

Synthesis of $\text{Na}^+, \text{CO}_3^{2-}$ -containing calcium phosphate nanoparticles and their thermal transformations

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The nanoparticles of $\text{Na}^+, \text{CO}_3^{2-}$ -containing hydroxyapatites have been prepared from aqueous solutions for system $\text{Na}^+ - \text{Ca}^{2+} - \text{NO}_3^- - \text{CO}_3^{2-} - \text{PO}_4^{3-}$ at molar ratio of $\text{Ca/P} = 1.67:1$ and $\text{CO}_3^{2-}/\text{PO}_4^{3-} = 0, 1.0, 2.0, 3.0$. Thermal transformations of the obtained phosphates have been established for the temperature range of $80-900^\circ\text{C}$. The obtained complex-substituted HAP have been investigated using IR spectroscopy, scanning electron microscopy, X-ray diffraction and thermogravimetry.

Синтезовані наночастинки $\text{Na}^+, \text{CO}_3^{2-}$ -содержащих гідроксиапатитів в водних розчинах системи $\text{Na}^+ - \text{Ca}^{2+} - \text{NO}_3^- - \text{CO}_3^{2-} - \text{PO}_4^{3-}$ (мольні співвідношення $\text{Ca/P} = 1.67$ і $\text{CO}_3^{2-}/\text{PO}_4^{3-} = 0, 1.0, 2.0, 3.0$). Розглянуто термічні перетворення синтезованих зразків в температурному інтервалі $80-900^\circ\text{C}$. Розглянуто термічні перетворення синтезованих зразків в температурному інтервалі $80-900^\circ\text{C}$. Отримані складнозаміщені гідроксиапатити досліджені з використанням методів ІК-спектроскопії, скануючої мікроскопії, порошкової рентгенографії та термогравиметрії.

Синтез наночастинок $\text{Na}^+, \text{CO}_3^{2-}$ -вмісних кальцій фосфатів та їх термічні перетворення. *А.І.Малишенко, Н.Ю.Струтинська, І.В.Затовський, М.С.Слободяник, М.Еппле, О.Примак.*

Синтезовано наночастинки $\text{Na}^+, \text{CO}_3^{2-}$ -вмісних гідроксиапатитів у водних розчинах системи $\text{Na}^+ - \text{Ca}^{2+} - \text{NO}_3^- - \text{CO}_3^{2-} - \text{PO}_4^{3-}$ (мольні співвідношення $\text{Ca/P} = 1.67$ та $\text{CO}_3^{2-}/\text{PO}_4^{3-} = 0, 1.0, 2.0, 3.0$). Розглянуто термічні перетворення синтезованих зразків у температурному інтервалі $80-900^\circ\text{C}$. Одержані складнозаміщені гідроксиапатити досліджено з використанням методів ІЧ-спектроскопії, скануючої електронної мікроскопії, порошкової рентгенографії та термогравиметрії.

1. Introduction

Apatite-related calcium phosphates have wide applications in medicine as an implants or dental materials due to their high biocompatibility [1–4]. For this reason many research are dedicated to investigation of calcium phosphates formation pecu-

liarities and their properties. It is known, that complex substituted hydroxyapatite (HAP, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is a basic component of bone inorganic part [1–3, 5]. The main substitutes of calcium atoms in HAP structure are sodium, magnesium (from 0.5 to 1.0 mas.%) and less amount of potassium (0.03–0.1 mas.%) [4, 6–9]. At the

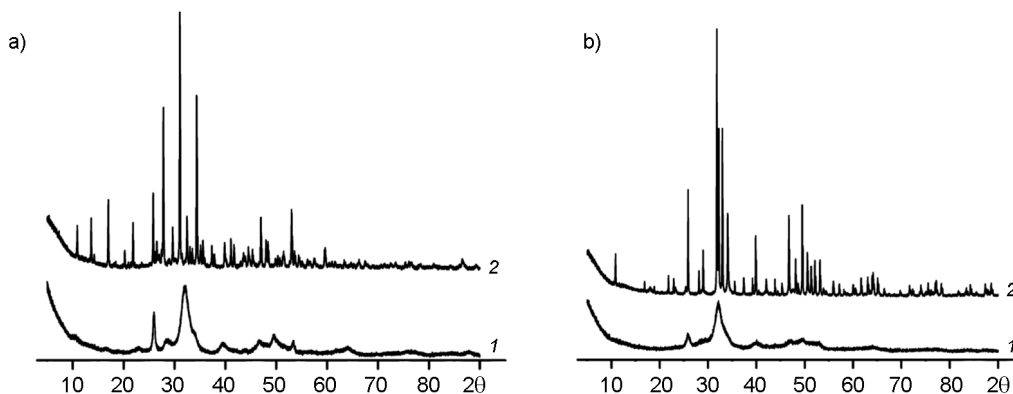


Fig. 1. XRD patterns of samples No.1 (a) and No.3 (b), dried at 80°C (1) and heated to 700°C (2).

same time, some part of phosphate groups is substituted by carbonate (to 8.0 mas.%) [5, 6]. Such cation-anion substitution influences on physical and chemical properties of biohydroxyapatite. It should be noticed, that nowadays there are plenty of manuscripts dedicated to obtaining of complex substituted apatites [1–5, 12, 13] including Na⁺,CO₃²⁻-containing HAP [4, 6–11]. However correlation between synthesis conditions, composition, morphology and fractional composition of particles is poorly studied issue. An establishment of possibility of thermal treatment influence on characteristics mentioned above is also interesting. Detailed investigation of such correlations is one of the key aspects in the development of methodology for obtaining materials not only with a desired composition, but also with controlled particle size of the complex substituted calcium phosphates.

Herein, the results of investigation of Na⁺,CO₃²⁻-containing calcium phosphates formation in aqueous solutions of system Na⁺-Ca²⁺-NO₃⁻-CO₃²⁻-PO₄³⁻ (molar ratios Ca/P = 1.67 and CO₃²⁻/PO₄³⁻ = 0, 1.0, 2.0, 3.0) are represented. Peculiarities of the thermal transformations of obtained samples have been studied in the temperature range of 80–900°C. Prepared complex substituted HAPs have been characterized by FTIR-spectroscopy, scanning electron microscopy, X-ray powder diffraction and thermogravimetry.

2. Experimental

Synthesis of the samples was carried out from aqueous solutions for system Na⁺-Ca²⁺-NO₃⁻-CO₃²⁻-PO₄³⁻ at fixed molar ratio Ca/P = 1.67 and different containing

of carbonate in initial solution CO₃²⁻/PO₄³⁻ = 0, 1.0, 2.0, 3.0 (samples No.1–4).

Preparation of the samples was done in two steps. At the first step, solutions of Ca(NO₃)₂·4H₂O, Na₂CO₃ and Na₂HPO₄ was mixed, then obtained amorphous precipitates were filtrated, washed up with deionized water and dried at 80°C. At the next step, obtained powders were heated to 400, 700 and 900°C during one hour.

Peculiarities of thermal transformations of the obtained HAP were investigated by thermogravimetry (STA 449 F3 Jupiter). FTIR-spectra were obtained using both FTIR Nicolet Nexus and VERTEX X70 in the range of 400–4000 cm⁻¹ for the samples pressed into disk of KBr. Phase compositions of the obtained samples and products of their thermal transformations were established using X-Ray powder diffraction (diffractometers Shimadzu XRD-6000 and Bruker D8 ADVANCE, CuKα-radiation, λ = 1.5418 Å and range 2θ from 5.0 to 90.0°).

Morphology of the fracture surface, shape and compositions of particles of the obtained samples were observed by scanning electron microscopy (SEM) with the energy-dispersive X-Ray analyzer (Zeiss Gemini 1540XB).

3. Results and discussion

3.1. Characterization of the obtained samples. The XRD patterns for the obtained dried at 80°C samples show two wide reflexes in the range 2θ = 20–60° (Fig. 1 — curve a,1 for sample No.1 and curve b,1 for sample No.3), which is characteristic for formation of the particles of calcium phosphates with nanoscale size. The fact of the nanoparticles obtaining is confirmed by scanning electron microscopy data (Fig. 2 —

Table 1. Phase composition and particles size of obtained from aqueous solutions samples, heated to 400, 700 and 900°C, for systems Na⁺-Ca²⁺-NO₃⁻-CO₃²⁻-PO₄³⁻ (Ca/P = 1.67).

Sample number	CO ₃ ²⁻ /PO ₄ ³⁻ in initial solution	Dried at 80°C	Heated to 400°C	Heated to 700°C	Heated to 900°C	
1	0	Phase composition	Calcium phosphate	Calcium phosphate	Whitlockite Ca ₃ (PO ₄) ₂	Whitlockite Ca ₃ (PO ₄) ₂
		Particles size, nm	14–20	23–30		
2	1	Phase composition	Calcium phosphate	Calcium phosphate	HAP+CaO	HAP+CaO
		Particles size, nm	11–23	18–27	425–480	
3	2	Phase composition	Calcium phosphate	Calcium phosphate	HAP+CaO	HAP+CaO
		Particles size, nm	12–27	13–23	80–150	
4	3	Phase composition	Calcium phosphate+CaCO ₃	–	HAP+CaCO ₃	HAP+CaCO ₃ +CaO

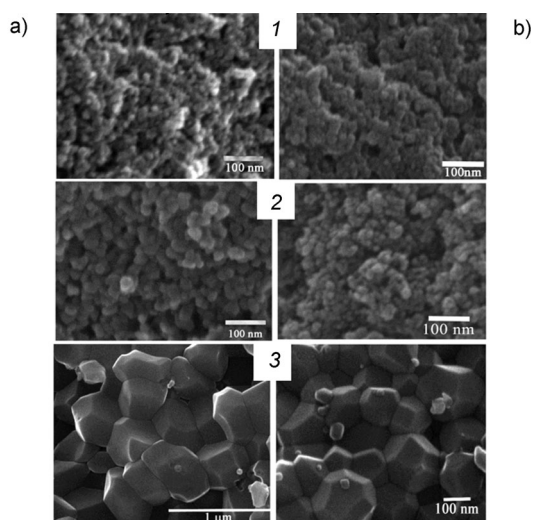


Fig. 2. Scanning electron microscopic observation of samples No.2 (a) and No.3 (b), dried at 80°C (1), heated to 400°C (2) and 700°C (3).

(a,b) 1). The particles are characterized by a spherical shape and its size distribution is in sufficiently narrow range (Table 1).

XRD pattern for sample No.4, obtained under the highest content of carbonate ion in solution (CO₃²⁻/PO₄³⁻ = 3.0), shows additional reflexes, corresponding to the crystalline phase of CaCO₃. Due to this reason this sample was not investigated in the recent work (Table 1).

FTIR spectra for samples No.1–3 (Fig. 3) in the ranges of 560–600 cm⁻¹ and 1000–1100 cm⁻¹ show the set of bands, related to PO₄-groups, the bands at 3480 and 600 cm⁻¹ are specified to OH-groups vibration. Its frequency positions are characteristic for

apatites [12–13]. In the ranges of 1500–1400 cm⁻¹ (ν₃) and 880–870 cm⁻¹ (ν₂) there is also presence of the bands corresponding to carbonate groups. It should be noticed, that for sample No.1 (Fig. 3 — curve 1), obtained without carbonate ion in the initial solution, the related intensity of these bands is very low and it is caused by the presence of insignificant quantity of absorbed from the air carbonate during synthesis process. However the intensity of these bands is significantly increasing while carbonate content in the initial solution becomes higher (Fig. 3a). In the spectra for all samples the broad band in region 3200–3600 cm⁻¹, indicated on the significant amount of absorbed water in their composition, is also observed.

3.2. Characterization of products of the samples thermal transformations. Thermogravimetry results demonstrate that mass losing for all samples occurs stepwise and can be divided conditionally on the intervals of 80–350°C, 450–650°C and above 700°C (Fig. 4). Literature data analysis for the thermal treatment of carbonated HAP permits to assume that on the first step (80–350°C) elimination of absorbed water takes place, than simultaneous CO₂ and water losing, and above 650°C present process can be accompanied by the samples destruction. Considering this data, the thermal treatment regimes for synthesized samples were chosen (400, 700 and 900°C).

The samples mass losing at 400°C is 8–28 % (Table 2). FTIR spectra of such samples show changing of bands relative intensities namely decrease for the band

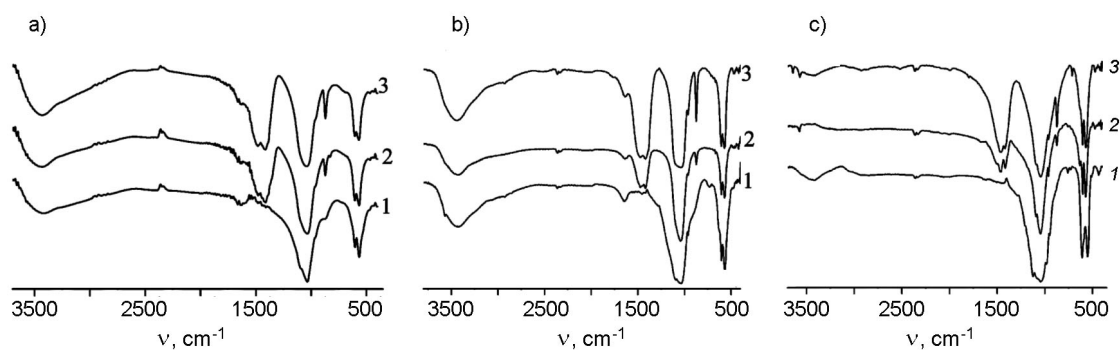


Fig. 3. FTIR-spectra of samples No.1, No.2 and No.3, dried at 80°C (a), heated to 400°C (b) and 700°C (c).

Table 2. Mass changes for obtained samples under heating at different temperatures

Sample number	Δm , %		
	400°C	400–700°C	700–900°C
1	8.8	2.7	0.36
2	8.7	5.8	1.2
3	19.0	6.5	6.1
4	28.0	4.8	6.5

3200–3600 cm⁻¹, corresponded to absorbed water. Wherein the phase and fractional composition of the thermal treatment products changes insignificantly, that is verified by the XRD and SEM data (Fig. 2). The particles save spherical shape, and their size increases approximately on 20 %. Herewith the fractional size distribution of the particles even narrows slightly, for instance, for the sample No.3 from 30 % to 15 %.

EDX results for heated at 400°C illustrate that sodium quantity in the obtained samples composition increases under rising of its concentration in the initial solution (Table 3).

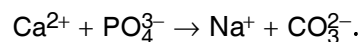
Further heating of the samples to 700°C leads to mass losing from 2 to 7 % depending on their composition (Table 2). Correlation between the mass losing value and carbonate quantity in the samples composition should be noticed. Sample No.4 is an exception due to consistence of stable calcium carbonate at these conditions. Wherein crystallinity of the samples and their phase composition are changing significantly. According to the phase analysis data heating of sample No.1 leads to formation of hetero-substituted calcium orthophosphate of whitlockite type with cell parameters $a, b =$

Table 3. EDX results for heated to 400°C samples

Sample number	Na [wt.%] 400	Ca [wt.%] 400	P [wt.%] 400	Molar ratio Ca/P
1	0.28	34.40	18.76	1.48
2	2.49	31.44	12.99	1.88
3	2.77	35.47	13.03	2.11

10.440(9) Å, $c = 37.301(6)$ Å. In the other cases sodium- and carbonate-containing calcium orthophosphates of apatite type are obtained (hexagonal symmetry, $\alpha, \beta = 90^\circ, \gamma = 120^\circ, a = b \neq c$). Thus, for heated to 700°C sample No.2 estimated cell parameters are $a, b = 9.4167$ Å, $c = 6.8919$ Å, to 900°C — $a, b = 9.3584$ Å, $c = 6.8524$ Å, for sample No.3 it has been established the formation of crystal lattice with parameters $a, b = 9.4148$ Å, $c = 6.8930$ Å for heated to 700°C and $a, b = 9.4106$ Å, $c = 6.8917$ Å for heated to 900°C.

Formation of the complex substituted calcium orthophosphates of apatite type for samples No.2 and No.3 envisages heterovalent substitution in cationic and anionic sublattices of the matrix according to the next scheme:



The scanning electron microscopy data for the heated to 700°C samples verify considerable particles enlargement from 100 to 480 nm (Fig. 2, (a,b — 3)). Bands related to water vibration are almost absent in their FTIR spectra, that confirms complete water elimination under heating to 700°C. The last fact could be a reason of observed particles aggregation. At the same time, FTIR

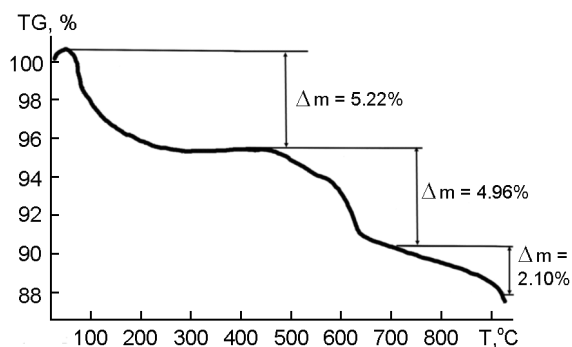


Fig. 4. Thermogravimetry for sample No.2.

spectra are characterized by more narrow bands, comparing to the case of dried at 80°C and heated at 400°C powders, that caused by increase of their crystallinity (Fig. 3c). It permits to determine more accurately the position of maximum for bands, related to carbonate group vibrations, in order to determine the carbonate localization in apatite matrix. It is known an existence of two types of CO₃²⁻-HAP depending on carbonate-ion position in apatite: substituting OH- (A-type) or phosphate-group (B-type). In the case of A-type CO₃²⁻ bands are observed at 1545, 1450 and 880 cm⁻¹, whereas for B-type — near 1455, 1410 and 875 cm⁻¹ [12, 13]. The position of the carbonate bands in FTIR spectra of investigated samples confirms the B-type substitution.

Analysis of the samples mass changing under their heating to 900°C demonstrates that the lowest value (to 0.5 %) is obtained for sample No.1. This fact indicates on stability of the formed under heating to 700°C whitlockite phase. Meanwhile increasing of the mass losing for the rest samples correlates with carbonate content in the samples composition, that gives evidence on reduction of Na⁺,CO₃²⁻-containing HAP thermal stability under rising of degree of phosphate-on-carbonate substitution. Their estimated crystalline lattice parameters decrease comparing to corresponding phosphates heated to 700°C, that reveal the lattice compression under the partial carbonate losing.

4. Conclusions

The nanoparticles of Na⁺,CO₃²⁻-containing HAP have been prepared by wet precipi-

tation method in aqueous media under ambient temperature and investigated using X-ray powder diffraction, FTIR-spectroscopy, thermogravimetry and scanning electron microscopy.

The relationships between molar ratio of the components in initial solutions and content of sodium and carbonate in the samples composition have been established. The influence of the samples heating to 400, 700 and 900°C on their particles size has been shown. It should be noticed, that heating of Na-containing calcium phosphate obtained without carbonate in solution caused elimination of absorbed water and formation of the whitlockite crystalline phase, while in other cases the complex substituted calcium orthophosphates are obtained. All obtained results illustrated the additional possibilities for synthesis of the nanoparticles of complex substituted calcium phosphates. Their size can be programmed by the way of the samples thermal treatment that is important for manufacturing of the new biomaterials and sorbents.

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