Study of thermal effects of silicate-containing hydroxyapatites

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Abstract. The possibility of modifications of hydroxyapatite silicate ions, from the extracellular fluid prototype solution under near-physiological conditions has been studied. Formation of silicon-structured hydroxyapatite with different extent of substitution of phosphate groups in the silicate group has been established through chemical and X-ray diffraction analyses, FTIR spectroscopy and optical microscopy. The results obtained are in agreement and suggest the possibility of substitution of phosphate groups for silicate groups in the hydroxyapatite structure when introducing different sources of silica, tetraethoxysilane and sodium silicate, in the reaction mixture. Growth in the amount of silicon in Si-HA results in the increase in the thermal stability of the samples. The greatest mass loss occurs at temperatures in the range of 25–400 ^{0}C that is caused by the removal of the crystallization and adsorption water and volatile impurities. It is shown that the modified apatites are of imperfect structure and crystallize in a nanocrystalline state.

1. Introduction
Hydroxyapatite (HA) is widely used for orthopedic implant manufacturing which employs an ion-plasma magnetron technique and electrochemical deposition, therefore, the temperature pattern in different processes is an important property of the material. The thermal analysis [1] indicates that pure HA is thermally less stable compared to its anion-exchanged modifications including silicon-substituted hydroxyapatite (HA-Si) of different extent of substitution.

It is known that silicon plays a bridging role in physiological processes of growth and re-construction of bone and cartilaginous tissues; therefore, the development of the techniques for silicon-substituted hydroxyapatite (Si-HA) synthesis is a relevant physical-chemical problem [2]. For complete physiological response of the organism when restoring a damaged bone, hydroxyapatite chemical modification should be carried out in the near-physiological solutions.

Model systems with the electrolyte content identical to biological fluids used as an initial solution are considered to be promising for composite biomaterials production. For this purpose, we have chosen a composition of the extracellular fluid model solution "Simulated Body Fluid" (SBF), which can be used for synthesis of calcium phosphates, as well as for evaluation of their biological activity [3]. No data on the possibility of producing silicon-substituted hydroxyapatite in this system is available.

An important characteristic of synthesized Si-HA is its thermal stability. [4] In [5] it was found that heat treatment of the biological bone at 1000 ºC provides formation of silicon-magnesium-substituted oxyapatite which transforms into hydroxyapatite upon cooling, retains a balanced composition of natural nanoimpurities that support the stability of the structure, phase and chemical composition to ensure the best features of the biocoatings on titanium implants under all application techniques

(electrochemical, plasma, slip processing). In [6], it was found that heat treatment of silicon-substituted hydroxyapatite at t = 500^0S within 1 day results in Si-HA crystalline phase. The data obtained through scanning microscopy indicated bimodal (inter-aggregate and intergranular) porosity of the sample, and the grain size was 20 to 60 nm, which theoretically facilitates osteoinduction [6].

An important factor is that, regardless of the degree of the texture and stoichiometry of the Si-HA sample, the obtained nanohardness varies in the range from 11 to 12 GPa, and thermal stability and uniformity of the chemical composition are provided. However, the most important characteristic is preservation of bioactivity, which allows full use of these samples [7.8].

The paper aims to study the process of thermal transformation of Si-HA-based samples produced through deposition from the model solution of the SBF and SBF + SiO_4^{4-} extracellular fluid under varying concentration and the nature of the silicate ion supplier.

2. Materials and methods

The SBF model solution was used as a prototype of the extracellular fluid. The solid phase was prepared by deposition from aqueous solutions, wherein $CaCl_2$, $MgCl_2$, K_2HPO_4, $NaHCO_3$, Na_2SO_4 and $NaCl$ were used as the initial system components [9].

The main compounds, suppliers of silicate groups, were Na_2SiO_3 and tetraethoxysilane (TEOS). Silicate ions were doped in the form of $Na_2SiO_3 \cdot 5H_2O$ and TEOS (tetraethoxysilane, alcohol solution). The weight content of silicon was varied in the range of 0.5 ÷ 5.0. %. The chosen ratio Ca/P = 1.67 was similar to that specified for production of stoichiometric hydroxyapatite [10]. While preparing the reaction mixture, the solution containing K_2HPO_4 and Na_2SiO_3/TEOS was the last introduced in the mixture. The synthesis was carried out at room temperature (t = 25 °C). The silicate-phosphate solution was introduced into calcium solution at a rate of 4.5–5.0 ml/min under continuous mixing of the reaction mixture. After 48 hours, the residuas were filtered under vacuum, dried at 80 ° C, weighed, and examined using a group of physical and chemical techniques.

Solid precipitates were analyzed via FTIR spectroscopy and X-ray diffraction (XRD) analysis – qualitative and quantitative phase analysis and calculation of the crystallite sizes (coherent scattering regions (CSR)). IR spectra were recorded with the FT-801 spectrometer (the samples were prepared as KBr pellets). XRD analysis of the powder samples was performed with the Bruker D8 Advance diffractometer, and the diffraction patterns were interpreted with the EVA Bruker software. After that, the thermogravimetric analysis was performed. The samples Si-HA m = 0.2000 ± 0.0005 g were placed in crucibles and then in a muffle furnace for 2 hours. The calcination temperature varied from 200 to 1000 ^{0}C with 200 ^{0}C space.

3. Results and Discussion

The results of the X-ray diffraction analysis of the solid phases indicate the formation of hydroxyapatite [11,12]. No other calcium phosphates were found. High intensity of the background in all the diffraction patterns can be related to the features of the SBF solution which is of more complex ion composition as compared to the systems used in conventional procedures for preparation of hydroxyapatite-based compounds [13]. When the concentration of silicate ions in the system increases, the peaks observed in the region of $2\theta = 25°–35°$ broaden due to low degree of sample crystallinity.

It should be noted that the diffraction patterns corresponding to solid phases with different sources of the silicate groups Na_2SiO_3/TEOS are similar. Thus, the nature of the reagent containing SiO_4^{4-} ions does not affect the hydroxyapatite structure.

The sizes of the produced modified hydroxyapatite crystallites are 6.1 ÷ 7.1 nm, which indicate the formation of compound in a nanocrystalline state.

The presence of silicon ions in the obtained powders was determined by the chemical analysis of the supernatant fluid after solid phase mineralization (Table 1). As the initial concentration of silicate ions in the system increases, the number of silicon ions significantly grows leads to the reduction of the ratio Ca/P+Si. The ratio Ca/P in the synthesized compounds exceeds the given value of 1.67 typical of stoichiometric hydroxyapatite, and corresponds to the phase of excess calcium HA. This indicates the

decrease in the amount of phosphate ions in the resulting solid phases, which we believe is due to the possible replacement of phosphate groups by silicate ones.

Table 1. Concentration of silicate-ions in a solid phase, solid phase composition

C Si init., %	C Si in solid ph., %		Ca/P+Si		Ca/P		Solid phase composition
	Na_2SiO_3	TEOS	Na_2SiO_3	TEOS	Na_2SiO_3	TEOS	
0.5	0.0076	0.0024	2.44	2.32	2.48	2.34	excess calcium HA
2.5	0.11	0.11	1.92	1.88	2.31	2.23	

Investigation of the modified hydroxyapatite samples by the thermo-gravimetric analysis showed a continuous mass loss (Tables 2). Silicon-containing hydroxyapatites formed in the sodium silicate medium are of the highest thermal stability. It is found that increase in the silicon content in the solid phase results in the reduction of the total mass loss during heating up to 1000°C. The analysis of the obtained data revealed that hydroxyapatite is the prevailing phase within the entire temperature range (Fig. 1, 2). The greatest reduction in the sample mass corresponds to the temperature range of 25–400°C which is caused by the removal of the crystallization and adsorption water and volatile impurities in samples with the organic additive of silicon ions.

Table 2. Sample mass loss

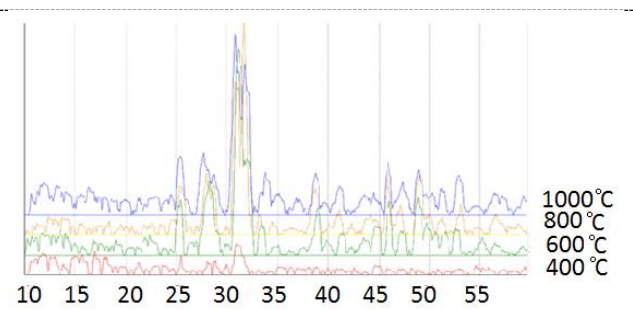| T (^{0}C)	Samples SBF+Na_2SiO_3 init. (%)					Sample SBF+TЭC init. (%)				
	0.50	1.00	1.50	2.50	5.00	0.50	1.00	1.50	2.50	5.00
	m (g)					m (g)				
200	0.0110	0.0299	0.0105	0.0062	0.0113	0.0608	0.0259	0.0105	0.0104	0.0102
400	0.0137	0.0223	0.0116	0.0143	0.0155	0.0159	0.0263	0.0148	0.0174	0.0130
600	0.0252	0.0332	0.0296	0.0325	0.0383	0.0782	0.0442	0.0383	0.0311	0.0268
800	0.0356	0.0385	0.0339	0.0244	0.0355	0.0804	0.0348	0.0358	0.0354	0.0389
1000	0.0289	0.0355	0.0507	0.0357	0.0384	0.0840	0.0514	0.0400	0.0389	0.0447

Comparison of the data from Tables 2 and 3 showed that a great mass loss was observed for Si-HA samples produced in the presence of TEOS due to the removal of the organic component from the structure under temperature increase. It should be noted that the greatest mass loss is observed at low concentrations of TEOS as the HA structure is not stabilized by silicate ions, probably, due to the predominant influence of the organic component decomposition. Further removal of carbonate ions from the apatite structure and partial decomposition of the excess calcium HA followed by formation of the stoichiometric compound and phase of β-tricalcium phosphate occurs in the temperature range of 600–1000 [10].

As can be seen from the diffraction patterns (Fig. 3), the beginning of phase transition and Si-HA peak splitting are observed at 600°C, and splitting of the peak from singlet into doublet can be clearly seen at 800°C. However, the temperature increase up to 1000°C does not cause further changes in the phase composition of samples. Increase in the content of silicate ions in HA is beneficial for thermal activity of samples (Fig. 4). As can be seen from the comparison of the XRD spectra presented above, the form of doublets in the angular range (30–32) 2θ is different that indicates their different thermal

stability at the given temperature. Thus, the presence of SiO_4^{4-} groups in the HA structure enhances thermal stability of HA-based materials. Fig. 5 shows IR absorption spectra for samples produced under variation of the silicate ion concentration and the product of their calcination (at 800°C) synthesized at C Si init. = 0.5%. The absorption bands corresponding to those for hydroxyapatite are observed in IR spectra of the obtained products [9]. The bands at 1020–1080 (v_3), 960, 840 (v_2), 600, 570 (v_4) and 473 (v_2) cm^{-1} correspond to the vibrations of the phosphate groups, the bands at 3570 and 630 cm^{-1} correspond to the vibrations of the hydroxyl groups, the bands at 1650, 1410–1570 (v_3), 880 and 873 (v_2) cm^{-1} correspond to the vibrations of the carbonate groups. The presence of the carbonate groups indicates the presence of all silicon substituted apatites in the structure, which is caused by the presence of HCO_3 ions in the initial synthesized solution. The peak of deformation vibrations of the OH^- groups at 3570 cm^{-1} is observed in the background of the high intensity band in the region of 3200–3700 cm^{-1}, which may be due to the presence of the adsorbed water in the produced apatite form [10]. As the silicate concentration in the reaction medium grows, the mode intensities of OH^- ions HA vibrations (3570 cm^{-1}) decrease.
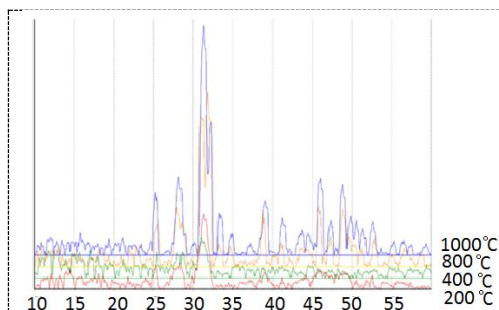
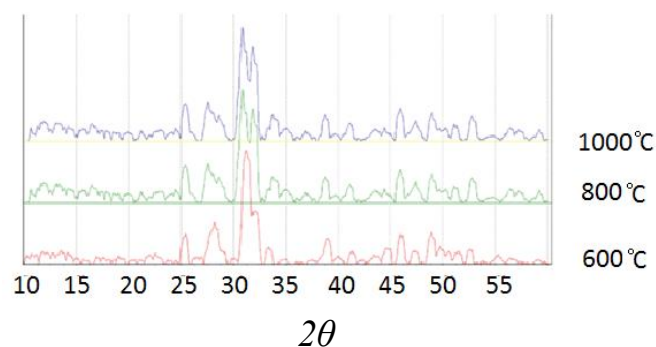| |
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| **Figure 1.** Diffraction patterns of Si-HA with different heat treatment (agent of silicate ions is Na_2SiO_3). |

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| **Figure 2.** Diffraction patterns of Si-HA with different heat treatment (agent of silicate ions is TEOS). |

The presence of SiO_4^{4-} groups in precipitates can be determined by the low intensity peaks with maxima at 504 cm^{-1} and 800 cm^{-1}, which correspond to the modes of deformation vibrations of Si-O bonds and symmetric valent vibrations of Si-O-Si bridges in SiO_4 tetrahedra. [9]. Insignificant increase in their intensity can be observed with the increase of silicon content in the initial reaction medium. Simultaneous decay of the vibrational modes of OH^- ions HA (3570 cm^{-1}) indicates the substitution of phosphates for silicates with the hydroxyl groups involved: $PO_4^{3-} + OH^- \Leftarrow SiO_4^{4-} + \square_{OH}$ that agrees with the literature data [1, 9–13].


2θ

Figure 3. Diffraction patterns of Si-HA with different heat treatment (agent of silicate ions is TEOS)

Broadening of the band in the region of 3570 cm^{-1} is typical of the hydroxyapatite samples modified by silicate ions from the tetraethoxysilane structure, which we believe is due to the

superposition on the absorption band at 2800–2900 cm^{-1} that corresponds to the vibrations of C-H groups. The occurrence of these bands in the spectra can be attributed to the fact that the synthesis was carried out in the TEOS alcohol solution. The IR absorption spectrum of the calcination product of silicon-substituted HA at 800°C is characterized by an intense narrow band at 3570 cm^{-1} typical of crystalline calcium hydroxyapatite. The IR spectrum contains the bands of valent and deformation vibrations 1020–1080, 960, 840, 600, 570 and 473 cm^{-1}. Thus, the thermal effect on the synthesized samples causes the removal of carbonate ions from the HA structure.

2θ
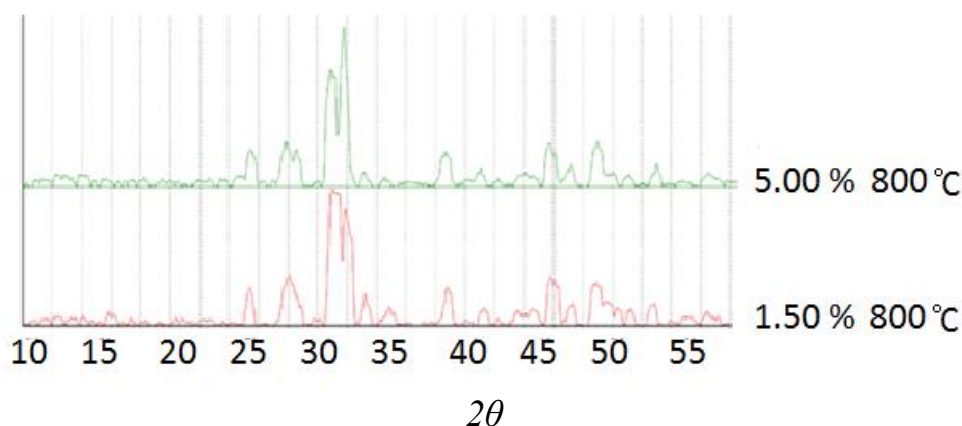
Figure 4. Comparison of Si-HA spectra with different extent of substitution (agent of silicate ions is Na$_2$SiO$_3$).

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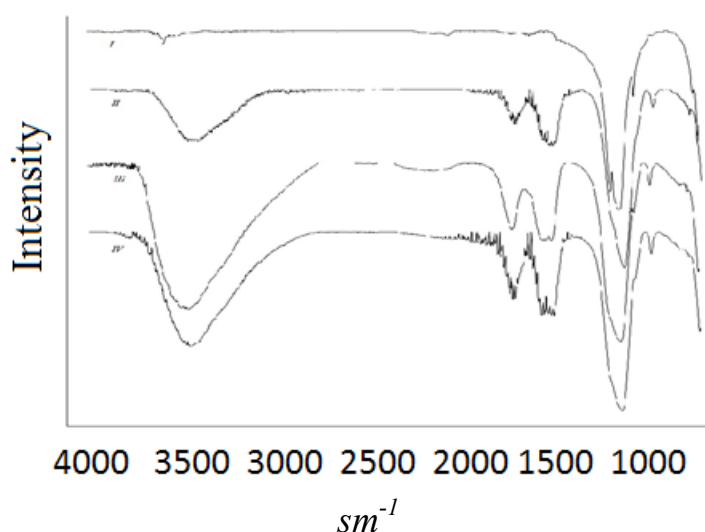
Figuire 5. IR spectra of HA samples modified (mass fraction (C%)): (*I*) Na$_2$SiO$_3$ is Si init. 0.5% at 800ºC; (*II* and *III*) TEOS is Si init. 0.5 and 1.0%, respectively; (*IV*) Na$_2$SiO$_3$ is Si init. 0.5%.

4. Conclusion

The following conclusions can be drawn based on the thermogravimetric analysis of Si-HA:

1. Formation of silicon-substituted hydroxyapatite from the model solution of human extracellular fluid was found via the chemical method, and XRD and FTIR analyses. No significant difference in the structure of the formed solid phases was identified due to different types of reagents containing SiO$_4^{4-}$. The results of all the analyses are in agreement and indicate the possibility of substitution of

phosphate groups for silicate groups in the HA structure when introducing various sources of silicon such as tetraethoxysilane and sodium silicate into the reaction mixture.

2. As the amount of silicon in Si-HA grows, thermal stability of the samples increases. The greatest mass loss is observed at temperatures of 25–400 °C, which is apparently caused by the removal of the crystallization and adsorption water and volatile impurities.

3. The structure of the modified apatites is imperfect and they crystallize in a nanocrystalline state.

These properties together with the synthesis carried out under near-physiological conditions, potentially increase the extent of resorption, solubility and bioactivity of the material based on the obtained silicon-substituted hydroxyapatite capable of the bone tissue integration.

Acknowledgments

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