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Role of the Composition of Starting Compounds in the Process of the Mechanochemical Synthesis of Zirconium-Substituted Apatite

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Abstract

The possibility to obtain a zirconium-substituted apatite by the method of mechanochemical synthesis was studied. It was established that zirconium oxide or zirconium hydroxide could be used as the source of zirconium for this synthesis. It is preferable to use zirconium hydroxide, as in the process of the mechanochemical synthesis, the major part of the oxide remains in the initial state. In case of the hydroxide, the intermediate phase of the double oxide contributing to further synthesis is formed.

Key words: mechanochemical synthesis, zirconium-substituted apatite

INTRODUCTION

The apatite structure (brutto formula is $Me_{10}(RO_4)_6X_2$) possesses by unique properties that allow a wide range of substitutions and provide various areas of its practical use. Three rows of isomorphic varieties of apatite are known: fluorapatite $Ca_{10}(PO_4)_6F_2$, hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ and chlorapatite $Ca_{10}(PO_4)_6Cl_2$ [1]. Fluorapatite, composing phosphate ores, is virtually the sole source of the preparation of phosphorus and its compounds. Depending on the composition apatites are applied as catalysts, ion-exchangers, absorbers of radiation wastes and phosphors [2–4]. Hydroxyapatite (HAP), the composition of which is close to the mineral part of bones and teeth of a man, is especially actual as a material for coating medical implants, manufacturing of biocompatible ceramics and cement used in traumatology, orthopedics, dental implantology and maxillofacial surgery. It is also widely used for filling the de-

fect of bones, as therapeutic, cosmetics and a component of therapeutic toothpastes [5].

If earlier in traumatology and orthopedics as materials for coating implants and biocompatible ceramics, stoichiometric HAP or its mixture with β -tricalcium phosphate were used, then in recent years, various substitutions in the structure of HAP are being researched. Thus, with the purpose of increasing the biological efficiency when implanting implants in the structure of HAP, silicate ions partially that substitute phosphate [6] or bactericide components – silver, copper, zinc ions and other ions with the purpose of the prevention of inflammatory processes after operative measure, are introduced [7–9].

Along with metal implants, there currently expanding the use of corundum and zirconia ceramics for the manufacture of individual parts of the implants or completely ceramic products used in traumatology and orthopedics. In this connection, a search for new composi-

tions of materials for coating ceramic implants and bioresorbable ceramics is necessary. One of the possible phosphate substituents in the structure of HAP is zirconate. In the literature, yet there are no data on phosphate substitution in the structure of HAP by the zirconate ion (ZrO_4^{4-}). There are works on the synthesis of composites from HAP and zirconium oxide doped by yttrium, in the form of a mechanic mixture and followed by its annealing [10]. As a result, composites from a mixture of these components with an impurity of calcium zirconate and β -tricalcium phosphate formed when annealing were obtained [11]. Additionally, bactericide properties of zirconium on staphylococcal cultures were investigated [12], however, the data on the biocompatibility and effect of zirconium ions on the healthy cells were not found. In this connection, it is actual to investigate not only the possibility of such a substitution, but and obtain the material, prospective as a coating of implants from zirconia ceramics or the precursor of phosphate-zirconia ceramics.

The goal of the present work is the study of the substitution possibility of a part of the phosphate in the structure of HAP on the zirconate at the mechanochemical synthesis using various zirconium compounds as starting components.

EXPERIMENTAL

As starting reagents for the synthesis of zirconium-substituted HAP (further – Zr-HAP), CaHPO_4 of the Ch. D. A (analytically pure) reagent grade, CaO (Ch. D. A.) calcined at 900°C , and three different zirconium compounds: oxychloride $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Ch. D. A.), oxide ZrO_2 (Ch. D. A.) and hydroxide $\text{Zr}(\text{OH})_4$ (97 % H_4ZrO_4) of the company Aldrich (USA). The choice of a number of starting zirconium compounds for the synthesis was made with the aim of establishing their impact on possibility of substituting phosphate by zirconate and on the composition of the final product. The mechanical activation of the reaction mixtures was conducted in a planetary mill AGO-2 water-cooled steel drums with a rotation frequency of 1200 min^{-1} , capacity of 150 mL, with steel balls of the mass of 200 g for 20 min. The ratio of the sample weight of the reaction mixture and of mass

of the balls was 1 : 20. To avoid the contamination of the product before the synthesis, preliminary fettling of the working zone of the mill was conducted by the reaction mixture of the components of the same composition, as that of the synthesized sample. As a result of “fettling”, the surface of the balls and walls of the drum was covered by this mixture, its rest was discarded after 1 min of the activation, and the synthesis of the samples was further carried out. The content of iron in the samples of HAP mechanochemically synthesized during 30 min did not exceed 0.05 mass % according to the analysis data by the method of atomic absorption. All the synthesized samples were annealed in a high-temperature electric furnace chamber PVK-1.4-8 (Russia) at 1000°C for 5 h.

The products of the mechanochemical synthesis before and after annealing were investigated by the following methods:

1) IR spectroscopy (IRS) on an Infracum-801 spectrometer (samples were analyzed in the form of pills obtained by the standard technique by pressing with KBr);

2) X-ray diffraction on a D8 Advance powder diffractometer, recording radiographs was performed in the geometry of Bragg–Brentano (CuK_α radiation, nickel K_β filter and ultra-fast position sensitive one-dimensional detector Lynx-Eye with the angle of capturing of 3°);

3) high-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray microanalysis (EDXMA) on a transmission electron microscope JEOL JEM 2010.

X-ray phase analysis of the compounds synthesized was carried out using a program EVA [13] using the database of ICDD powder X-ray patterns [14]. The refinement of unit cell parameters of substituted HAP and quantitative analysis by the Rietveld method were performed using the program TOPAS [15].

RESULTS AND DISCUSSION

Synthesis of Zr-HAP using $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ as the starting component

The mechanochemical synthesis of HAP with a given composition of the partial substitution of phosphate on zirconate using zirconium

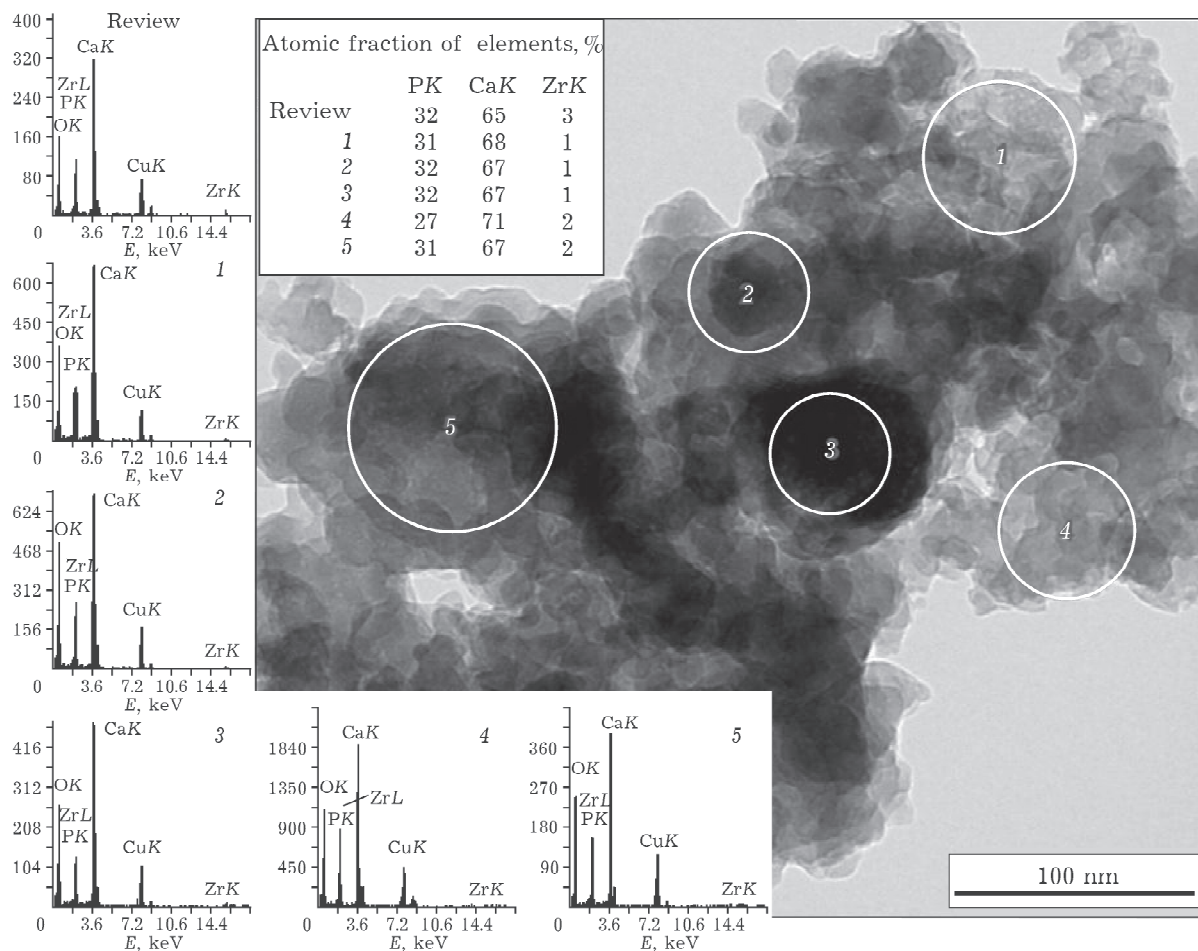
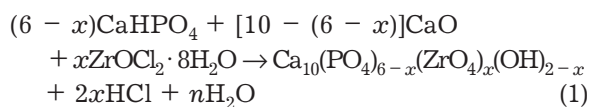


Fig. 1. Electron microscope image and EDXMA data of sample 3A (see Table 1).

um oxychloride was carried out according to the reaction



where $x = 0.1, 0.25, 0.5$ mol.

The products mechanochemically synthesized represented a nanocrystalline powder with aggregates of the size of 50–100 nm (Fig. 1). According to the data of XPA (Table 1), the products synthesized represent HAP with a small admixture of zirconium oxide that was apparently formed as a result of the decomposition of the starting zirconium oxychloride at the mechanical activation. The determination of the elemental composition of the product of the mechanochemical synthesis by the method of EDX showed that it was heterogeneous. Thus, on the review TEM picture (see Fig. 1) with the introduction of zirconium at the rate of 0.25

mol per the unit cell, the specified composition of the product should correspond to the elementary ratio of components (%): Ca 62.5, P 36.875, Zr 1.5. It can be seen (see Fig. 1, insertion) that the composition of particles of the sample is characterized by an increased con-

TABLE 1

Phase composition of samples synthesized with the introduction of zirconium oxychloride before annealing

Samples	Zr, mol	Content, mass %	
		HAP	<i>o</i> -ZrO ₂ *
1A	0	100	–
2A	0.1	100	–
3A	0.25	98	2
4A	0.5	96	4

Note. Here and in Tables 2–6, the amount of zirconium introduced at the synthesis is indicated.

* Orthorhombic modification.

TABLE 2

Phase composition of samples synthesized with the introduction of zirconium oxychloride after annealing

Samples	Zr, mol	Content, mass %		
		Chl-HAP*	CaO	CaZrO ₃
1A-T	0.0	99	1	–
2A-T	0.10	95	3	2
3A-T	0.25	90	4	6
4A-T	0.50	86	4	10

*Chl-HAP – chlorohydroxyapatite.

tent of calcium in comparison with a given composition. In Fig. 1 (fragment 4), the isolation of calcium oxide in the form of nanocrystalline particles is noted, which can be explained by a partial evaporation of phosphorus under the influence of the electron beam of the device during the decomposition of the synthesized apatite, which is accompanied by an elevated content of calcium in the product and registered by the data of EPXMA.

The samples mechanochemically synthesized with a various amount of zirconium oxychloride added have radiographs with reflexes, characteristic for apatite, corresponding to HAP and contain a small number of new phases.

After annealing these samples, their phase composition changed (Table 2). Calcium zirconate, the content of which increases up to 10 % with increasing the amount of zirconium introduced, was discovered in the samples. The comparison of unit cell parameters of the sam-

ples of Zr-HAP and HAP stoichiometric composition indicates their strong difference (Fig. 2). As the starting component of the reaction mixture, the reagent that contains chlorine was used. In this regard, in the process of the mechanochemical synthesis, chlorapatite Ca₁₀(PO₄)₆(Cl)₂ or chlorohydroxyapatite with a partial substitution on the chlorine ion of the group OH[–] that is localized in the structure of HAP along the axis 6₃ was apparently formed. The parameters of unit cells of two isomorphous varieties of apatite are significantly different: for HAP, $a = b = 9.422 \text{ \AA}$, $c = 6.881 \text{ \AA}$, and for chlorapatite, $a = b = 9.598 \text{ \AA}$, $c = 6.776 \text{ \AA}$ [1]. The values of unit cell parameters of the sample with the introduction of 0.5 mol of zirconium oxychloride amounted to: $a = b = 9.518 \text{ \AA}$, $c = 6.842 \text{ \AA}$, which testifies probable entering of chlorine in the structure of apatite.

The composition of the samples after annealing was also investigated by the methods of TEM, HREM and EDXMA. From the data of Fig. 3, it follows that the samples by composition are non-homogenous: crystalline particles of HAP without substitution (see Fig. 3, particle 3) with the elemental composition of components, close to the theoretical atomic composition of apatite (31.7 % P, 68.3 % of Ca, see Fig. 3, particle 3) are present. The particles probably with a partial substitution of phosphate on zirconate can also be seen on the picture; however, their composition is different from given. Thus, the sample at the given sub-

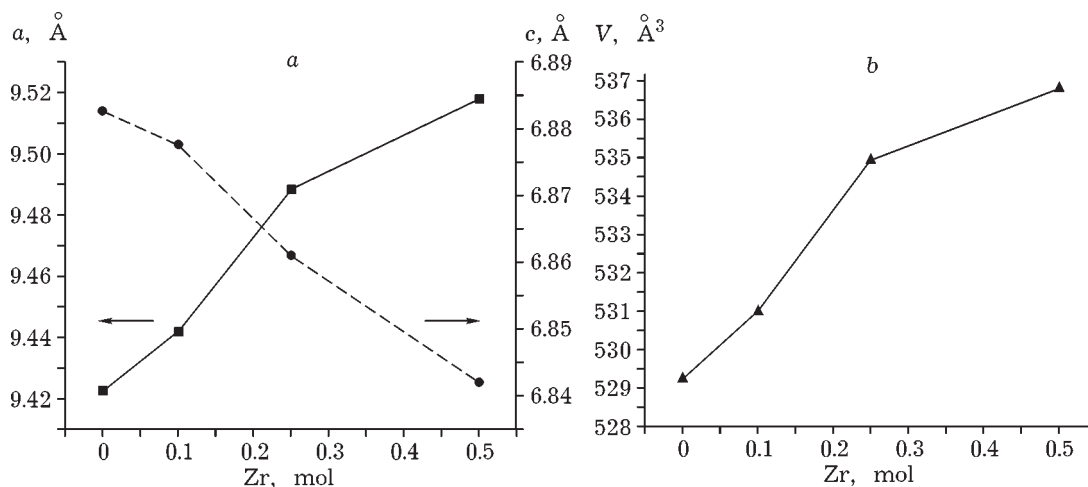


Fig. 2. Change of parameters a and c (a) and of volume (V) of the unit cell of the apatite phase (b) after annealing the samples synthesized with the introduction of zirconium oxychloride.

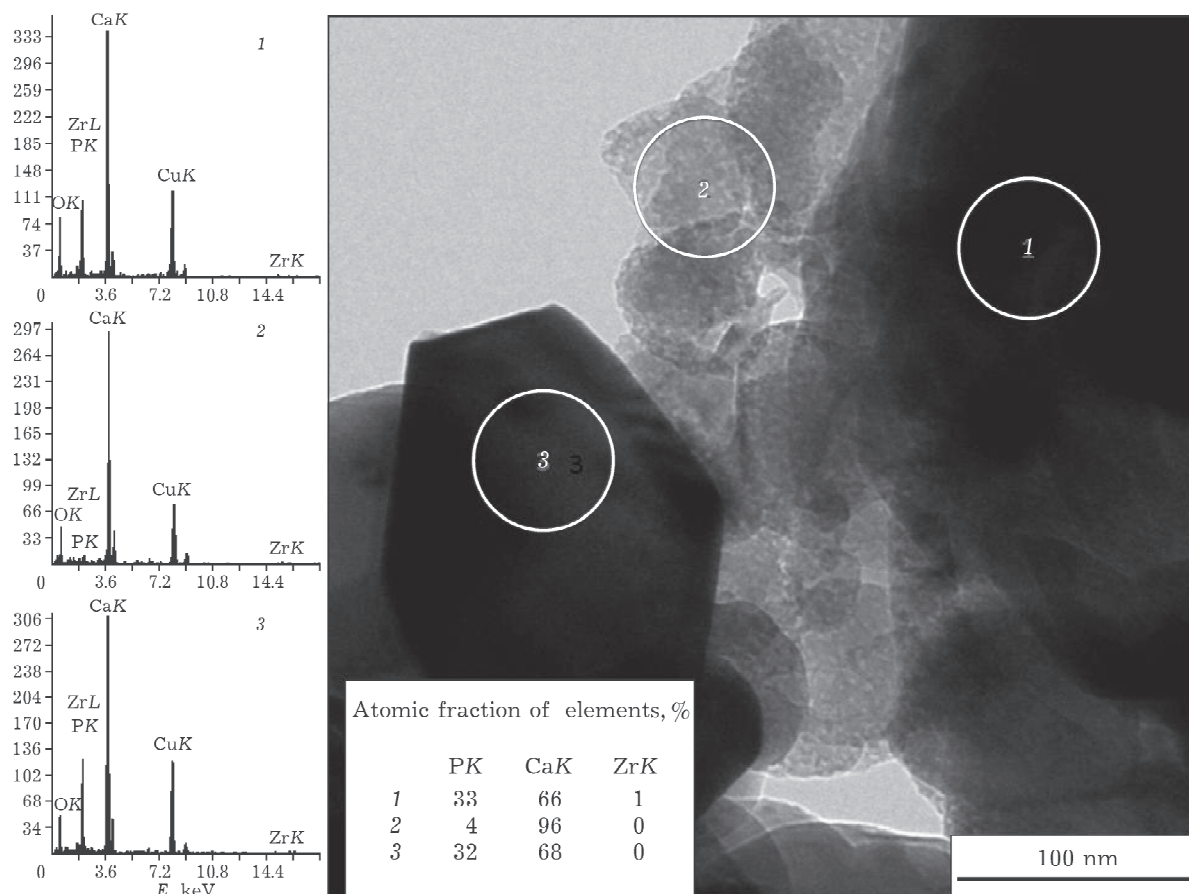


Fig. 3. Electron microscope image and EDXMA data of sample 2A-T.

stitution of 0.1 mol of phosphate on zirconate ion should have the elemental composition (at. %): Ca 62.5, P 36.9, Zr 0.6.

In some samples, after annealing, calcium oxide in the form of nanoparticles (*e. g.*, see Fig. 3, region 2) that was apparently formed when decomposing the apatite under the influence of an electronic beam of the microscope was discovered.

According to the data on the synthesis of Zr-HAP using zirconium oxychloride, the synthesis product represents not HAP, and chlorapatite. Therefore, other starting zirconium-containing reagents are necessary for the synthesis of zirconium-substituted HAP.

Synthesis of Zr-HAP using ZrO₂ as the starting component

To exclude the formation of chlorapatite, the synthesis using ZrO₂ as a starting component in an amount of from 0.2 to 2.0 mol of

zirconium (Table 3) was conducted. The synthesis reaction corresponds to the formula $(6 - x)\text{CaHPO}_4 + [10 - (6 - x)]\text{CaO} + x\text{ZrO}_2 \rightarrow \text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{ZrO}_4)_x(\text{OH})_{2-x} + n\text{H}_2\text{O}$ (2) where $x = 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.6, 2.0$ mol.

On radiographs of Zr-HAP samples mechanochemically synthesized at the introduction of zirconium oxide, addition to the reflexes of the apatite, reflexes of the original unreacted zirconium oxide appear. Its content in the sample obtained when introducing 2 mol of zirconium, exceeds 20 % (see Table 3). One can suggest that zirconium oxide did not enter into reaction with the rest of the components of the reaction mixture. However, at the comparative analysis of the unit cell parameters of the synthesized samples it was discovered that with increasing the concentration of introduced zirconium the parameter a is decreased and the parameter c is somewhat increased. Possibly, the carbonate ion enters the structure of HAP (what is typical when synthesizing in air envi-

TABLE 3

Phase composition of the samples synthesized with introducing zirconium oxide before annealing

Samples	Zr, mol	Content, mass %				
		HAP	CaO	<i>m</i> -ZrO ₂ *	<i>t</i> -ZrO ₂ **	Ca(OH) ₂
1B	0.2	95	–	4	1	–
2B	0.4	93	–	6	1	–
3B	0.6	90	–	8	2	–
4B	0.8	86	–	12	2	–
5B	1.0	83	–	14	3	–
6B	1.2	78	1	17	4	–
7B	1.6	74	2	20	2	2
8B	2.0	67	4	23	3	3

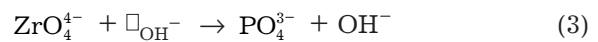
* Monoclinic modification.

** Tetragonal modification.

ronment) with the formation of carbonate-apatite, for which the parameter *a* is considerably lower in comparison with hydroxyapatite. However, in IR spectra of these samples only weak bands of the adsorption of the bonds C–O of the carbonate ion in the structure of apatite, the quantity of which was not able to affect significantly on lattice parameters are fixated [16]. Apparently, an insignificant amount of the zirconate ion can enter into the structure of HAP in the process of mechanochemical synthesis when using zirconium oxide as a component of the reaction mixture.

After annealing the samples, the parameter *a* of the unit cell is increased (Fig. 4), which can be explained by the inclusion of a zircon-

ate ion into the structure of HAP, because of its large ionic radius compared to the phosphate. In favour of a partial substitution of phosphate by zirconate, and the data of IR spectroscopy testify (Fig. 5). At the heterogeneous substitution of phosphate on zirconate, the charge compensation may occur due to the formation of vacancies in the positions of OH groups of the structure of HAP according to the scheme



In IR spectra (see Fig. 5), there is a decrease in the intensity of the absorption bands of bending vibrations of the O–H bonds in the structure of HAP (630–635 cm⁻¹) and their stretching vibrations (3570–3575 cm⁻¹) with

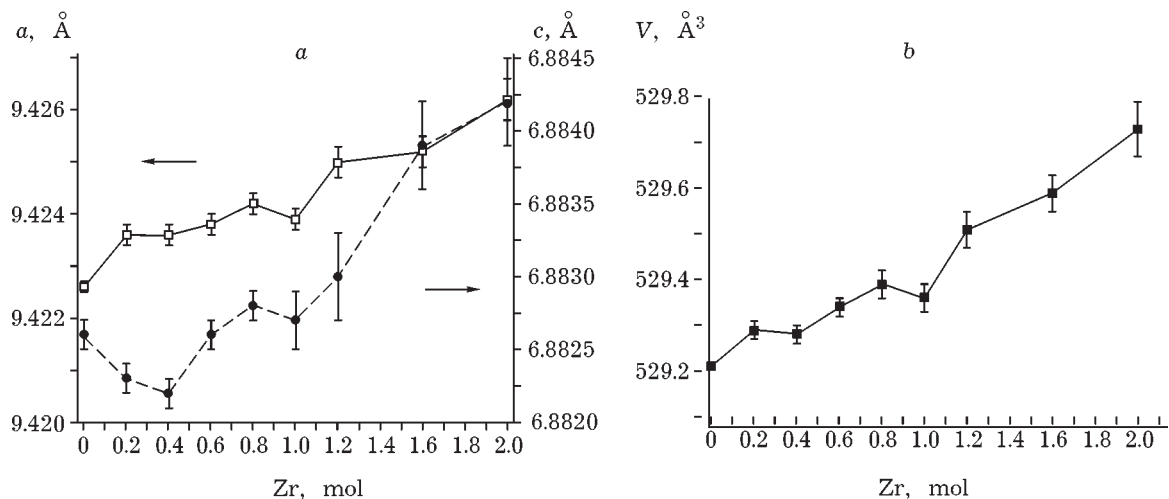


Fig. 4. Change of parameters *a* and *c* (a) and of volume (*V*) of the unit cell of the apatite phase (b) after annealing the samples synthesized with the introduction of zirconium oxide.

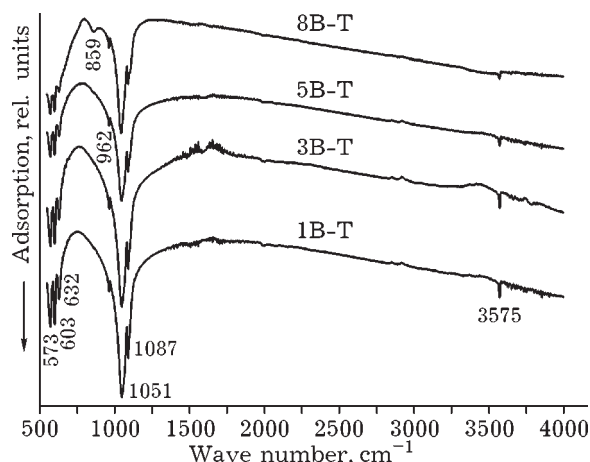


Fig. 5. IR spectra of the samples synthesized with the introduction of zirconium oxide after annealing.

increasing the amount of introduced zirconium. Apparently, this is due to the formation of vacancies in the position of the OH groups when compensating the charge of the heterogeneous substitution of phosphate by zirconate.

The composition of obtained Zr-HAP can be described by the formula $\text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{ZrO}_4)_x(\text{OH})_{2-x}$, where $x = 0.2\text{--}2.0$ mol. However, it follows from the data about the phase composition of the samples after annealing that, along with substituted HAP, in the process of annealing, calcium zirconate CaZrO_3 is formed, the amount of which with increasing the concentration of injected zirconium oxide increases up to 32 mass % (Table 4). Due to this, a given amount of the introduced zirconate cannot enter into the structure of HAP. It is important to note that the parameters of the unit cell a and c are changed unevenly with increasing the amount

TABLE 4

Phase composition of the samples synthesized with the introduction of zirconium oxide after annealing

Samples	Zr, mol	Content, mass %		
		HAP	CaO	CaZrO ₃
1B-T	0.2	94	1	5
2B-T	0.4	92	1	7
3B-T	0.6	88	2	10
4B-T	0.8	84	3	13
5B-T	1.0	80	3	17
6B-T	1.2	76	4	20
7B-T	1.6	70	5	25
8B-T	2.0	62	6	32

of introduced zirconium: the parameter a increases, the parameter c decreases up to the concentration of 0.4 mol, then increases (see Fig. 4). This can be explained by a various character of deformations proceeding when substituting phosphate on zirconate depending on the concentration of the starting reagent ZrO_2 .

After annealing, calcium oxide, which was able to form when decomposing a small amount of the carbonate group entering into the structure of apatite at the synthesis, is present in samples (see Table 4).

Thus, the possibility of the mechanochemical synthesis of Zr-HAP with a partial substitution of phosphate on zirconate using zirconium oxide as the starting component was shown. As a result of the synthesis when introducing small concentrations of zirconium oxide (up to 1 mol), HAP is formed with a partial substitution of phosphate on zirconate and the phase of starting zirconium oxide, which does not enter into the reaction, is preserved. At large concentrations of entered zirconium oxide, initial CaO and $\text{Ca}(\text{OH})_2$ are also present in the samples (see Table 3). When annealing the samples the unreacted zirconium oxide interacts with calcium oxide and hydroxide forming calcium zirconate (see Table 4).

Synthesis of Zr-HAP using $\text{Zr}(\text{OH})_4$ as the starting component

The mechanochemical synthesis of Zr-HAP using zirconium hydroxide as the starting component was carried out following the reaction: $(6-x)\text{CaHPO}_4 + [10 - (6-x)]\text{CaO} + x\text{Zr}(\text{OH})_4 \rightarrow \text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{ZrO}_4)_x(\text{OH})_{2-x} + n\text{H}_2\text{O}$ (4) where $x = 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.6, 2.0$ mol.

X-ray phase analysis of mechanochemically synthesized samples showed that on the diffractograms, alongside with the reflexes of apatite, the phase of $\text{Ca}_{1.5}\text{Zr}_{0.5}\text{O}_{18.5}$ appeared. The composition of this phase corresponds to the double oxide. The double oxide content increases with the increase of the concentration of introduced zirconium and reaches 20 % in the sample of 8V (Table 5). The major product of the synthesis is HAP. The lattice parameters of the apatite phase in the samples before annealing are changed: with increasing concen-

TABLE 5

Phase composition of the samples synthesized with the introduction of zirconium hydroxide before annealing

Samples	Zr, mol	Content, mass %	
		HAP	$\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$
1V	0.2	88	2
2V	0.4	97	3
3V	0.6	96	4
4V	0.8	94	6
5V	1	91	9
6V	1.2	89	11
7V	1.6	85	15
8V	2	80	20

tration of introduced zirconium, the parameter a decreases and the parameter c is increased, herewith, the volume of the crystal lattice varies. Judging by the change of unit cell parameters of mechanochemically synthesized samples of HAP with zirconium hydroxide as a component-substituent, on the stage of the mechanical activation of the reaction mixture of phosphate, apparently, is partially substituted by zirconate with the formation of Zr-HAP. However, the given quantity of zirconium cannot enter in the structure of HAP, since a part of the substituent forms the double oxide $\text{Ca}_{1.5}\text{Zr}_{8.5}\text{O}_{18.5}$.

After annealing, on roentgenograms of mechanochemically synthesized samples, clear apatite reflexes can be seen. Herewith, the

phase of the double oxide was not discovered, but sufficiently intense reflexes of zirconate calcium were observed. The phase composition of the samples after annealing is presented in Table 6. It can be seen that aside from HAP, calcium zirconate in large amounts and small – calcium oxide is contained in the sample.

After annealing, the parameter of the unit cell a of the sample with a concentration of entered zirconate of 0.2 mol significantly exceeds that for the sample without substitution (Fig. 6). When increasing the concentration of the entered zirconium hydroxide this parameter gradually increases, as and parameter c .

The change of the unit cell parameters of the Zr-HAP phase for the samples after annealing testifies the substitution of phosphate by zirconate. IR spectroscopic data testify that heterogeneous substitution most likely occurs by the scheme (3): with the increase of the concentration of the substituent on IR spectra, the intensity of adsorption bands of deformational fluctuations of bonds of the group O–H (630 cm^{-1}) and their stretching vibrations (3570 cm^{-1}) is decreased, analogously to the data of Fig. 5.

Thus, the use of zirconium hydroxide as the starting component of the reaction mixture at the mechanochemical synthesis of zirconium-substituted HAP allows obtaining the finished product with the inclusion of zirconium ions in its structure. Judging by the dynamics change of unit cell parameters in HAP structure in the process of

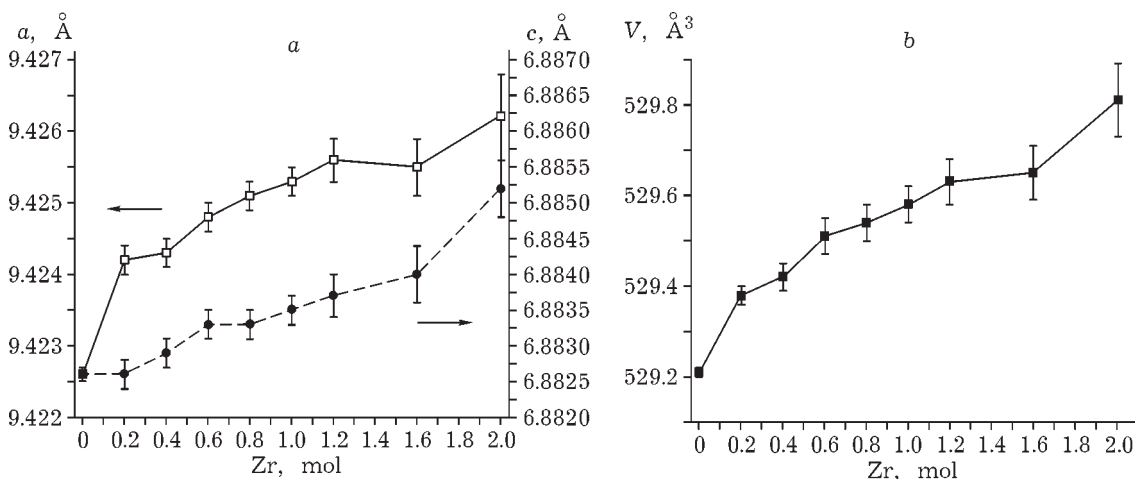


Fig. 6. Change of parameters a and c (a) and of volume (V) of the unit cell of the apatite phase (b) after annealing the samples synthesized with the introduction of zirconium hydroxide.

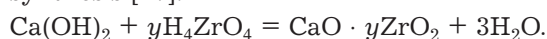
TABLE 6

Phase composition of the samples synthesized with the introduction of zirconium hydroxide after annealing

Samples	Zr, mol	Content, mass %		
		HAP	CaO	CaZrO ₃
1V-T	0.2	95	1	4
2V-T	0.4	92	1	7
3V-T	0.6	88	2	10
4V-T	0.8	85	2	13
5V-T	1.0	80	3	17
6V-T	1.2	76	4	20
7V-T	1.6	69	5	26
8V-T	2.0	61	6	33

the mechanochemical synthesis, not more than 0.6–0.8 mol of zirconate ion per unit cell enters.

Supposedly, the formation of the side product that is the double oxide $\text{Ca}_{1.5}\text{Zr}_{0.85}\text{O}_{1.85}$ in the process of the mechanical activation of the reaction mixture is conditioned by the fact that at the mechanical activation in the air environment, calcium oxide included in the reaction mixture interacts with water vapours of the air and is transformed into $\text{Ca}(\text{OH})_2$. Zirconium hydroxide represents *ortho*-zirconium acid H_4ZrO_4 . The interaction of these components with the formation of the double oxide occurs by the reaction of the soft mechanochemical synthesis [17]:



CONCLUSIONS

By the mechanochemical method directly in a planetary mill during 20 min of the activation of the reaction mixture, samples of hydroxyapatite modified by zirconate ions were synthesized. The change of the unit cell parameters of mechanochemically synthesized samples indicates that already at the stage of the mechanical activation of the reaction mixture, the entry of zirconate ion in the structure of hydroxyl-apatite occurs.

A comparative study using the reaction mixture of three different zirconium compounds as the starting component was carried out: oxychloride $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, oxide ZrO_2 , and hydroxide $\text{Zr}(\text{OH})_4$.

The synthesis of modified HAP using zirconium oxychloride in the process of annealing is accompanied by entering of chlorine in the apatite structure localized on the axis 6_3 , in the position of OH group of HAP. Entering chlorine in the apatite structure facilitates a significant increase of the parameter of the unit cell a and decrease of the parameter c . Due to this, when using zirconium oxychloride the synthesis product represents not hydroxyapatite, and chloro-apatite or hydroxyapatite.

The synthesis of HAP using zirconium oxide in process of the mechanical activation is accompanied by the formation of hydroxyapatite. According to the data of X-ray structural analysis, some amount of the zirconate ion is included in the structure of HAP on the stage of the mechanochemical synthesis. The largest part of unreacted ZrO_2 remains in the product of the mechanochemical synthesis. The samples after annealing consist of a mixture of hydroxyapatite, calcium zirconate and calcium oxide. Thus, using zirconium oxide one can synthesize hydroxyapatite modified by the zirconate ion, however, the content of zirconate in the synthesis product probably will not exceed tenths of a mole.

The mechanochemical synthesis using zirconium hydroxide, which represents weak *ortho*-zirconic acid, is accompanied by the formation of apatite and a double oxide of the composition of $\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$. After annealing the samples, the synthesis product consists of modified hydroxyapatite, calcium zirconate and an impurity of calcium oxide.

The carried out study showed that entering the zirconate ion substituting the phosphate in the structure of hydroxyapatite was fundamentally possible. However, due to a large radius of the zirconate ion, substitution apparently will not exceed 0.5–0.8 mol per the unit cell. When selecting the starting component for the synthesis one can use the oxide and hydroxide, however, the advantage is remained for the use of zirconium hydroxide, since in the process of the mechanochemical synthesis, the major part of the oxide remains in the initial state. In case of the hydroxide, an intermediate phase, which contributes to the further synthesis, is formed. When using zirconium oxychloride as a modifier, chlorine is a part of the

apatite structure and the synthesis product is chlorapatite, and not hydroxyapatite.

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