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Anionic Substitutions in the Mechanochemical Synthesis of Hydroxyapatite

M. V. CHAIKINA[1], N. V. BULINA[1], I. YU. PROSANOV[1], A. V. ISHCHENKO[2,3]

[1]*Institute of Solid State Chemistry and Mechanochemistry,*
Siberian Branch of the Russian Academy of Sciences,
Novosibirsk, Russia

E-mail: chaikinam@solid.nsc.ru

[2]*Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences,*
Novosibirsk, Russia

[3]*Novosibirsk State University,*
Novosibirsk, Russia

Abstract

An overview of possible anionic substitutions in the structure of hydroxyapatite for the mechanochemical method of synthesis is presented. It was revealed that single-phase nanocrystalline varieties of anion-substituted hydroxyapatite are formed during mechanochemical synthesis. A series of the samples of carbonate-, silicate-, aluminate-, zirconate-substituted hydroxyapatites with different concentrations of the substituent ion were obtained. It was established that additional high-temperature annealing leads to a partial loss of the substituent ion, which results in the formation of impurity phases. Silicate-, aluminate-, and zirconate-containing hydroxyapatite species may be of interest as coatings of medical implants made of metal and zirconium-corundum ceramics.

Keywords: mechanochemical synthesis, carbonate-, silicate-, aluminate-, zirconate-substituted hydroxyapatite

INTRODUCTION

Hydroxyapatite (HAP) $Ca_{10}(PO_4)_6(OH)_2$ is widely used in medicine as an analogue of the mineral component of bone and dental tissues [1], serves as a material for medical ceramics, for filling the defects of bone tissues, for implant coatings, it is used in stomatology, and also as therapeutic means and cosmetics [2, 3]. Organogenic HAP does not correspond to the idealized formula presented above and always contains cation and anion substitutions at a level of several hundredths to several mass percent. These substitutions play an essential biological part [4, 5]. The structure of apatite allows carrying out a broad range of substitutions in the anion and cation sublattices [6]. The variation of HAP composition is accompanied by the changes of its properties. Within the recent decade, many works dealing with the synthesis of HAP with various substitutions were published. Analysis of the biological role of some ions and their antibacterial properties exhibited after the introduction into hydroxyapatite structure was considered in reviews [7, 8]. The authors of [4] demonstrated that a substituent in HAP structure, even at a level of several hundredths of a percent, affects its physicochemical properties and the properties of the resulting bioceramics. When HAP is used as a material for implants, the composition of the substituent in HAP structure may affect adhesion with the substrate, accelerate implantation and even decrease the possibility of malignant neoplasms [9]. In particular, according to numerous literature data cited in [10], silicon is a necessary element for osteosynthesis. The use of HAP modified with silicate as a coating for implants promotes faster implantation. The presence of carbonate ions in HAP structure causes an increase in its solubility [6]. It may be assumed that a coating made of HAP modified with aluminate and zirconate will exhibit higher adhesion to the surface of medical implants made of corundum and zirconium ceramics. From this point of view, we chose anions as substituents (dopants) and synthesized HAP samples with partial anion substitution of phosphate ions for carbonate, silicate, aluminate or zirconate ions.

The goal of the present work was to investigate the degree of substitution during the mechanochemical synthesis of HAP varieties with the introduction of dopants – carbonate, silicate, aluminate and zirconate ions playing essential biological roles, with the outlooks to use them as the materials for implant coatings, for bioceramics, and composites for medical purposes. The effect of the chemical composition of substituents on the substitution degree and the composition of the synthesized product was studied.

EXPERIMENTAL

The basis for all substituted HAP samples was monetite $CaHPO_4$ (Ch. reagent grade, Vekton) and freshly calcined calcium oxide CaO (Ch.D.A. reagent grade, Vekton). The sources of substituting ions were reagents (Ch.D.A. grade): calcium carbonate $CaCO_3$, amorphous silicon oxide $SiO_2 \cdot 0.7H_2O$, aluminium oxide Al_2O_3, zirconium oxychloride $ZrOCl_2 \cdot 8H_2O$, zirconium oxide ZrO_2 and zirconium hydroxide $Zr(OH)_4$. Mechanochemical synthesis of the samples of carbonate-(CO_3-HAP), silicate- (Si-HAP), aluminate- (Al-HAP) or zirconate-substituted HAP (Zr-HAP) was carried out in AGO-2 planetary mill in water-cooled steel jars with the rotation frequency of 1200 r.p.m., 150 mL in volume, with steel balls 200 g in mass, for 30 min. The mass ratio of the reaction mixture to the balls was 1 : 20. To avoid product contamination, the preliminary lining was carried out in the working zone of the mill by the reaction mixture with the same composition as the sample to be synthesized [11]. To study the structure of the resulting materials, the synthesized samples were annealed at a temperature of 1000 °C for 5 h in a PVK 1.4-8 electric furnace (Russia). The samples of anion-substituted HAP were marked as CE-HAP (here C is dopant concentration, in mol of substituting ions per one mole of HAP, and E is the element of substituent anion).

The samples after mechanochemical synthesis and after annealing were studied by means of X-ray structure analysis, IR spectroscopy and high-resolution electron microscopy (HREM). X-ray diffraction patterns were recorded with a Bruker D8 Advance diffractometer (Germany) in Bragg–Brentano configuration with CuK_α radiation, NiK_β filter and superfast position-sensitive one-dimensional detector Lynx-Eye (capture angle 3°). X-ray phase analysis of the compounds was carried out using the powder diffraction database ICDD PDF-4 (2011). Refinement of unit cell parameters, crystallite size, and calculation of phase concentrations were carried out using Rietveld procedure in Topas 4.2 software (Bruker, Germany). IR spectra were recorded with an Infralyum-801 spectrometer (Russia), tablets of the samples were made using a standard procedure by pressing with KBr. Investigation of the samples by means of HTEM was performed with a JEM-2010 electron microscope (JEOL, Japan) with the accelerating voltage 200 kV. The particles were deposited by dispersing the suspension of the sample in alcohol onto a copper substrate using an ultrasonic dispergator. Local analysis of the elemental composition of the samples was carried out with the help of energy-dispersive spectroscopy (EDS) with a QUANTAX 200-TEM spectrometer (Bruker, Germany) with an XFLASH detector.

RESULTS AND DISCUSSION

Substitution of phosphate ions by carbonate ions

Anion substituents in apatite structure may be arranged in two positions: in the positions of complex phosphate ions or monovalent anions at the 6_3 axis, where OH groups are localized. Heterovalent substitution often takes place. An example may be the substitution of phosphate and hydroxide ions by carbonate ions with the formation of carbonate hydroxyapatite of B and A type, respectively [6].

Carbonate hydroxyapatite of B type with the general formula $Ca_{10-x}(PO_4)_{6-x}(CO_3)_x(OH)_{2-x}$ is usually formed during the synthesis of HAP according to various procedures in the air due to the presence of carbon dioxide in the air [10]. During mechanochemical synthesis according to reaction $6CaHPO_4 + 4CaO = Ca_{10}(PO_4)_6(OH)_2 + 2H_2O$, which is also carried out in the air, a definite amount of carbonate ions substituting phosphate ions is present in HAP structure. This process is essentially dependent on air humidity and is explained as follows. Calcium oxide in the reaction mixture interacts with water vapour in the air during the first second of mechanical activation and is partially transformed into calcium hydroxide $CaO + H_2O = Ca(OH)_2$, then it reacts with atmospheric carbon dioxide forming calcium carbonate: $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$, which enters the structure of the compound to be synthesized, with the formation of carbonate hydroxyapatite. In the case of low air humidity (during the heating season), the formed calcium hydroxide reacts completely with calcium hydrophosphate. At this, the source of calcium hydroxide is exhausted, the reaction with carbon dioxide does not proceed, therefore, carbonate ions to not enter apatite structure. An example may be HAP samples synthesized at the air humidity of 15 and 75 %. Their IR spectra shown in Fig. 1. The concentration of carbonate ions in the samples determined by means of volumetry was 1 and 3 mass %, or 0.2 and 0.6 mol of carbonate ions per 1 mol of HAP, respectively. It should be noted that the mineral part of human and animal bone and dental tissues is composed of B type carbonate hydroxyapatite. During sample annealing, carbonate ions leave the HAP structure within the temperature range 500–1200 °C. The X-ray phase analysis data showed that monophase HAP is formed in both cases.

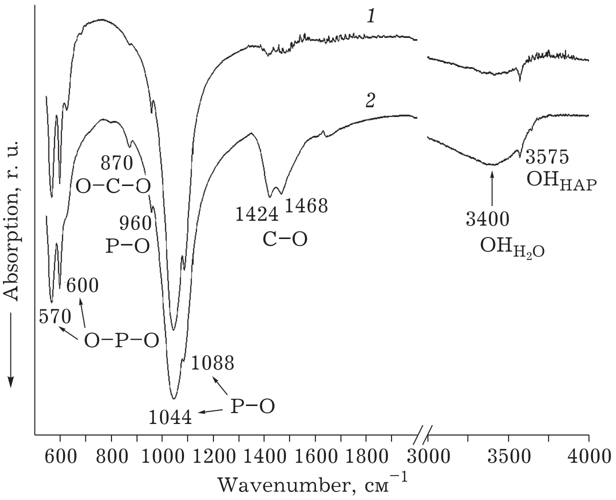
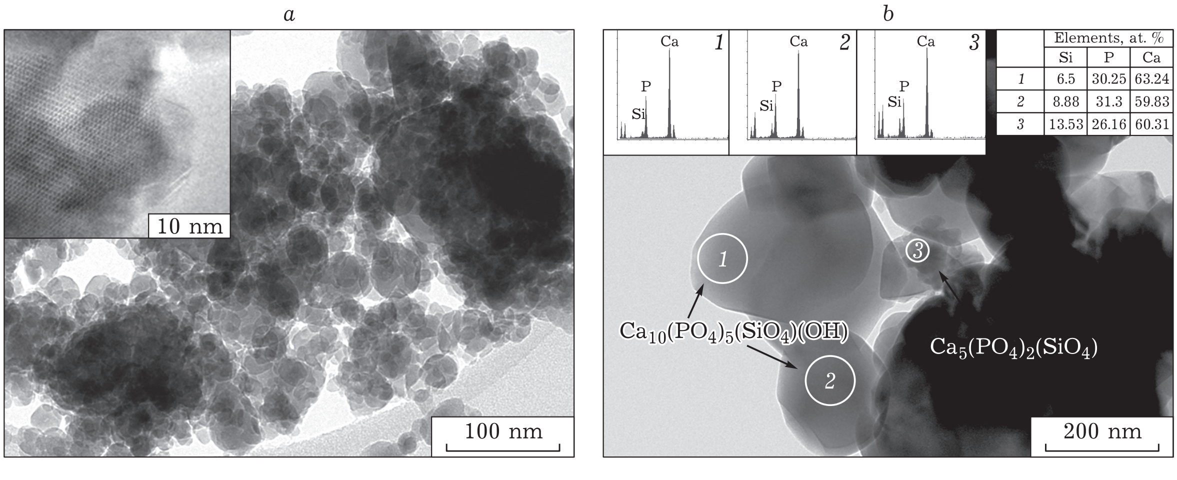


Fig. 1. IR spectra of mechanochemically synthesized HAP sample obtained at the air humidity of 15 (*1*) and 75 % (*2*).

Substitution of phosphate ions by silicate ions

In the case of heterovalent substitution of phosphate ions by silicate ions, charge compensation occurs due to the formation of vacancies (V) in the positions of OH groups localized at the 6_3 axis in HAP structure according to the scheme: $SiO_4^{4-} + V_{OH} \rightarrow PO_4^{3-} + OH^-$. As a result of this substitution, substantial deformation of the lattice is observed, with its gradual rearrangement from hexagonal into orthorhombic [12]. It was revealed that up to 2 mol of silicate ions per 1 mol of HAP may enter the HAP structure during mechanochemical synthesis. The product is a monophase nanosized silicate-substituted HAP (Si-HAP) (Fig. 2, *a*). However, annealing of the resulting material involves crystallite growth. As a result, in the samples with the high concentration of silicate ions, a part of these ions leaves HAP lattice, which leads to the formation of the second phase silicocarnotite $Ca_5(PO_4)_2(SiO_4)$ (see Fig. 2, *b*, particle 3). As shown above, the phase transition of Si-HAP into silicocarnotite starts at a temperature of 970 °C [13]. The concentration



	Elements, at. %		
	Si	P	Ca
1	6.5	30.25	63.24
2	8.88	31.3	59.83
3	13.53	26.16	60.31

Fig. 2. HTEM images of mechanochemically synthesized silicate-substituted HAP: *a* – before annealing (insert shows nanoparticles with extended lattice); *b* – after annealing at 1100 °C for 15 h (insert shows EDS data with the table of elemental composition).

of silicocarnotite in the sample depends on the amount of the inserted silicate ion, temperature and annealing time [13].

X-ray diffraction patterns of Si-HAP with different amounts of the introduced silicon oxide after annealing at 1000 °C for 10 h are shown in Fig. 3. One can see that silicocarnotite is formed in noticeable amounts when 1.2 mol of silicate ions are introduced per 1 mol of HAP. For these annealing conditions, Si-HAP remains monophase until the substitution degree 0.8. With an increase in annealing temperature to 1200 °C, the monophase nature is conserved within the concentration range 0–0.6 mol of silicate ion per 1 mol of HAP [12].

Substitution of phosphate ions by aluminate ions

We are unaware of works on the synthesis of HAP with reliable data on the substitution of phosphate by aluminate ions in the literature. The authors of [14] studied co-precipitation of three-valent cations including aluminium during the synthesis of apatite for the purpose of substituting calcium ions. On the basis of the data of IR spectroscopy, the authors believe that aluminium ions are sorbed at the surface interacting with OH groups of apatite. The synthesis of HAP according to the sol-gel method was reported, with the introduction of the substituent in the form of the solution of aluminium nitrate in ethanol in the amount of 10 to 40 mass % [15]. The product obtained in the form of powder was pressed in a tablet and annealed at 900 °C. After annealing, the sample turned out to be monophase, it was composed of aluminium and calcium phosphates: $AlPO_4$, CaP_4O_{11}, $Al_3(PO_4)_2(OH)_3(H_2O)_5$ and $Ca_2Al(PO_4)_2(OH)$ [15].

We synthesized the samples of HAP using mechanochemical method, with the introduction aluminium oxide into the reaction mixture in the amount of 0.1–1.5 mol of aluminate ions per 1 mol of HAP (Table 1). X-ray phase analysis results showed that a monophase product – nanosized HAP is formed during mechanochemical synthesis of aluminate-substituted HAP (*C*Al-HAP) within the whole range of concentrations *C* (see Table 1). After the introduction of 0.1–0.25 mol of aluminate ions per 1 mol of HAP, a small change of HAP unit cell parameters is observed. At higher concentrations, the parameters remain unchanged, which is the evidence of insignificant insertion of aluminate ions into the HAP structure during mechanochemical synthesis.

After sample annealing, X-ray diffraction patterns contain narrow intense reflections corresponding to the HAP phase, which points to the high degree of product crystallinity (Fig. 4). After the introduction of aluminium oxide into the reaction mixture in the amount of 0.5 mol of aluminate ions and more per 1 mol of HAP, reflections

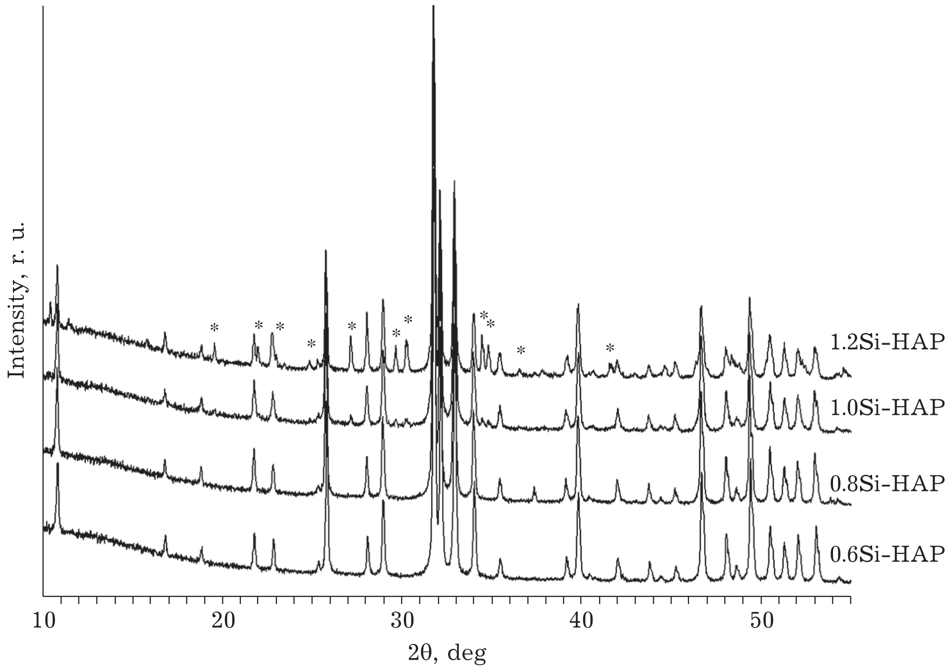


Fig. 3. X-ray diffraction patterns of mechanochemically synthesized samples of silicate-substituted HAP (CSi-HAP) after annealing at a temperature of 1000 °C for 10 h.

TABLE 1

Phase composition of the samples of mechanochemically synthesized HAP with the substitution of phosphate ions by aluminate ions

Sample	Introduced Al_2O_3, mol	HAP concentration, %	Crystallinity degree, %	Crystallite size, nm	HAP unit cell parameters		
					a, Å	c, Å	V, Å^3
HAP	0	100	72	29	9.409	6.895	528.7
0.1Al-HAP	0.1	100	72	23	9.43	6.90	531
0.25Al-HAP	0.25	100	70	25	9.42	6.91	531
0.5Al-HAP	0.5	100	69	21	9.42	6.91	531
0.8Al-HAP	0.8	100	63	21	9.42	6.91	531
1.0Al-HAP	1.0	100	57	18	9.42	6.91	531
1.5Al-HAP	1.5	100	56	18	9.42	6.91	531

related to the phase of calcium aluminate $Ca_3Al_2O_6$ appear in the diffraction patterns of the samples.

The content of calcium aluminate increases with an increase in the amount of Al_2O_3 introduced. In addition, X-ray diffraction patterns of all annealed samples contain reflections corresponding to calcium oxide (see Fig. 4). The formation of CaO during annealing of the samples may be explained by the decomposition of carbonate-substituted HAP formed during mechanochemical synthesis.

When planning experiments, we calculated the ratio of components for obtaining the necessary product in the form of a stoichiometric compound in which aluminium is present in apatite structure in the form of aluminate ion $(AlO_3)^{3-}$, according to reaction: $(6 - x)CaHPO_4 + (4 + x)CaO + 0.5xAl_2O_3 = Ca_{10}(PO_4)_{6-x}(AlO_3)_x(OH)_2$.

According to the data of IR spectroscopy, the complex aluminate ion in HAP structure has a tetrahedral coordination, which is more probable with the substitution of the tetrahedron of phosphate ion. If we assume that the phosphate ion is substituted by $(AlO_4)^{5-}$, then charge compensation should proceed due to the formation of vacancies in the positions of OH groups according to the scheme: $(AlO_4)^{5-} + 2V_{OH} \rightarrow (PO_4)^{3-} + 2OH^-$. With this scheme, the content of OH groups in

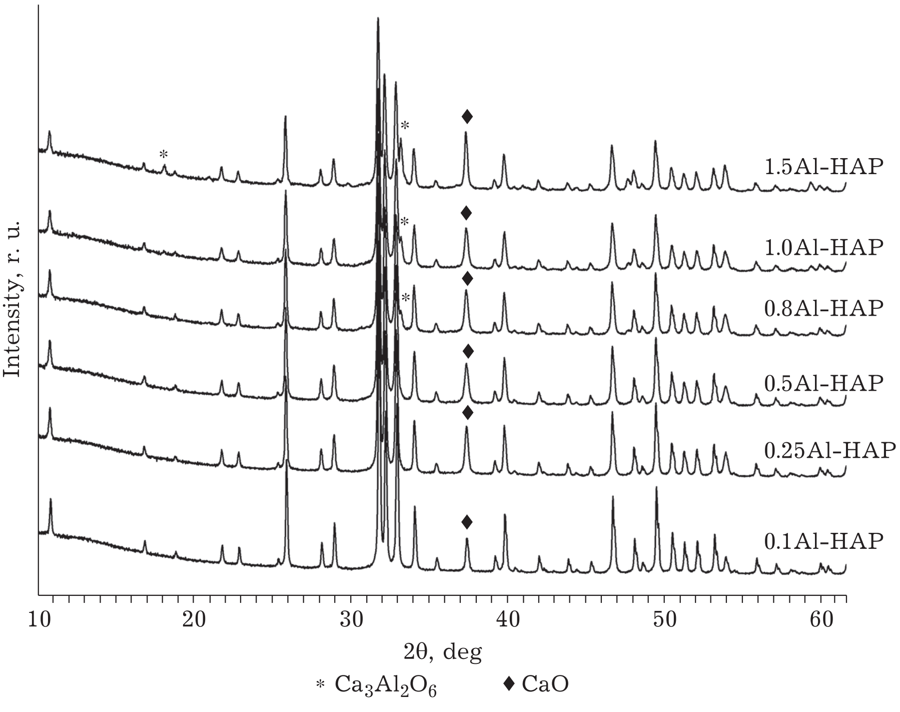


Fig. 4. X-ray diffraction patterns of mechanochemically synthesized samples of aluminate-substituted HAP (CAl-HAP) after annealing at a temperature of 1000 °C for 10 h.

HAP structure should decrease, which will be observed as a decrease in the intensity of bands at 630 and 3575 cm^{-1} related to the vibrations of the bonds of OH group with an increase in the concentration of the introduced Al_2O_3, however, this was not observed (Fig. 5). The authors of [16] analyzed the IR spectrum of calcium aluminate and determined that absorption bands at 705, 720, 780, 820, 865 and 900 cm^{-1} relate to AlO_4 tetrahedrons, while the bands at 410, 460, 510 and 520 cm^{-1} are due to the presence of AlO_6 octahedrons in $Ca_3Al_2O_6$. In the IR spectra of the samples synthesized by us with the concentration of the introduced aluminium oxide 1.0–1.5 mol per 1 mol of HAP, some bands appeared with the wavenumbers 745, 819, 866 and 900 cm^{-1} (see Fig. 5). These wavenumbers are close to the data reported in [16] for the tetrahedral surroundings of aluminate ions.

So, in the case of the synthesis of Al-HAP, most probably, substitution leading to the formation of vacancies occurs. These vacancies destabilize HAP structure. This may explain the fact that the $Ca_3Al_2O_6$ phase is released during annealing in the case when more than 0.5 mol of aluminate ions is introduced into HAP samples.

Substitution of phosphate ions by zirconate ions

Along with metal implants, at present, the application of corundum and zirconium ceramics for the manufacture of separate details of implants or completely ceramic products for use in traumatology and orthopedy broadens. In this connection, search for new compositions is necessary to make the materials for coatings of ceramic implants and bioresorbable ceramics. One of the possible substituents of phosphate ions in HAP structure may be zirconate ions according to the scheme: $ZrO_4^{4-} + V_{OH} \rightarrow PO_4^{3-} + OH^-$, with the formation of vacancies in the positions of OH groups for charge compensation.

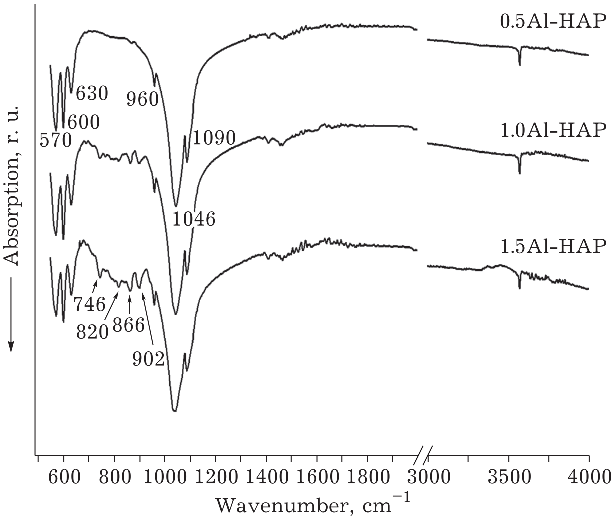


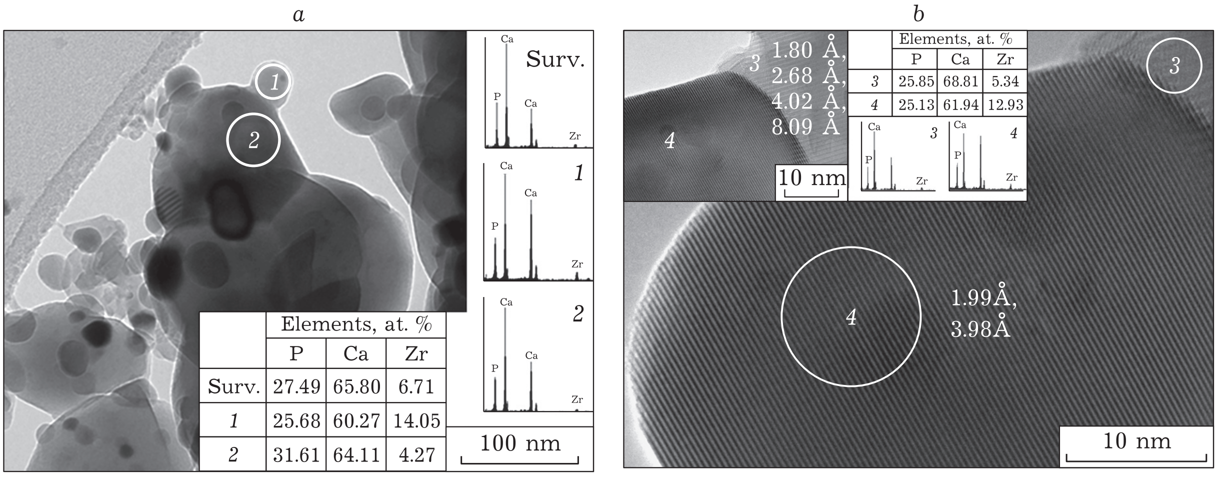
Fig. 5. IR spectra of the annealed samples of substituted HAP (CAl-HAP).

Some data on calcium substitution by zirconium in HAP structure were published [17], but the data on the substitution of phosphate ions by zirconate ions ZrO_4^{4-} are absent yet. It is interesting not only to study the possibility of this substitution but also to obtain the material for coating the implants made of zirconium ceramics or for use as a precursor of phosphate-zirconium ceramics.

We synthesized the samples of zirconium-substituted hydroxyapatite Zr-HAP using zirconium oxychloride, oxide and hydroxide as precursors of zirconate ions. After the introduction of zirconium oxychloride into the reaction mixture, mechanochemically synthesized samples were composed of HAP with an insignificant admixture of zirconium oxide, maybe due to the partial decomposition of initial zirconium oxychloride during mechanical activation. After annealing of Zr-HAP samples, their unit cell parameters changed substantially. It should be stressed that the unit cell parameters of two isomorphous apatite varieties differ substantially: for HAP, $a = b = 9.422$ Å, $c = 6.881$ Å, while for chloroapatite ($Ca_{10}(PO_4)_6Cl_2$), $a = b = 9.598$ Å, $c = 6.776$ Å. The unit cell parameters for the Zr-HAP sample synthesized by us, with the introduction of zirconium oxychloride in the concentration of 0.5 mol of zirconate ion per 1 mol of HAP, are: $a = b = 9.518$ Å, $c = 6.842$ Å, which is the evidence of the insertion of chloride ion into apatite structure at the position of OH groups with the formation of chlorohydroxyapatite.

Mechanochemical synthesis of the samples with the introduction of zirconium oxide is accompanied by the formation of HAP without the substitution of phosphate ions by zirconate ions. However, after annealing, some amount of zirconate ions enter the HAP structure, as suggested by an increase in the lattice parameters of HAP.

When zirconium hydroxide is used as a dopant, Zr-HAP is formed as early as at the stage of mechanical activation of the reaction mixture. Zirconium that did not enter HAP structure forms a double oxide of the composition $Ca_{0.15}Zr_{0.85}O_{1.85}$. Judging from the dynamics of unit cell parameters in HAP, not more than 0.6–0.8 mol of zirconate ions per 1 mol of HAP enter HAP structure during mechanochemical activation. After annealing, the samples contain $CaZrO_3$ and CaO in



	Elements, at. %		
	P	Ca	Zr
Surv.	27.49	65.80	6.71
1	25.68	60.27	14.05
2	31.61	64.11	4.27

	Elements, at. %		
	P	Ca	Zr
3	25.85	68.81	5.34
4	25.13	61.94	12.93

Fig. 6. HTEM images and elemental composition according to EDS data for mechanochemically synthesized sample of zirconate-substituted HAP (0.8Zr-HAP) after annealing at a temperature of 1000 °C for 5 h (concentration of zirconate ion 0.8 mol per 1 mol of HAP): *a* – nanoparticle *1* with high Zr content (table in the insert) grown on crystal *2*; *b* – nanoparticle *4* with extended lattice and high Zr content (table in the insert) grown on crystal *3*, zirconate ion content in HAP 5.34 at. %.

addition to HAP. Phases in the form of nanoparticles with the high content of zirconate ions (10–15 at. %) were also revealed. These phases grow during sample annealing on HAP crystals with lower amount of zirconate ions substituting phosphate ions. Figure 6, *a* shows the data of electron microscopy and EDS examination of the Zr-HAP sample in which nanoparticles with zirconate ion content 14 at. % (see Fig. 6, *a*, particle *1*) were formed on HAP crystal containing 4.27 at. % zirconate ions (see Fig. 6, *a*, particle *2*). Figure 6, *b* shows nanoparticle *4* containing 12.93 at. % zirconate ions and 25.12 at. % phosphate ions with extended lattice and interplanar spacings characteristic of calcium zirconate (corresponding to card PDF [35-0790] of the ICDD database). The particle was formed on HAP crystal (particle *3*) containing 5.34 at. % zirconate ions, with the interplanar spaces corresponding to the lattice of HAP. These phases may be related to the substitution-type solid solutions.

So, a comparison of the results of the mechanochemical synthesis of Zr-HAP with the introduction of three different zirconium compounds showed that an optimal dopant is zirconium hydroxide. The introduction of zirconium hydroxide as a precursor of zirconate ions allows us to obtain zirconate-substituted HAP samples as early as at the stage of mechanical activation.

CONCLUSIONS

1. HAP samples with anion substitutions of phosphate ions by carbonate, silicate, aluminate or zirconate ions were obtained with the help of the mechanochemical method. The obtained samples are nanosized powder materials ready for subsequent application.

2. Under the conditions of the mechanochemical synthesis of carbonate-substituted HAP, the concentration of carbonate ions is 0.2 and 0.6 mol per 1 mol of HAP. The decomposition of carbonate-substituted HAP starts at a temperature of 500 and is completed at 1200 °C.

3. With the heterovalent substitution of phosphate ions by silicate ions, mechanochemical synthesis allows obtaining a monophase product after the addition of up to 2 mol of silicate ions per 1 mol of HAP. The thermal stability of the samples decreases with an increase in the concentration of the substituting anion. The maximal substitution degree giving a monophase product during annealing at 1100 °C for 15 h is 0.6 mol of silicate ions per 1 mol of HAP.

4. For the mechanochemical synthesis of the samples of aluminate-substituted HAP, the possibility of the insertion of up to 0.25 mol of aluminate ions per 1 mol of HAP was revealed. The release of $Ca_3Al_2O_6$ and CaO is observed during annealing of the samples with the concentration of introduced aluminate ions more than 0.5 mol per 1 mol of HAP.

5. During mechanochemical synthesis with zirconium hydroxide used as a dopant, zirconate-substituted HAP is formed, with zirconate ion concentration not more than 0.6–0.8 mol per 1 mol of HAP, and a double oxide $Ca_{0.15}Zr_{0.85}O_{1.85}$. After annealing, in addition to the substituted HAP,

the samples contain $CaZrO_3$ and CaO. Phases in the form of nanoparticles with the high zirconium content (10–15 at. %) were revealed.

6. HAP varieties with anion substitutions may be interesting as the coating materials for medical implants made of corundum and zirconium ceramics and bioceramics.

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