophasic (Fig. 3b-e).

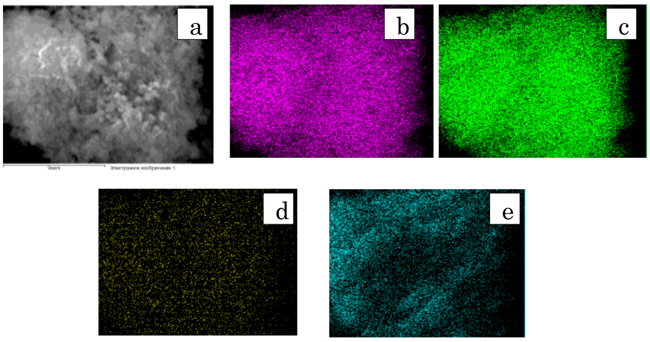

Fig. 3 – (a) SEM image of $Ca_{10}[(PO_4)_{5.5}(SiO_4)_{0.5}](OH)_{1.5}$ surface. SEM images of $Ca_{10}[(PO_4)_{5.5}(SiO_4)_{0.5}](OH)_{1.5}$ surface under characteristic X-ray irradiation: (b) P, Кα_1, (c) Ca, Кα_1, (d) O, Кα_1, (e) Si, Кα_1

X-ray phase analysis of compounds with 1.4-4.3 wt % Si revealed the presence of HA-phase where diffraction maxima are shifted towards lower θ as the contents of silicon increases (see Fig. 4). Evidently, it is caused by the changes in the lattice parameters and supports the fact that the silicate groups are incorporated into the structure. Absence of other phosphate and silicate phases, as well as EDX analyses data (see above) witness that the obtained products are monophasic.

FTIR spectra of Si-HA obtained via both routes contain all characteristic bands for HA (Fig. 5). Thus, absorption at 1050-1090 (ν_3), 962 (ν_1), 603, 570 (ν_4) and 473 (ν_2) cm^{-1} correspond to phosphate, and bands at 3570 and 630 cm^{-1} correspond to –OH groups oscillation. It is worth to notice, that the latter band is overlapped with the wide signal at 3200-3700 cm^{-1}, that is, together with the absorption at 1630 cm^{-1}, might indicate the presence of the adsorbed water. Additional bands at 1650 and 1419-1457 cm^{-1} (ν_3) witness the presence of carbonate groups, and are present in all Si-HA obtained. As it is mentioned in [10], air is the source of CO_3^{2-}, and it is involved in the synthesis to compensate an excessive negative charges occurring at substitution of triple-charged PO_4^{3-} to tetra-charged SiO_4^{4-}. Oscillations of the latter cause the appearance of weak absorption bands at 892, 800 and 500 cm^{-1}.

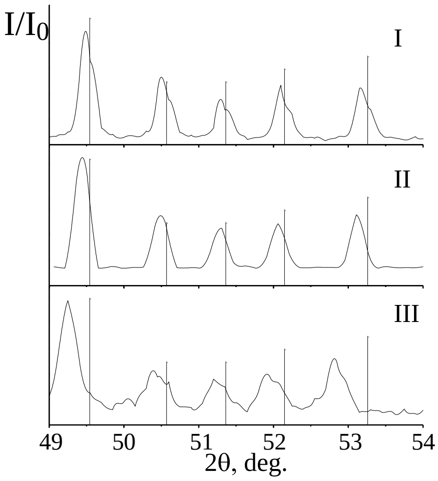

Fig. 4 - XRD spectra of 0.5 Si-HA (1.4 wt. % Si) (**I**), 1.0 Si-HA (2.85 wt. % Si) (**II**), 1.5 Si-HA (4.3 wt. %Si) (**III**)

Noteworthy, the intensity of P-O and O-H absorption bands at 962 cm^{-1} and 3570 cm^{-1}, respectively, decreases with an increase of silicon contents from 1.4 to 4.3 wt % in the samples (0.5-1.5) Si-HA(I, II). It is closely related to the partial substitution of phosphate groups with silicate ones, as well as loss of part of the hydroxyl-groups caused by aiming of Si-HA molecules to preserve their electroneutrality. All of the above support the formation of Si-HA with formula $Ca_{10}[(PO_4)_{6-x}(SiO_4)_x](OH)_{2-x}$, where $x = 0.5$; 1.0 and 1.5 (Table 2).

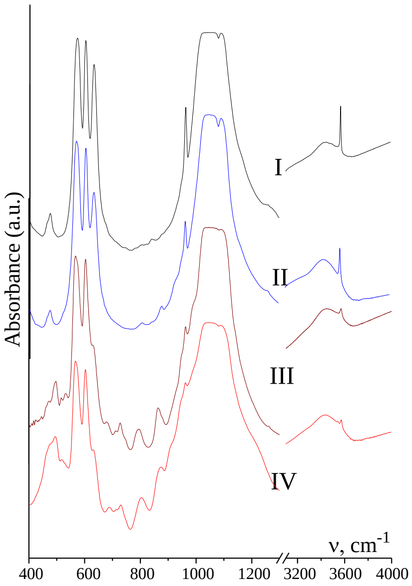

Fig. 5 – FTIR spectra: I) HA; II) 0.5 Si-HA; III) 1.0 Si-HA; IV) 1.5 Si-HA

4. CONCLUSIONS

In this report, we investigated the influence of initial Si-containing components, solutions mixing sequence, pH, reaction and work–up temperatures on the formation and precipitation of Si-HA from aqueous solutions. The synthetic procedure towards nanodisperse Si-HA powders (1.4-4.3 wt % Si) was developed and optimized. It was found, that by variation of the silicon source, i.e. sodium silicate or tetraethoxysilane, allowed obtaining materials with particle size of 100-200 nm or 40-100 nm, respectively. Uniform distribution of P, Ca, Si and O on the surface, imaged by SEM in characteristic irradiation, indicates formation of monophase products in both routes. Therefore, chemical and physical analyses witness the formation of monophase crystalline products with apatite structure, corresponding to the formula $Ca_{10}[(PO_4)_{6-x}(SiO_4)_x](OH)_{2-x}$, where $x = 0.5$, 1.0 and 1.5 (1.4-4.3 wt % Si).

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