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Sodium, magnesium and carbonate-containing calcium phosphates: synthesis and investigation

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The results of calcium phosphates formation in an aqueous solution of Ca^{2+}-Mg^{2+}-Na^+-PO_4^{3-}-CO_3^{2-}-NO_3^- systems at different molar ratios of Ca^{2+}:Mg^{2+}:Na^+:PO_4^{3-}:CO_3^{2-} = (10-*x*-*y*/2–*z*/2) : *x* : *y* : (6-*z*) : *z*, (*x* = 0.25, 0.5, 0.75; *y* = 0.25, 0.5, 0.75, 1.0; *z* = 0.5, 1.0) at a temperature of 25°C with subsequent heating at 600°C for 2 hours are presented. In the case of a system with molar ratios Ca^{2+}:Mg^{2+}:Na^+:PO_4^{3-}:CO_3^{2-} = (10-*x*-*y*/2–*z*/2) : *x* : *y* : 5.5 : 0.5 for *x* = 0.25 regardless of the amount of sodium cations (*y* = 0.25–1.0), modified apatite-type calcium phosphates (hexagonal system, space group $P6_3/m$) were obtained. For system at a fixed sodium content (*y* = 0.25), with an increase of magnesium amount (*x* = 0.5, 0.75), the formation of biphasic calcium phosphates (a mixture of phases based on β-$Ca_3(PO_4)_2$ – trigonal system, space group *R-3c* and $Ca_{10}(PO_4)_6(OH)_2$) was founded. An increase in the amount of carbonate in the initial solution to a molar ratio of PO_4^{3-}:CO_3^{2-}= 5 : 1 also led to the formation of biphasic calcium phosphates with different contents of main components ((47-65wt%) (β-$Ca_3(PO_4)_2$ + (53–35wt%) $Ca_{10}(PO_4)_6(OH)_2$) with an increase in the amount of sodium from *y* = 0.5 to 1.0. FTIR spectroscopy data confirmed the partial substitution of phosphate-anion by carbonate groups in the structure of apatite-type calcium phosphate. It was found that biphasic calcium phosphates containing a complex of trace elements are characterized by higher activity in a model solution than monophasic apatite-related carbonate-containing calcium phosphates of similar composition, and can be used in the future to restore bone tissue.

Keywords: trace elements; magnesium; sodium; hydroxyapatite; tricalcium phosphate.

Натрій, магній та карбонат-вмісні кальцій фосфати: синтез та дослідження. *Н.Ю. Струтинська, Є.О. Комащенко, О.В. Лівіцька, І.І. Гринюк, Д.К. Прохоренко*

У роботі досліджено формування кальцій фосфатів у водному розчині систем Ca^{2+}-Mg^{2+}-Na^+-PO_4^{3-}-CO_3^{2-}-NO_3^- за різних мольних співвідношень Ca^{2+}:Mg^{2+}:Na^+:PO_4^{3-}:CO_3^{2-}= (10-x-y/2–z/2):x:y:(6-z):z, (x = 0.25, 0.5, 0.75; y = 0.25, 0.5, 0.75, 1.0; z = 0.5, 1.0) при температурі 25°C з подальшим їх нагріванням при 600°C впродовж 2 годин. Встановлено, що для систем з мольними співвідношеннями Ca^{2+}:Mg^{2+}:Na^+:PO_4^{3-}:CO_3^{2-}= (10-*x*-*y*/2–*z*/2):*x*:*y*:5.5:0.5, для *x* = 0.25 незалежно від кількості катіонів натрію (*y* = 0.25–1.0) формуються модифіковані кальцій фосфати апатитового типу (гексагональна сингонія, просторова група $P6_3/m$), а для фіксованого вмісту натрію (*y* = 0.25) при збільшенні кількості магнію (*x* = 0.5, 0.75) формуються біфазні кальцій фосфати (суміш фаз на основі β-$Ca_3(PO_4)_2$ (тригональна сингонія, просторова група *R-3c*) та $Ca_{10}(PO_4)_6(OH)_2$). При зростанні кількості карбонату у вихідному розчині до значення мольного співвідношення PO_4^{3-}:CO_3^{2-}= 5 : 1 формування біфазних

кальцій фосфатів ((45-65мас%)(ß-$Ca_3(PO_4)_2$ + (53–35мас%) $Ca_{10}(PO_4)_6(OH)_2$) виявлено при зростанні кількості натрію від $y = 0.5$ до 1.0. Дані ІЧ-спектроскопії підтверджують реалізацію часткового заміщення фосфату на карбонат у структурі апатитового типу. Показано, що біфазні кальцій фосфати характеризуються вищою активністю у модельному розчині, ніж монофазні карбонатвмісні кальцій фосфати апатитового типу, що мають близький вміст мікроелементів та можуть бути в подальшому використані для відновлення кісткової тканини.

1. Introduction

The search for materials for various purposes for the restoration of bone tissue or the healing of defects in orthopedics, including apatite-related calcium phosphates or ß-tricalcium phosphates, requires a systematic study of the conditions of their formation in a wide range of the ratios of initial components as well as the establishment of correlations between their composition and functional properties. Calcium phosphates (in particular, hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ and ß-$Ca_3(PO_4)_2$) have attracted great attention due to their wide application in many areas of medicine (artificial bone grafts, dental implants, drug delivery systems, toothpastes), industry (catalysts of organic reactions, luminescent materials) and ecology (effective adsorbents for heavy metals removal). These compounds have a wide variety of compositions, structural types and properties. The crystal structure of calcium phosphates is very flexible, therefore, various types of substitutions (homo- and heterovalent in cationic and anionic sublattices) are realized in its frameworks. This fact makes it possible to influence the physico-chemical (solubility, thermal stability, mechanical behavior) and biological properties (biocompatibility, bioactivity, osteoconductivity) of future materials [1–7].

Hydroxyapatite is a base of inorganic part of bone tissue. Its main features in biological systems are nanosized particles, high specific surface area, non-stoichiometric composition (calcium deficiency), the presence of CO_3^{2-}-ions (to 8%) and other microelements (Na^+, K^+, Mg^{2+}, Zn^{2+}). The incorporation of carbonate groups in the apatite structure leads to lattice distortion and crystal defects, a decrease in crystallinity and an increase in solubility and bioactivity [8–11].

Magnesium ions play an important part in the regulation of ion channels, DNA stabilization, enzyme activation, stimulation of cell growth and proliferation. In recent years, this metal has gained great popularity in orthopedics. The presence of Mg^{2+}-ions in bone minerals and body fluid can affect bone mineral metabolism, formation and crystallization processes, and dissolution rate [12–13]. Many investigations are devoted to the incorporation of magnesium ions in the structure of calcium phosphates and the creation of composites, as well as its effect on the properties of phosphates or materials based on them [14–18].

The purpose of this work was to study the features of calcium phosphate formation in aqueous solutions at a wide range of molar ratios Ca^{2+}:Mg^{2+}:Na^+:PO_4^{3-}:CO_3^{2-}= (10-x-y/2–z/2):x:y:(6-z):z, (x = 0.25, 0.5, 0.75; y = 0.25, 0.5, 0.75, 1.0; z = 0.5, 1.0) at temperature of 25°C followed by heating the samples at 600°C during 2 hours. It was important to establish correlations between the chemical composition of the obtained modified calcium phosphates and their activity in a model solution to assess the prospects of their use for bone tissue restoration.

2. Experimental

Synthesis of calcium phosphates doped with trace elements. Modified calcium phosphates have been synthesized from an aqueous solution of Ca^{2+}-Mg^{2+}-Na^+-PO_4^{3-}-CO_3^{2-}-NO_3^- at different molar ratios Ca^{2+}:Mg^{2+}:Na^+:PO_4^{3-}:CO_3^{2-}= (10-*x*-*y*/2–*z*/2) : *x* : *y* : (6-*z*) : *z*, (*x* = 0.25, 0.5, 0.75; *y* = 0.25, 0.5, 0.75, 1.0; *z* = 0.5, 1.0) at a temperature of 25ºC followed by heating the solid powders to 600ºC during 2 hours. As initial components, the compounds $Ca(NO_3)_2{\cdot}4H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$, $NaNO_3$, $(NH_4)_2HPO_4$ and NH_4HCO_3 were used. All of them were of the analytical grade. Calculated amounts of initial components were dissolved in deionized water and then the solution containing sodium, calcium, magnesium cations was mixed with a solution containing phosphate and carbonate anions at room temperature. The obtained precipitates were stirred for 5 min and 3 ml of $NH_3{\cdot}H_2O$ was added. Then the water was evaporated and solid powders after grinding were annealed at 600°C in a SNOL-7.2/1100 muffle furnace (TermoPro-601 temperature controller).

Methods of characterization. The phase composition of samples was investigated using X-ray powder diffraction. XRD patterns were recorded using a Shimadzu XRD-6000 \\\\\\

Table 1. Types and amounts of phases obtained in aqueous solutions of the system Ca^{2+}:Mg^{2+}:Na^+:PO_4^{3-}:CO_3^{2-}= (10-*x*-*y*/2–*z*/2) : *x* : *y* : (6-*z*) : *z*, (*x* = 0.25: *y* = 0.25, 0.5, 0.75, 1.0; *y* = 0.25: *x* = 0.5, 0.75, *z* = 0.5, 1.0) and heated at 600°C for 2 hours.

Molar ratios		Type of phase
PO_4^{3-}:CO_3^{2-}	Ca^{2+}:Mg^{2+}:Na^+	
11 : 1	9.375 : 0.25 : 0.25	$Ca_{10}(PO_4)_6(OH)_2$
	9.25 : 0.25 : 0.5	
	9.125 : 0.25 : 0.75	
	9.0 : 0.25 : 1.0	
	9.125 : 0.5 : 0.25	ß-$Ca_3(PO_4)_2$ (35 wt%) + $Ca_{10}(PO_4)_6(OH)_2$(65 wt%)
	8.875 : 0.75 : 0.25	ß-$Ca_3(PO_4)_2$ (42 wt%) + $Ca_{10}(PO_4)_6(OH)_2$(68 wt%)
5 : 1	9.125 : 0.25 : 0.25	$Ca_{10}(PO_4)_6(OH)_2$
	9.0 : 0.25 : 0.5	ß-$Ca_3(PO_4)_2$ (47 wt%) + $Ca_{10}(PO_4)_6(OH)_2$ (53 wt%)
	8.875 : 0.25 : 0.75	ß-$Ca_3(PO_4)_2$ (55 wt%) + $Ca_{10}(PO_4)_6(OH)_2$(45 wt%)
	8.75 : 0.25 : 1.0	ß-$Ca_3(PO_4)_2$ (65 wt%) + $Ca_{10}(PO_4)_6(OH)_2$(35 wt%)
	8.875 : 0.5 : 0.25	$Ca_{10}(PO_4)_6(OH)_2$
	8.625 : 0.75 : 0.25	$Ca_{10}(PO_4)_6(OH)_2$

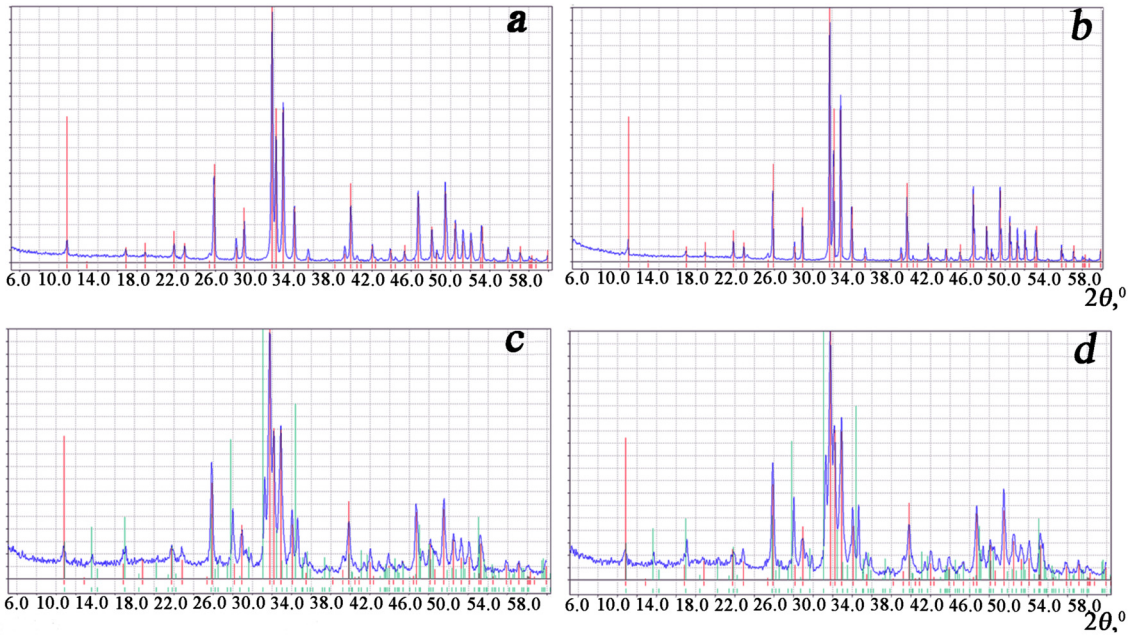

Fig. 1. XRD patterns for calcium phosphates prepared at molar ratios Ca^{2+}:Mg^{2+}:Na^+:PO_4^{3-}:CO_3^{2-}= (10-*x*-*y*/2–*z*/2) *: x : y* : 5.5 : 0.5, (*x* = 0.25: *y* = 0.25 (a), 1.0 (b); *y* = 0.25: *x* = 0.5 (c), 0.75 (d) and heated at 600°C for 2 hours.

diffractometer (continuous *θ–2θ* scanning method at a rate of 1.2 deg/min, 2*θ* = 5-60 degrees). The crystalline phase was identified using the ICDD (International Center for Diffraction Data) database for hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (PDF2 #01–089-6495). The lattice parameters and crystallite sizes for modified calcium phosphates were calculated using the FullProf program and the Debye-Scherrer equation, respectively.

The presence of various anions in the synthesized phases was confirmed by infrared Fourier spectroscopy of samples pressed into KBr tablets in the frequency range of 400-4000 cm^{-1} (PerkinElmer Spectrum BX spectrometer).

The *in vitro* activity of synthesized calcium phosphates modified with different amounts of trace elements (sodium and magnesium) was studied by soaking them in the phosphate-buffered saline (PBS) at pH = 7.4 and a tempera-

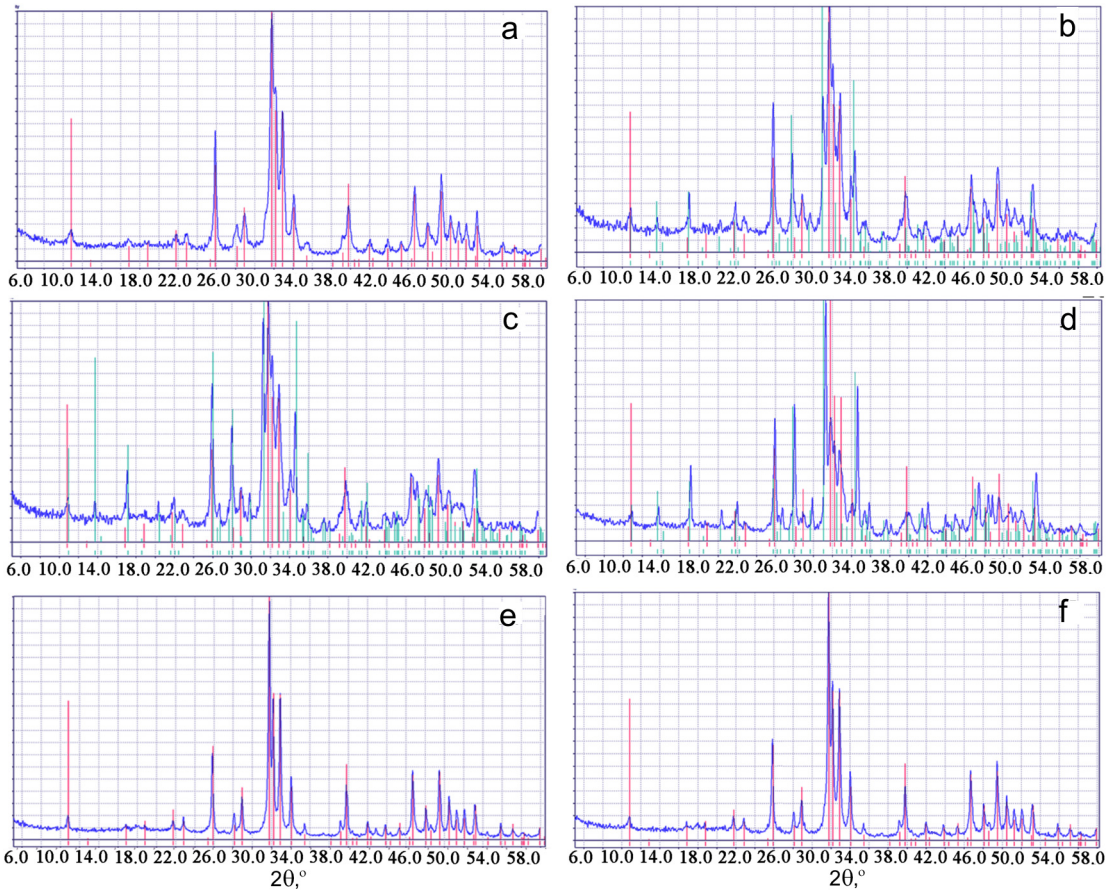

Fig. 2. XRD patterns for calcium phosphates prepared at molar ratios Ca^{2+}:Mg^{2+}:Na^{+}:PO_4^{3-}:CO_3^{2-}= (10-x-y/2–z/2) : x : y : 5 : 1, (x = 0.25: y = 0.25 (a), 0.5 (b), 0.75 (c), 1.0 (d); y = 0.25: x = 0.5 (e), 0.75 (f) and heated at 600°C for 2 hours.

ture of 37 °C. The pH values of the PBS solution with the sample were measured every 24 hours using a pH meter (OHAUS Started 2100).

3. Results and Discussion

The possibility of complex aliovalent substitution of atoms in the cationic and anionic sublattices of apatite-related calcium phosphate according to the principle $Ca^{2+} + PO_4^{3-} \rightarrow Na^{+} + Mg^{2+} + CO_3^{2-}$ during the interaction of components in an aqueous solution in a wide range of molar ratios of the initial components was investigated. It was found that heating of samples to 600°C led to the formation of different types of phases depending on the amount of magnesium cations and carbonate-anions in the initial solution (Fig. 1, Fig.2, Table 1).

In the case of systems with a molar ratio of PO_4^{3-} : CO_3^{2-}= 11 : 1, single-phase modified calcium phosphates containing 0.6wt% of magnesium and (0.5–2.4wt%) of sodium have been obtained, which belong to the hexagonal system, space group $P6_3/m$ (apatite-related $Ca_{10}(PO_4)_6(OH)_2$ – PDF2 #00-074-0565). An increase in the magnesium amount above 1wt% led to the formation of biphasic calcium phosphates (a mixture of phases based on $Ca_{10}(PO_4)_6(OH)_2$ – PDF2 #00-074-0565 and ß-$Ca_3(PO_4)_2$ – trigonal system, space group R-$3c$, PDF2 #00-070–2065) (Fig. 1 c, d).

The formation of biphasic calcium phosphates was also detected with an increase in the amount of carbonate in solutions to values of the molar ratio PO_4^{3-}:CO_3^{2-}= 5 : 1 and a change in the sodium content from 1wt% to 2.5wt% and a fixed amount of magnesium equal to 0.6wt% (Fig. 2 b-d). It should be noted, that an increase in the amounts of sodium in the initial solutions at molar ratios Ca^{2+}:Mg^{2+}:Na^{+}:PO_4^{3-}:CO_3^{2-}= (9.25-y/2) : 0.25 : y : 5 : 1, (y = 0.5, 0.75, 1.0) led to an increase in the amount of the phase based on ß-$Ca_3(PO_4)_2$ from 47 to 65 wt% in the composition of biphasic phosphates (Fig. 2b-d, Table 1).

In the system with a fixed amount of sodium cations at the molar ratio of Ca^{2+}:Mg^{2+}:Na^{+}:PO_4^{3-}:CO_3^{2-}= (9.375-x) : x : 0.25 : 5 : 1, (x = 0.5, 0.75), an increase in the amount of magnesium

Table 2. Calculated lattice parameters for calcium phosphates obtained at molar ratios Ca^{2+}:Mg^{2+}:Na^{+}:PO_4^{3-}:CO_3^{2-}= (10-*x*-*y*/2–*z*/2) : *x* : *y* : 5.5 : 0.5, (*x* = 0.25: *y* = 0.25, 0.5, 0.75, 1.0; *y* = 0.25: *x* = 0.5, 0.75) and heated at 600°C for 2 hours. Hexagonal system, space group $P6_3/m$.

Phosphate	Parameters	
	a, Å	*c*, Å
$Ca_{9,375}Mg_{0,25}Na_{0,25}(PO_4)_{5,5}(CO_3)_{0,5}(OH)_2$	9.405(3)	6.879(9)
$Ca_{9,25}Mg_{0,25}Na_{0,5}(PO_4)_{5,5}(CO_3)_{0,5}(OH)_2$	9.395(5)	6.873(8)
$Ca_{9,125}Mg_{0,25}Na_{0,75}(PO_4)_{5,5}(CO_3)_{0,5}(OH)_2$	9.394(5)	6.870(8)
$Ca_9Mg_{0,25}Na(PO_4)_{5,5}(CO_3)_{0,5}(OH)_2$	9.393(2)	6.867(4)
$Ca_{9,125}Mg_{0,25}Na_{0,25}(PO_4)_5(CO_3)(OH)_2$	9.413(8)	6.873(8)
$Ca_{8,875}Mg_{0,5}Na_{0,25}(PO_4)_5(CO_3)(OH)_2$	9.428(1)	6.878(6)
$Ca_{8,625}Mg_{0,75}Na_{0,25}(PO_4)_5(CO_3)(OH)_2$	9.426(1)	6.891(3)

contributed to the formation of a phase based on $Ca_{10}(PO_4)_6(OH)_2$ (Fig. 2e-f, Table 1). Thus, the substitution of 8mol% (3wt%) of phosphate anions and calcium with a carbonate group and a complex of magnesium (0.6wt%) and sodium (0.5–2.4wt%) did not change phase composition of products, whereas an increase in the amount of magnesium to 1.2–2wt% contributed to the formation of biphasic calcium phosphates and an increase in the amount of the phase based on ß-$Ca_3(PO_4)_2$ to 43wt% with an increase in the magnesium content in the initial solution.

In the case of an increase in the degree of substitution to 17 mol% in the anionic sublattice ($PO_4^{3-} \rightarrow CO_3^{2-}$) of calcium phosphate, the apatite-type structure, on the contrary, was retained with an increase in the magnesium content in the phosphate composition within the range of (0.6–1.8)wt.% and a fixed sodium content of 0.6 wt% (Table 1). When attempting to increase the sodium content above 0.6 wt% to (1.2–2.5) wt%, two-phase calcium phosphates are formed, and the content of the phase based on ß-$Ca_3(PO_4)_2$ increases from 47 wt% to 65 wt%. For these systems, an increase in the degree of substitution in the anionic sublattice entails the formation of vacancies in the cationic sublattice and a decrease in the Ca/P molar ratio, which is closer to that for tricalcium phosphate and promotes the formation of biphasic calcium phosphates.

The calculated lattice parameters for single-phase apatite-related calcium phosphates are given in Table 2. Analysis of the obtained data and their comparison with the lattice parameter for pure $Ca_{10}(PO_4)_6(OH)_2$ confirmed the partial substitution of calcium atoms by trace elements in the initial calcium phosphate. The particle sizes of monophasic calcium phosphates were calculated using the Debye-Scherrer equation and their nanosize was found to be in the range of 30-45 nm, regardless of the composition of the initial solution.

The FTIR spectra of the synthesized phosphates are shown in Figure 3. Vibrational modes of phosphate tetrahedra are observed in the frequency ranges of 550-670 cm^{-1} (ν_4) and 1000–1150 cm^{-1} (ν_1 and ν_3) and OH groups at 3490 cm^{-1} (Fig. 3). The bands in the range of 3210-3600 cm^{-1} are attributed to the vibrations of sorbed water, while the modes in the frequency ranges of 1355–1490 cm^{-1} (ν_3) and 880-890 cm^{-1} (ν_2) belong to the vibrations of carbonate groups. The positions of the latter modes confirmed the partial substitution of $PO_4^{3-} \rightarrow CO_3^{2-}$ (B-type) in the structure of hydroxyapatite.

The results of *in vitro* activity tests of synthesized apatite-type calcium phosphates containing different amounts of sodium (0.5–1.0 wt%), magnesium (0.5–1.0 wt%) and CO_3^{2-} (3wt%), as well as biphasic calcium phosphate (47 wt% ß-$Ca_3(PO_4)_2$ and 68 wt% $Ca_{10}(PO_4)_6(OH)_2$) containing sodium (0.5 wt%) and magnesium (0.5 wt%) are presented in Figure 4 as a change of the pH value over 192 hours of testing. The obtained results showed that in all cases after the first 24 hours, an increase in pH was observed in the range (2–45%) depending on the composition of the samples. The most extreme increase in pH was observed for biphasic calcium phosphate (ß-$Ca_3(PO_4)_2$ (47wt%) + $Ca_{10}(PO_4)_6(OH)_2$ (68wt%) containing 0.6wt% sodium and 1.9wt% magnesium (Fig. 4, curve 1). In the case of modified apatite-type calcium phosphates, the increase in pH during first

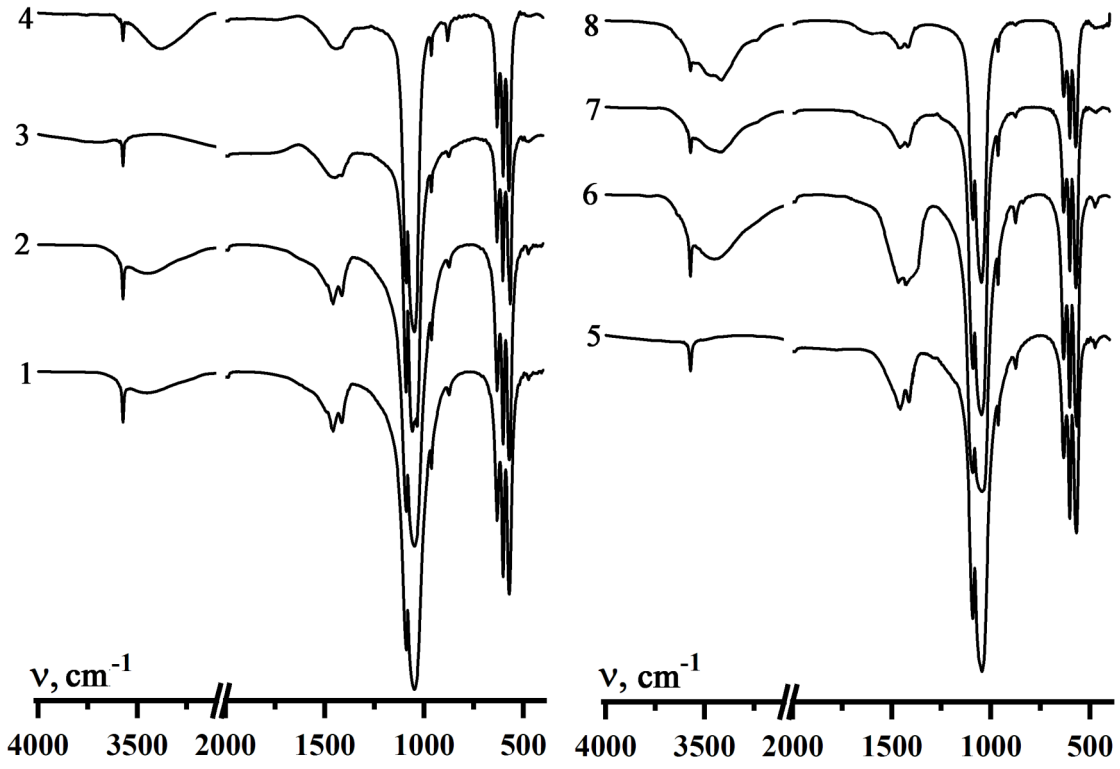

Fig. 3. FTIR spectra of modified calcium phosphates prepared at molar ratios: Ca^{2+}:Mg^{2+}:Na^{+}:PO_4^{3-}:CO_3^{2-} = (10-*x*-*y*/2–*z*/2) : *x* : *y* : (6-*z*) : *z*, (*x* = 0.25: *y* = 0.25 (a), 1.0 (b); *y* = 0.25: *x* = 0.5 (c), 0.75 (d) *z* = 0.5 (a) and 1.0 (b) and heated at 600°C for 2 hours.

24 hours is less significant, but can be regulated by the sodium content in calcium phosphate. Over the next 24 hours, an increase in pH is also observed for all samples, without a significant change in the subsequent hours of the study. An increase in the pH of the model solution in the presence of calcium phosphates with different contents of trace elements indicates their partial dissolution and, accordingly, may indicate the influence of the modification of calcium phosphates on their activity. A feature of apatite-type calcium phosphate containing 0.5wt% sodium and 0.5wt% magnesium (Fig. 4, curve 3) is a slight decrease in pH after 192 hours of testing, which may indicate the limits of material dissolution processes (Fig. 4, curve 3).

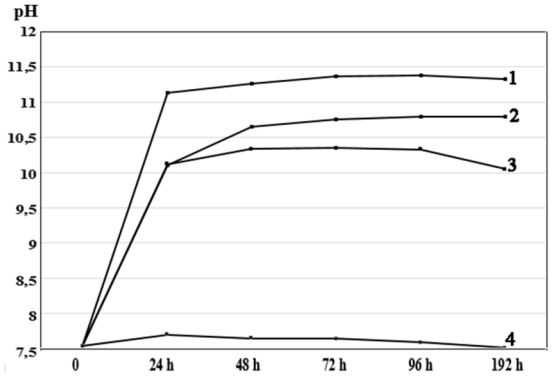

Fig. 4. Change in the pH of a model solution at 37°C in the presence of modified calcium phosphates prepared at molar ratios: Ca^{2+}:Mg^{2+}:Na^{+}:PO_4^{3-}:CO_3^{2-}= (10-*x*-*y*/2) : *x* : *y* : (6-z) : *z*, *z* = 0.5: *x* = 0.75, *y*=0.25 (curve 1); *x* = 0.25: *y* =0.75 (curve 2), *y* =0.25 (curve 3) and *z* = 1: *x* = 0.25, *y* = 0.25 (curve 4).

4. Conclusions

The conditions for obtaining monophasic apatite-type calcium phosphates and biphasic calcium phosphates (a mixture of phases based on β-$Ca_3(PO_4)_2$ and $Ca_{10}(PO_4)_6(OH)_2$) containing different amounts of trace elements: sodium (0.5–2.5wt%), magnesium (0.5–2.0wt%) and carbonate anion (3 or 6wt%) have been established. The results of FTIR spectroscopy confirmed the partial substitution of phosphate by a carbonate group. The study of the effect of modified calcium phosphates on the pH of a model solution at 37°C revealed an increase in the activity of the samples over 192 hours with an increase in the content of sodium cations from 0.5 to 1wt% in their composition. It should be noted that biphasic calcium phosphates are characterized by a higher rate of dissolution in the model solution than monophasic apatite-re-

lated carbonate-containing calcium phosphates, which have a similar content of microelements and can be used in the future to restore bone tissue.

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References

1. S. Bhat, U.T. Uthappa, T. Altalhi, H.-Y. Jung, M. D. Kurkuri, *ACS Biomater. Sci. Eng.*, 8, 10, 4039 (2022).
2. M. Gruselle, K. Tõnsuaadu, P. Gredin, C. Len, *Molecular Catalysis*, 519, 112146 (2022).
3. S. George, D. Mehta, V.K. Saharan, *Rev. Chem. Engin*, 36, 3, 369 (2020).
4. A. Fihri, C. Len, R.S. Varma, A. Solhy, *Coord. Chem. Rev.*, 347, 48 (2017).
5. E. Fiume, G. Magnaterra, A. Rahdar, E. Verné, F. Baino, *Ceramics*, **4**, 4, 542 (2021).
6. A. Galotta, Ö. Demir, O. Marsan, V.M. Sglavo, D. Loca, C. Combes, *J. Locs, Nanomaterials*, **14**, 5, 441 (2024).
7. T.H.M. Mysore, A.Y. Patil, C. Hegde, M.A. Sudeept, R. Kumar, M.E.M. Soudagar, I.M.R. Fattah, *European Polymer Journal*, **209**, 112842 (2024).
8. I. Cacciotti, *Int J Appl Ceram Technol*, **16**, 1864 (2019).
9. R. Yotsova, S. Peev, *Pharmaceutics*, 16, 2, 291 (2024).
10. K. Shikawa, K. Hayashi, *Sci Technol Adv Mater.*, 22, 1, 683 (2021).
11. S.L. Wong, C. Drouet, A. Deymier, *Materialia*, 29, 101795 (2023).
12. M. Nabiyouni, Y. Ren, S. B. Bhaduri, *Materials Science and Engineering: C*, **52**, 11 (2015).
13. J.-M. Yu, H.-C. Choe, *Applied Surface Science*, **432**, 294 (2018).
14. Z. Geng, R. Wang, Z. Li, Z. Cui, S. Zhu, Y. Liang, Y. Liu, B. Huijing, X. Li, Q. Huo, Z. Liu, X. Yang, *J. Biomat. App*, **31**, 1, 140 (2016).
15. A. Ezerskyte-Miseviciene, I. Bogdanoviciene, A. Zilinskas, A. Beganskiene, A. Kareiva, *J Aust Ceram Soc*, **56**, 839 (2020).
16. P.N. Lim, R.N. Lam, Y.F. Zheng, E.S. Thian, *Materials Letters*, **172**, 193 (2016).
17. B. Gayathri, N. Muthukumarasamy , D. Velauthapillai, S.B. Santhosh, V. Asokan, *Arab.J. Chem.*, **11**, 5, 645 (2018).
18. S. S. Singh, A. Roy, B. Lee, I. Banerjee, P. N. Kumta, *Mater.Sc.Eng: C*, **67**, 636 (2016).