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Effect of cations ($Mg^{2+,}$ Zn^{2+}, Cd^{2+}) on formation of the mineral phase in $Ca(NO_3)_2$-$Mg(NO_3)_2$-Na_2HPO_4-H_2O system

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Abstract. Synthesis of hydroxyapatite in the system $Ca(NO_3)_2$-$Me(NO_3)_2$-$NaHPO_4$-H_2O with pH in the range of 6-12.2 is performed, and hydroxyapatite of B-type is formed. The effect of magnesium, zinc and cadmium ions on the properties of hydroxyapatite is studied. It is shown that as the concentration of these ions increases, the crystallinity of hydroxyapatite and the Ca/P ratio decreases. It is found that in all the experiments Zn^{2+} cations affect the hydroxyapatite structure to a lesser extent which results in less structural defects, wherein the Ca/P ratio attains the highest values. It is shown that the solubility of the samples containing zinc ions is greater than that of the samples with other additives.

Keywords: Hydroxyapatite structure; Dissolution; Crystallization; Acidity; Cationic substitution.

1. Introduction

Millions of people are susceptible to bone tissue lesions as a result of pathological diseases, such as osteomyelitis, osteosarcoma, osteoporosis, or injury. Since ancient times health professionals has been searching for techniques to reconstruct the bone tissue by implanting the defect to allow normal functioning of the damaged organ, for example, to withstand physiological loading. The problem is to find the material for the implant. Ideally, the material should be biocompatible with the tissue, that is, cause an adequate response from the body, to be nontoxic. It should not cause negative immune and other types of body reactions, and not be rejected by the body as a foreign body. It should be biologically active, that is, form interaction with the biological system to form bone tissue on it or replace it by the bone tissue and, preferably, and to induce bone formation processes. The implant must maintain its functional qualities over a certain period of time without change in its structure and mechanical properties. A great number of materials have been tested for this purpose [1–10]. However, bioinert materials were limited in application in reconstructive surgery because of the inevitable rejection reactions [1–9].

In recent years, interest in biogenic apatite has significantly increased. One of the reasons is the fact that hydroxyapatite is close in chemical composition to the inorganic component of the bone, and therefore, it has similar physicochemical and mechanical properties. Therefore, it can be used as an implant in the form of ceramics, cements and composites [7, 8].

Another reason of great interest in studying these minerals is due to the fact that apatite is the part of the majority of pathogenic biominerals, and the cause and mechanism of their formation has not yet been found. Unfortunately, data on the composition and structural features of biogenic apatite are very few in number. At the same time, the literature data [7–10] suggests a complex isomorphism which often causes considerable non-stoichiometry of the substance and significant variations in the parameters of the crystal lattice.

The aim of the research is to study the effect of metal ions on patterns of formation and nature of the solid phase crystallized from aqueous solutions of specified pH and ionic composition.

2. Experimental techniques

The crystals of the substituted calcium phosphate were synthesized from aqueous solution at room temperature through spontaneous crystallization according to the chemical reaction:

$$10\ CaX_2 + 6\ M_2HPO_4 + MOH \rightarrow Ca_{10}(PO_4)6(OH)_2\downarrow + 20\ MX + 6\ H_2O \quad (1)$$

Crystallization was conducted at room temperature (22–25 °C) and under varying concentration of the metal cation dopant in the range of 0.0017–0.0255 mol/l (for Mg^{2+}) or 0.0009–0.0102 mol/l (for Zn^{2+} and Cd^{2+}). The crystallization time was 48 hours. In the liquid phase, the content of calcium and magnesium ions was determined by complexometric titration with two indicators (Eriochrome Black T and murexide, according to RD 52.24.403-2007); the final content of the metal ion dopant (Zn^{2+} according to GOST 18293-72 and Cd^{2+} by the photometric dithizone method) was found; the concentration of phosphate ions was evaluated by molybdene blue spectrophotometric method. The resulting solid phase was studied by physical and chemical analyses [8].

StatSoft Statistica 6.0 was used to perform statistical data processing.

3. Result and discussion

Hydroxyapatite was synthesized from the solution at varying pH and ionic strength. The results of X-ray diffraction analysis of the solid phase (Figure 1) indicated the formation of hydroxyapatite. Other calcium phosphates in the sediment were not found.

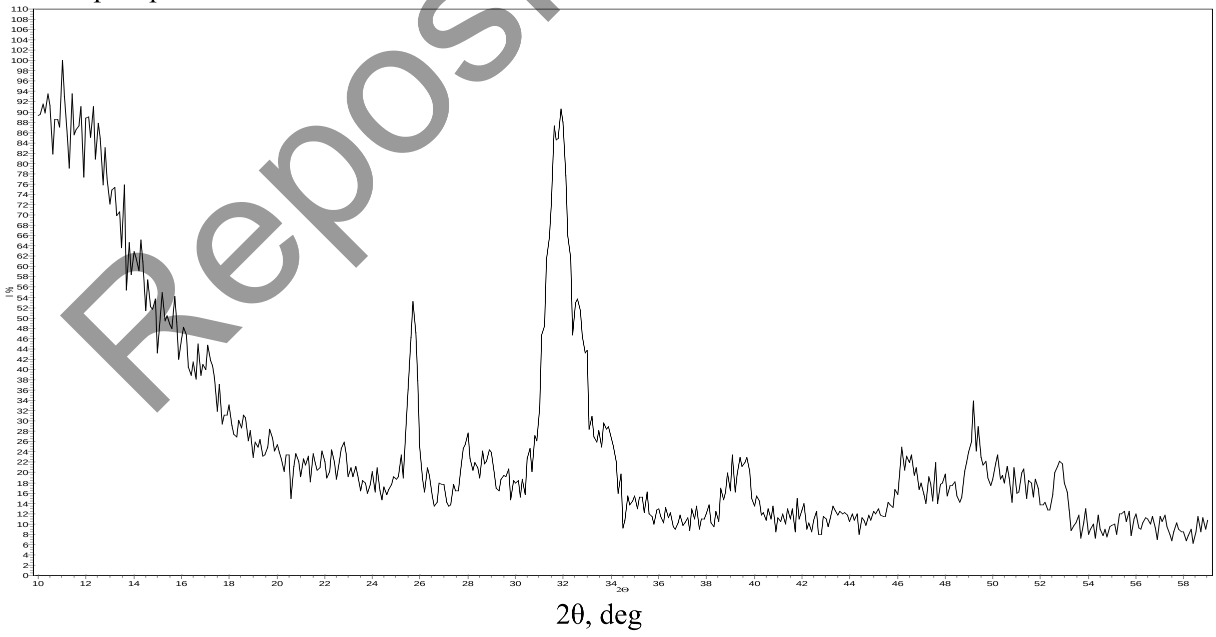


Figure 1. X-ray phase analysis of the samples produced by deposition: at pH = 9.0.

The characteristic main absorption bands caused by vibrations of O-P-O bonds in PO_4^{3-} tetrahedras are observed in the IR spectra (Figure 2). The maximum absorption in these bands is at 1087, 1040, 962, 601, 575 and 474 cm^{-1}. The peaks at ν = 1040 and 1087 cm^{-1} are caused by triply-degenerated antisymmetric valence vibrations of the O-P-O bonds, ν3. The absorption band at 962^{-1} refers to a non-degenerated symmetric valence mode, ν_1. The intensities with the maximum absorption at 601 and 575 cm^{-1} are caused by doubly-degenerated valence vibrations of the O-P-O bond, ν_4. Faint peak at 472 cm^{-1} is the component of the degenerated valence vibrations of the ν_2 mode. The peak with ν = 640 cm^{-1} and the intensity at 1650 cm^{-1} in the near spectrum region correspond to OH-group variations; the broad band at 3150–3400 cm^{-1} in the far spectrum region can be caused by the absorption of the molecular water adsorbed by apatite.

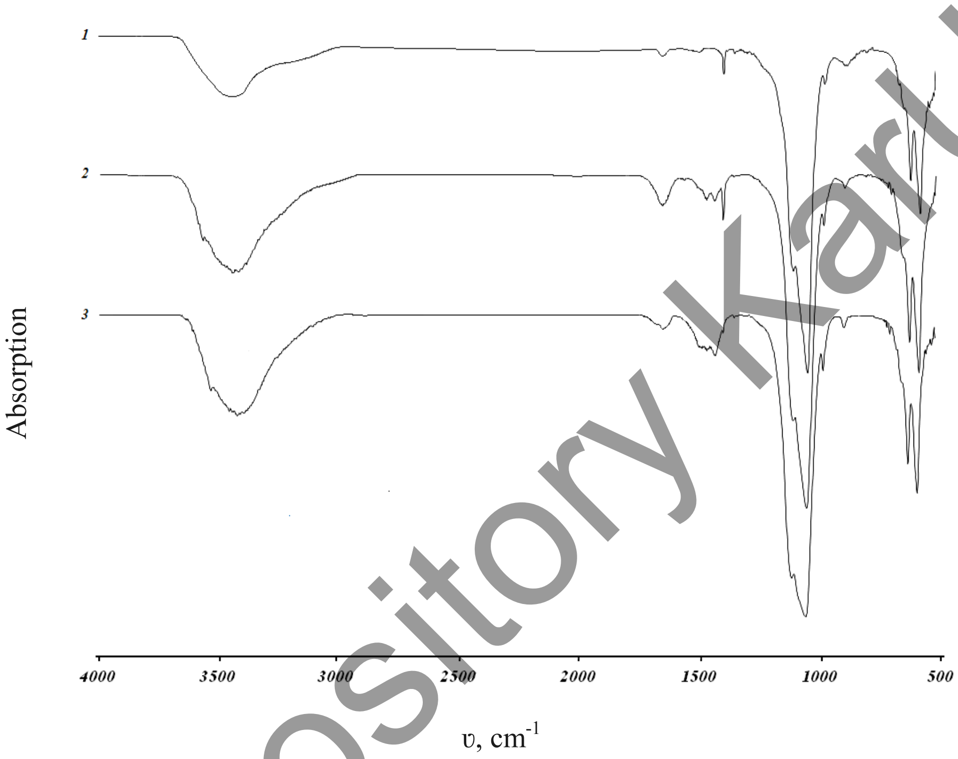


Figure 2. IR spectra of samples prepared by precipitation: 1 is at pH = 6.00, 2 is at pH= 9.00, 3 is pH = 12.00 (hydroxyapatite phase).

In the spectra of the synthesized hydroxyapatite, we can also observe the bands of the ν3 mode of CO_3^{2-} vibrations at 1420 and 1450 cm^{-1} and those of the ν2 mode at 873 cm^{-1}. These absorption bands in the spectra indicate partial substitution of RO_4^{3-} by carbonate ions in the hydroxyapatite structure of B-type. Thus, all the samples prepared at pH ≥ 7.00 are found to be carbonate -substituted hydroxyapatite of B-type [8].

The analysis data (table 1) showed that pH growth increases the precipitated mass of the resulted phase. At pH=12, precipitation is the largest. This indicates more favorable conditions for crystallization of the mineral phase.

Table 1. Data of the analysis of ions in the solution.

pH initial	m ave., g	Ca/P ave.
6.00±0.05	1.195±0.3563	1.35
9.00±0.05	1.335±0.0497	1.58
12.00±0.05	1.567±0.3476	1.68

An important characteristic of hydroxyapatite is stoichiometry of its composition which is usually expressed by the Ca/P ratio. To explain the deviations from the ideal stoichiometry Ca/P = 1.67 the hydroxylapatite composition is written by the formula $Ca_{10-x}(HPO_4)_{x}(PO_4)_{6-x}(OH)_{2-x}$ (1.5 <Ca/P <1.67, i.e. 0<x<1).

The chemical analysis showed that the Ca/P ratio in the prepared samples is from 1.35 to 1.68 depending on the initial concentrations. Table 1 shows the change in Ca/P at varying pH. These changes indicate that the data obtained at pH = 12 (Ca/P = 1.68) is the closest to the ideal stoichiometry. This data is in agreement with the thermodynamic results obtained earlier [8].

Comparison of possibility for crystallization of the mineral phase in $Ca(NO_3)_2$-$Mg(NO_3)_2$ - Na_2HPO_4-H_2O system containing (Mg^{2+}, Zn^{2+}, Cd^{2+}).

Cationic substitutions are known to have a significant impact on biological behavior of hydroxyapatite and are one of the known techniques to improve reabsorption (solvability) of hydroxyapatite materials. In addition, the elements of the apatite crystal lattice can exchange with ions of the solution surrounding the crystal and change due to the ions in this solution. In living systems, this property makes apatite highly sensitive to the ion composition of biological fluids. The ion exchange in the hydroxyapatite crystal lattice changes its properties, affects the strength and size of crystals.

For example, it is known that strontium apatite is formed in substitution of Ca by Sr^{2+} in the apatite crystal lattice. This disturbs the crystal structure. Kashin-Beck disease is reported to be accompanied by osseous lesion, meromicrosomia of limbs in humans and animals. In the radionuclide-contaminated areas, the negative effect of strontium apatite on a human being is caused by the possibility of radioactive strontium deposition.

In the case of filling the cation site, the determining factor is the nature of the chemical bond formed by the divalent cation in a specific position of the crystal structure. The factor that the substituting cation and calcium cation are similar in size is of less relevance.

We studied the effect of magnesium, zinc and cadmium ions as dopants in hydroxyapatite synthesis since the ionic radii of these cations are close in values to those of calcium ions (table 2). It was found that the highest values for Ca/P are obtained for zinc ion dopants (1.4), and the minimum values are typical of cadmium ion dopants (0.8). In the presence of magnesium ions in the hydroxyapatite structure, the Ca/P ratio takes intermediate values between zinc ion and cadmium ion dopants. It can be assumed that Zn^{2+} ions have a lesser effect on the hydroxyapatite structure and cause less imperfection of its structure.

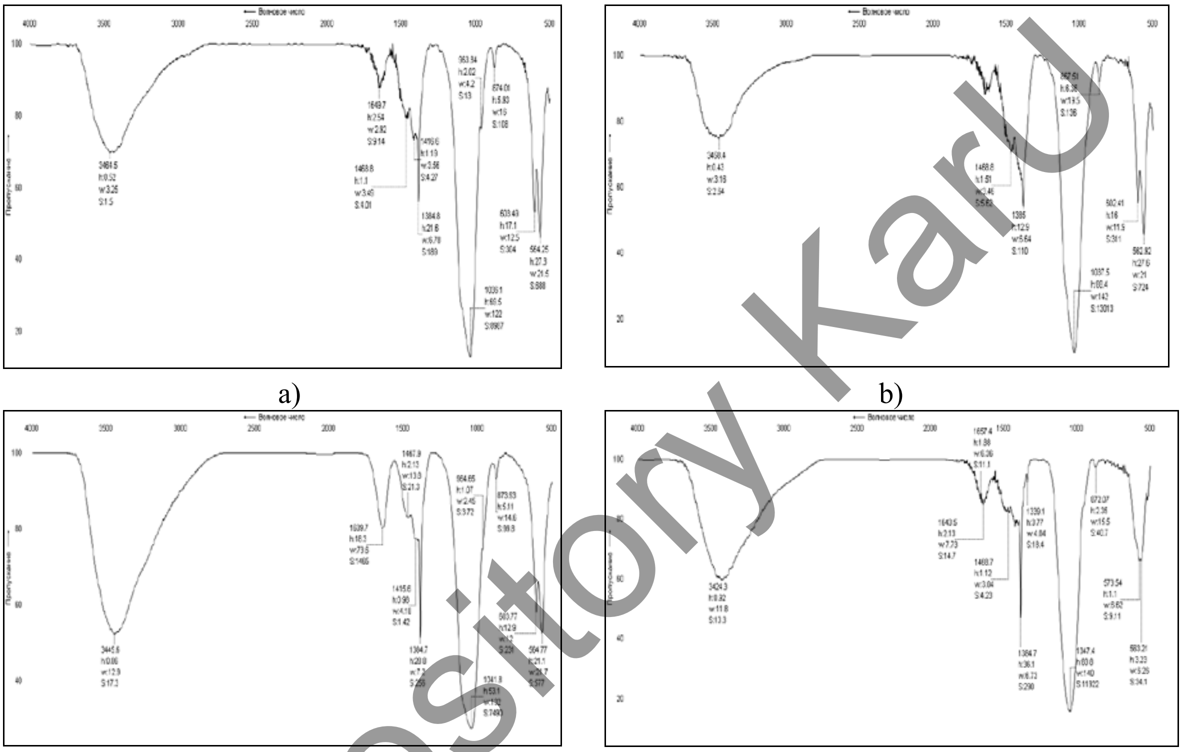
Table 2. Ion and metal radius.

Cation	Ion radius, Å
Ca	0.99
Mg	0.66
Zn	0.83
Cd	0.97

The analysis of the resultant solid phase weight indicated that Zn^{2+}, Mg^{2+} and Cd^{2+} ions present in the starting solution increase the precipitation mass. The minimal effect was observed for magnesium ions as dopants.

It is important to emphasize that the biological activity of hydroxyapatite samples doped with magnesium, zinc and cadmium ions is similar, but the greatest bioactivity is observed for precipitation containing zinc ions. All the solid phases with dopants exhibit higher solvability than hydroxyapatite samples without additives.

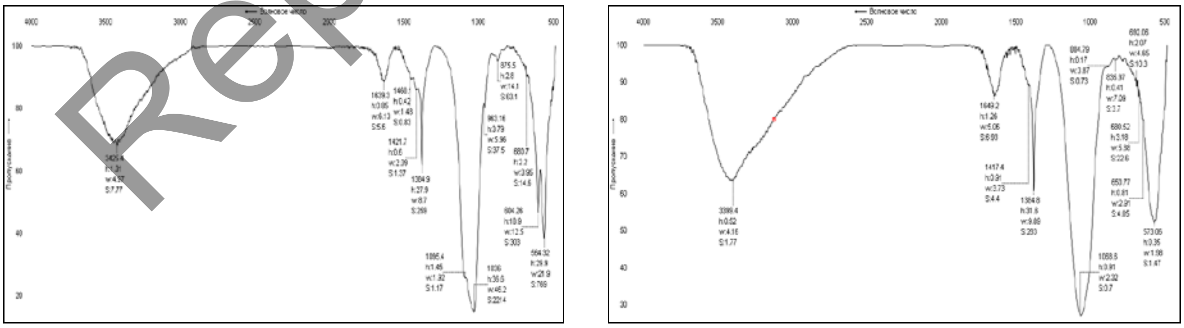
IR spectroscopy indicated that doping with ions and slight increase in their concentration in the starting solution does not virtually affect the IR spectra form (Figure 3 a–d); the B-type hydroxyapatite is observed in all the cases. In turn, sharp increase in dopant concentration (up to 75%) causes formation of the amorphous phase (Figure 4 a–b). Magnesium ions, whose ionic radius is significantly smaller as compared to calcium, may destabilize the apatite structure to a greater extent.



a) b)

c) d)

Figure 3. IR spectrum of the sample at pH=12: a) C(Cd)=2.5%; b) (Cd)=30%; c) C(Zn)=2.5%; d) C(Zn)=30%



a) b)

Figure 4. IR spectrum of the sample at pH=9 c a) C(Mg)=5%; b) C(Mg)=75%

4. Conclusions

1. Synthesis of hydroxyapatite in the $Ca(NO_3)_2$-$Me(NO_3)_2$-$NaHPO_4$- H_2O system with the initial ratio Ca/P = 1.70, with pH in the range of 6-12.2 has been performed.

2. The Ca/P ratio in synthetic samples is found to be from 1.35 to 1.68 depending on the initial concentration of the doped ions. The value for Ca/P, closest to the hydroxyapatite stoichiometry (1.67), can be obtained at pH = 12 with hydroxyapatite of B-type being formed.

3. The effect of magnesium zinc and cadmium ions on the properties of hydroxyapatite is studied. As the concentration of these ions increases, the hydroxyapatite crystallinity and Ca/P ratio are shown to decrease.

4. It is established that in all the experiments Zn^{2+} cations lead to less imperfection of the hydroxyapatite structure, and the Ca/P ratio attains its highest values.

5. It is shown that the bioactivity of the samples containing zinc ion dopants is greater than that of other dopants.

It is found that ion doping does not affect the IR spectra form.

5. Acknowledgements

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