

# Synthesis and Investigation of Calcium-Containing Phosphatosilicates with $\text{NaZr}_2(\text{PO}_4)_3$ Structure

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**Abstract**—Calcium-containing phosphatosilicates of the type  $\text{Ca}_{0.5(1+x)}\text{Zr}_2(\text{PO}_4)_{3-x}(\text{SiO}_4)_x$  were obtained by sol-gel method using the salting out process. Phase formation was studied, and optimal temperature and time regimes of synthesis providing the formation of one-phase reaction products were established. It is found that phases of NZP-structure are formed. Boundaries of phase stability of phosphatosilicates at the heterovalent isomorphic substitutions  $\text{P}^{5+} \rightarrow \text{Si}^{4+}$ :  $0 \leq x \leq 0.5$  are established. On the basis of powder X-ray analysis data the crystalline structure of  $\text{Ca}_{0.75}\text{Zr}_2(\text{PO}_4)_{2.5}(\text{SiO}_4)_{0.5}$  was refined by the full-profile analysis (Rietveld method). Hydrolytic stability of phosphatosilicates was studied.

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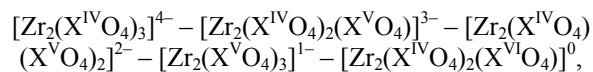
Principles of iso- and heterovalent isomorphic substitutions of atoms in different crystallographic positions of framework structures with mononuclear tetrahedral oxoanions and tetrahedral-octahedral frameworks described in [1–3] are the basic for the development of new materials with the properties regulated in the desired direction (“on a plan” materials). Orthophosphates with the structures of natural minerals such as kosnarite  $\text{KZr}_2(\text{PO}_4)_3$  [or  $\text{NaZr}_2(\text{PO}_4)_3$ , NZP type] and langbeinite  $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$  (LB) are primarily among them. Formula compositions of compounds regarded as probable structural analogs of NZP and LB are calculated, and many of such compounds are synthesized and studied [3–7].

Calcium-containing phosphates with NZP structure are studied recently as the basis of new materials. Among them there are luminophores (together with  $\text{Eu}^{\text{II}}$ , Sm) for light-emitting diodes technology of ecologically safe sources of white light of new generation [5–7], biocompatible nanocrystalline substances-luminophores (together with Er/Yb lanthanides) which are developed aiming at the use in bioimaging [8], ceramics with high characteristics of thermal, mechanical, and chemical stability [9, 10].

Classification scheme of formula types with the framework of  $[\text{T}_2(\text{XO}_4)_3]^g$  kind [where T are cations populating position 2 of the framework and having

oxidation state from 1+ to 5+ (in different ratios and combinations), X are cations forming tetrahedral oxoanions with the oxidation states from 4+ to 6+, g is the charge of the framework] which was developed in [11] may be used while planning new materials with the properties variable in the desired direction, and also with the expected new properties.

According to this scheme zirconium occupying two framework positions and known as the element stabilizing NZP structure may be present in the frameworks of the type:



where  $\text{X}^{\text{IV}}$ ,  $\text{X}^{\text{V}}$ ,  $\text{X}^{\text{VI}}$  are cations in the oxidation state 4+, 5+, and 6+ respectively. Therewith the occupancy of positions in the cavities must increase together with the growth of charge g from 0 to 4– (for the compensation of the charge at such charge variations up to  $g = 4+$ ).

It is evident that while designing compounds with calcium as the compensator of the framework charge its fraction will increase at the substitution of  $\text{X}^{\text{V}}$  with  $\text{X}^{\text{IV}}$ . At the transition from known phosphate  $\text{Ca}_{0.5}\text{Zr}_2(\text{PO}_4)_3$  to phosphatosilicates the atomic content may be increased 4-fold. It must be taken in mind that in this case only formal but not crystallochemical criteria are

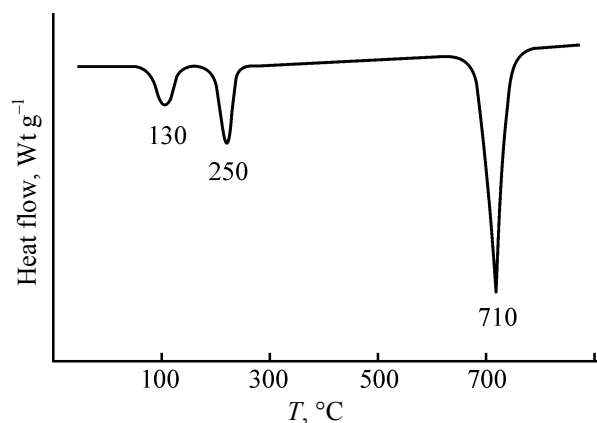
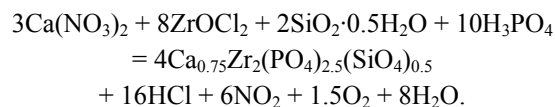


Fig. 1. Differential thermal analysis data for  $\text{Ca}_{0.75}\text{Zr}_2(\text{PO}_4)_{2.5} \cdot (\text{SiO}_4)_{0.5}$ .

considered. Increased fraction of calcium in the composition of compounds is important first of all in the development of materials of medical applications, and also with the purpose of alteration of the properties of other materials on the basis of these substances.

In this research we aimed to synthesize new calcium-containing compounds with the expected structure of  $\text{NaZr}_2(\text{PO}_4)_3$ , phosphatosilicates of the type  $\text{Ca}_{0.5(1+x)}\text{Zr}_2(\text{PO}_4)_{3-x}(\text{SiO}_4)_x$  from the above mentioned series with higher concentration of calcium as compared to known  $\text{Ca}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ , to optimize the conditions of the synthesis, and to study phase formation, crystalline structure, and the behavior in water systems.

The objects of investigation were phosphatosilicates of  $\text{Ca}_{0.5(1+x)}\text{Zr}_2(\text{PO}_4)_{3-x}(\text{SiO}_4)_x$  series (where  $x = 0, 0.1, 0.25, 0.5, 1.0, 2.0, 3.0$ ) including the total area of the assumed phases with the structure of  $\text{NaZr}_2(\text{PO}_4)_3$ . Their synthesis was carried out by the sol-gel method with the addition of ethanol, the salting out agent. Solutions, 1 M, of  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{ZrOCl}_2$ ,  $\text{H}_3\text{PO}_4$ , and silicosol  $\text{SiO}_2 \cdot 0.5\text{H}_2\text{O}$  were used as starting reagents. Their stoichiometric amounts were mixed under constant stirring and the obtained gel was dried for 5 h at  $90^\circ\text{C}$ . An example of this reaction is given below.



In Fig. 1 the curve of differential thermal analysis for the precursor with  $x = 0.5$  is presented. It is established that in the range  $25\text{--}800^\circ\text{C}$  irreversible

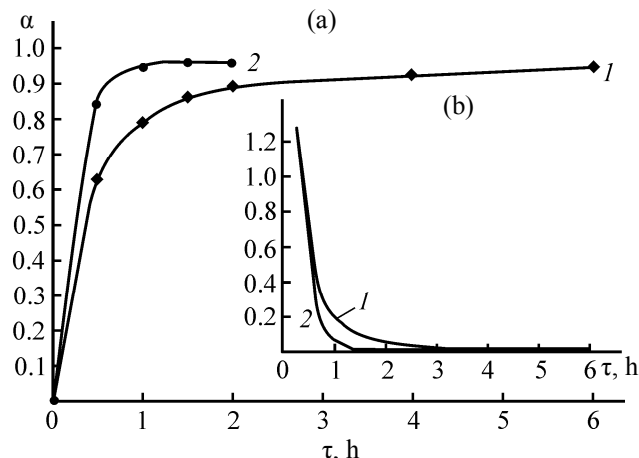
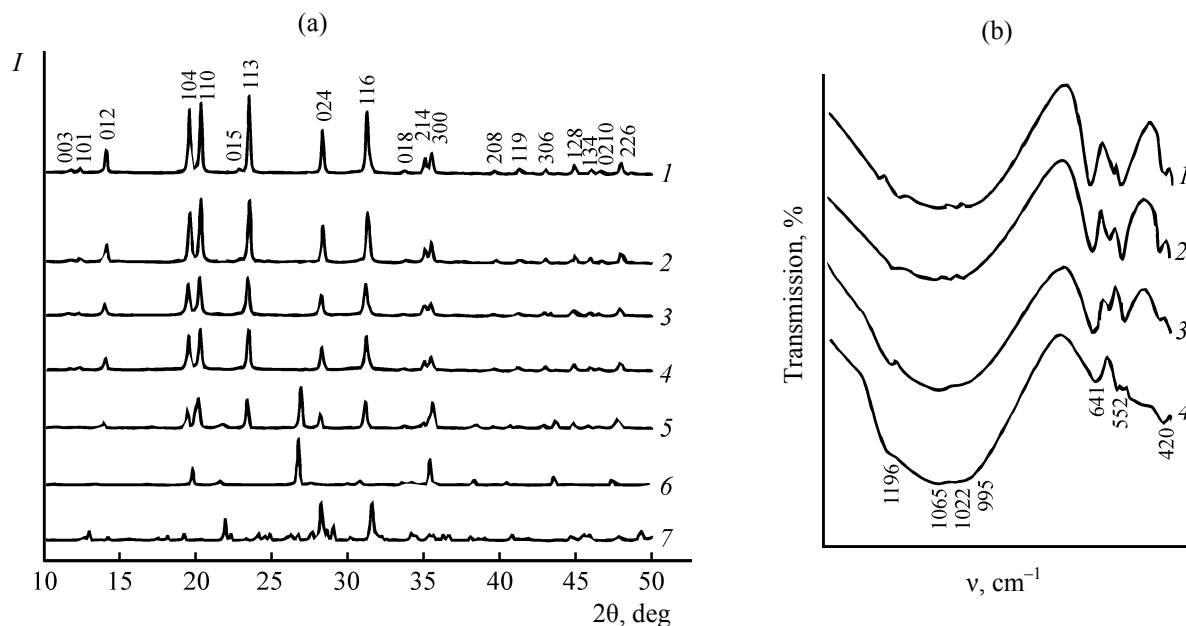


Fig. 2. Dependence of degree of transformation on time in the course of isothermal treatment:  $T = (1)$  700 and  $(2)$   $800^\circ\text{C}$  (a), and reaction rate (b) for  $\text{Ca}_{0.75}\text{Zr}_2(\text{PO}_4)_{2.5}(\text{SiO}_4)_{0.5}$ .

processes accompanied by *endo*-effects take place: at  $T = 130$  and  $250^\circ\text{C}$  (the liberation of crystallization water and the decomposition of phosphoric acid); at  $T = 710^\circ\text{C}$  (the formation of the target product). On the basis of these data temperatures 700 and  $800^\circ\text{C}$  were chosen for further experiments. The duration of the temperature treatment was established on the basis of kinetic dependencies obtained under isothermal conditions at  $T = 700$  and  $800^\circ\text{C}$  presented in Fig. 2.

In the course of the initial 0.5–2 h of isothermal annealing at  $700^\circ\text{C}$  according to X-ray phase analysis data the target NZP phase together with the additional phase of  $\text{ZrP}_2\text{O}_7$  intermediate was formed [17]. The rest intermediate compounds were in amorphous state and their reflexes in the X-ray photograph of the sample were absent. According to the data presented in Fig. 2 after 6 h of annealing the fraction of the target phase was 0.9496. At the increase in temperature to  $800^\circ\text{C}$  it reached 0.9623 after 2 h of isothermal treatment.  $R_{\text{wp}}$  values for each experiment were no more than 6%. Calcium-zirconium phosphatosilicates synthesized under these conditions were fine crystalline colorless powders. From the atomic force microscopy data size distribution  $r$  of particles is observed in the range  $0 < r \leq 350$  nm. From the statistic analysis of distribution function it follows that the average size of particles is  $100 \pm 60$  nm.

Results of X-ray phase analysis (Fig. 3a) show that in  $\text{Ca}_{0.5(1+x)}\text{Zr}_2(\text{PO}_4)_{3-x}(\text{SiO}_4)_x$  ( $0 \leq x \leq 3$ ) system there is a limited area of existence of solid solutions under the conditions  $0 \leq x \leq 0.5$ . Calculated parameters of unit cell varied in the range  $8.777 \leq a \leq 8.787$  Å,



**Fig. 3.** Characterization of phosphatosilicates  $\text{Ca}_{0.5(1+x)}\text{Zr}_2(\text{PO}_4)_{3-x}(\text{SiO}_4)_x$ : (a) X-ray phase analysis data where  $x = (1) 0, (2) 0.1, (3) 0.25, (4) 0.5, (5) 1.0, (6) 2.0$ , and  $(7) 3.0$ ; (b) IR spectra where  $x = (1) 0, (2) 0.1, (3) 0.25$ , and  $(4) 0.5$ .

$22.737 \leq c \leq 22.835 \text{ \AA}$ . At the increase in  $x$  an increase in the parameter  $a$  and decrease in the parameter  $c$  takes place. Phosphatosilicates with higher content of  $\text{SiO}_4$  group up to  $x = 2$  were not obtained as single phase products even at higher temperature and prolonged times of heating.

IR spectroscopy data (Fig. 3b) demonstrate the crystallization of obtained phosphatosilicates in NZP-structure and the absence of X-ray amorphous admixtures in the samples. The appearance of the IR spectra is characteristic of compounds of structural NZP type crystallizing in the space group  $R\bar{3}$ . According to the rules of selection in the spectra of such compounds two bands of stretching symmetric  $\nu_1$  ( $A_u, E_u$ ), four bands of bending symmetric  $\nu_2$  ( $2A_u, 2E_u$ ), and six bands each of stretching asymmetric and bending vibrations  $\nu_3$  ( $3A_u, 3E_u$ ) are possible. Bands related to vibrations of  $\text{PO}_4^{3-}$  and  $\text{SiO}_4^{4-}$  are located close to one another and overlap. In the presented spectrum absorption bands at  $1400\text{--}900 \text{ cm}^{-1}$  correspond to  $\nu_3$ , at  $850\text{--}800 \text{ cm}^{-1}$ , to  $\nu_1$ , and at  $650\text{--}500 \text{ cm}^{-1}$ , to  $\nu_4$  vibrations of these polyhedra.

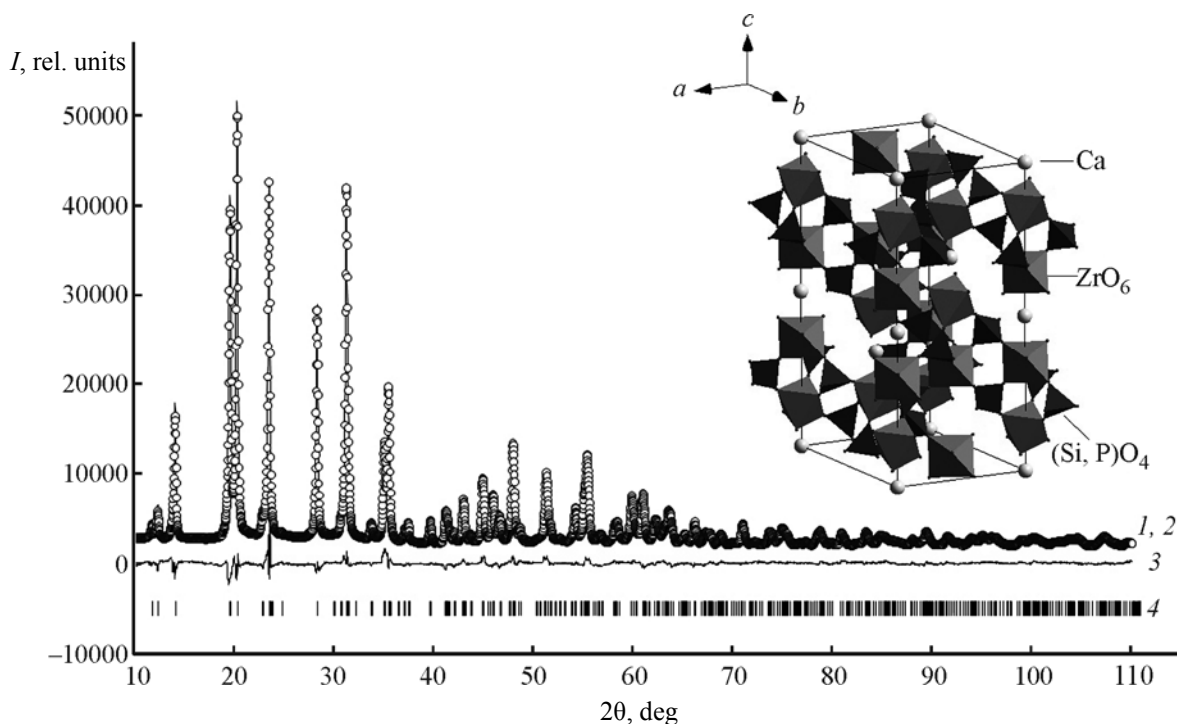
Specific density of  $\text{Ca}_{0.75}\text{Zr}_2(\text{PO}_4)_{2.5}(\text{SiO}_4)_{0.5}$   $\rho_{\text{exp}} = 3.1(1) \text{ g cm}^{-3}$  ( $\rho_{\text{teor}} = 3.25 \text{ g cm}^{-3}$ ) was evaluated by picnometric method.

Further we carried out the refining of the structure of this compound by Rietveld method. Atomic coordinates of  $\text{Ca}_{0.5}\text{Zr}_2(\text{PO}_4)_3$  were taken as a base model

[12]. Conditions of performing the experiment and primary crystallographic data are listed in Table 1. It is seen from Fig. 4 that good agreement of calculated X-ray photograph with the experimental one is observed. Obtained values of coordinates and parameters of heat vibrations of atoms are presented in Table 2. Results of refining show that silicon and phosphorus atoms are randomly distributed in the tetrahedral coordinated framework positions of structure (18f).

**Table 1.** Conditions of measuring and results of refining of crystalline structure of phosphatosilicate  $\text{Ca}_{0.75}\text{Zr}_2(\text{PO}_4)_{2.5}(\text{SiO}_4)_{0.5}$

Parameter	Value
Space group:	$R\bar{3} (148)$
$Z$	6
Cell parameters:	
$a, \text{ \AA}$	8.7870(3)
$c, \text{ \AA}$	22.7369(8)
$V, \text{ \AA}^3$	1520.35(9)
Angle range $2\theta$ , deg	10–110
Total number of points	5001
Number of reflexes	563
Number of refined parameters	43
Confidence factor, %:	
$R_{\text{wp}}, R_{\text{p}}$	6.09, 4.64
$S$	3.70



**Fig. 4.** Experimental (dotted line, 1), calculated (continuous line, 2), and differential (dash line 3), and X-ray diffraction diagram (4) of X-ray diffraction spectra of  $\text{Ca}_{0.75}\text{Zr}_2(\text{PO}_4)_{2.5}(\text{SiO}_4)_{0.5}$  and the fragment of its structure.

The structure of the compound under study (Fig. 4) corresponds to NZP type. It is formed by discrete polyhedrons,  $(\text{Si,P})\text{O}_4$  tetrahedrons and  $\text{ZrO}_6$  octahedrons, joined by structural  $\text{Zr-O-Si/P}$  bridges. Groups of two octahedrons and four tetrahedrons are oriented along the crystallographic axis  $c$ . Positions of cavities inside the polyhedron columns are of two types:  $3a$  and  $3b$ . Calcium atoms completely occupy

out-of-framework  $3a$  positions and half of alternating with them positions  $3b$ . Cavities between the polyhedron columns remain vacant.

Calculated interatomic distances and bond angles are listed in Tables 3, 4. From the comparison of structural data for compounds  $\text{Ca}_{0.75}\text{Zr}_2(\text{PO}_4)_{2.5}(\text{SiO}_4)_{0.5}$  and  $\text{Ca}_{0.5}\text{Zr}_2(\text{PO}_4)_3$  it follows that partial substitution of phosphorus with silicon in the framework of structure leads to insignificant distorting of structure-forming polyhedrons. It is seen in small alteration in bond lengths (about 7%) and bond angles (about 6%), which indicates the stability of total structural motive of the framework octahedron-tetrahedron scaffold.

**Table 2.** Coordinates, isotropic heat parameters of atoms ( $B_{\text{iso}}$ ) in the structure of  $\text{Ca}_{0.75}\text{Zr}_2(\text{PO}_4)_{2.5}(\text{SiO}_4)_{0.5}$  phosphate-silicate

Atom	Position	$x$	$y$	$z$	$B_{\text{iso}}, \text{\AA}^2$
$\text{Ca}^1$	$3a$	0	0	0	3.49(12)
$\text{Ca}^2$	$3b$	0	0	0.5	3.48(13)
$\text{Zr}^1$	$6c$	0	0	0.1491(5)	0.58(8)
$\text{Zr}^2$	$6c$	0	0	0.6417(6)	0.55(9)
Si, P	$18f$	0.2924(2)	0.0070(2)	0.2498(7)	0.47(8)
$\text{O}^1$	$18f$	0.1842(2)	-0.0057(7)	0.1919(1)	0.29(8)
$\text{O}^2$	$18f$	0.0664(6)	0.8467(2)	0.6957(3)	0.29(8)
$\text{O}^3$	$18f$	0.1765(4)	0.1860(2)	0.0869(1)	0.29(8)
$\text{O}^4$	$18f$	0.2165(5)	0.0650(5)	0.5971(6)	0.29(8)

For the investigation of hydrolytic stability ceramic samples obtained by pressing of  $\text{Ca}_{0.75}\text{Zr}_2(\text{PO}_4)_{2.5} \cdot (\text{SiO}_4)_{0.5}$  powder at  $p = 200$  MPa were heated and annealed at  $900^\circ\text{C}$  for 10 h. The duration of experiment was 21 day, samples were taken after 1, 2, 3, 7, 14, and 21 day of treatment. Rate of Ca leaching was calculated by the formula:

$$R = m / (c_{\text{sp}} \cdot S \cdot \tau),$$

where  $R$  is the leaching rate of element ( $\text{g cm}^{-2} \text{ day}$ ) for the time  $\tau$ ,  $m$  is the mass of element entering the solution in the course of time  $\tau$ ,  $c_{\text{sp}}$  is the specific

**Table 3.** Interatomic distances in polyhedrons of  $\text{Ca}_{0.75}\text{Zr}_2(\text{PO}_4)_{2.5}(\text{SiO}_4)_{0.5}$  structure,  $d$ , data of this work,  $d'$ , reported data for  $\text{Ca}_{0.5}\text{Zr}_2(\text{PO}_4)_3$  [16]

Bond type	$d$	$d'$	$\Delta d = (d - d')$ , Å	$ \Delta d /d$ , %
$\text{Ca}^1\text{--O}^3 (\times 6)$	2.539(2)	2.47133(6)	0.07	2.7
$\text{Ca}^2\text{--O}^4 (\times 6)$	2.781(11)	—	—	—
$\text{Zr}^1\text{--O}^1 (\times 3)$	1.911(8)	2.042980(30)	–0.13	6.9
$\text{Zr}^1\text{--O}^3 (\times 3)$	2.131(8)	2.12352(4)	0.01	0.4
$\text{Zr}^2\text{--O}^2 (\times 3)$	2.109(9)	2.0545(0)	0.05	2.6
$\text{Zr}^2\text{--O}^4 (\times 3)$	1.972(11)	2.0701(0)	–0.10	5.0
$\text{Si/P--O}^1$	1.595(13)	1.53531(4)	0.06	3.7
$\text{Si/P--O}^2$	1.597(14)	1.52184(4)	0.08	4.7
$\text{Si/P--O}^3$	1.550(3)	1.542480(30)	0.01	0.5
$\text{Si/P--O}^4$	1.596(6)	1.520410(30)	0.08	4.7

concentration of element in solid phase (g/g of solid phase),  $S$  is the area of ceramic sample ( $\text{cm}^2$ ),  $\tau$  is the time of leaching, days [14].

According to X-ray phase analysis data the phosphatosilicate after keeping in water retained its phase composition. Calcium leaching rate achieved on the 21st day was  $1 \times 10^{-8} \text{ g cm}^{-2} \text{ day}$  (see Fig. 5).

Hence, new calcium-containing phosphatosilicates of the  $\text{NaZr}_2(\text{PO}_4)_3$  structure are obtained. In the system under investigation limited substitution solid solutions of the type  $\text{Ca}_{0.5(1-x)}\text{Zr}_2(\text{PO}_4)_{3-x}(\text{SiO}_4)_x$ ,  $0 \leq x \leq 0.5$  are formed. The processes of their formation are studied. In the initial stage procedures of sol-gel technologies can be used with the subsequent treatment of the dry residue at  $800^\circ\text{C}$  for 2 h. By means of full profile analysis using the powder X-ray analysis data (Rietveld method) crystalline structure of  $\text{Ca}_{0.75}\text{Zr}_2(\text{PO}_4)_{2.5}(\text{SiO}_4)_{0.5}$  phosphatosilicate was refined. Tetrahedral positions in such compounds are statistically populated by silicon and phosphorus atoms.

On the whole the obtained results open additional possibilities of modeling complex compositions of solid solutions of NZP series on the basis of anionic heterovalence isomorphism for different use including the biological and medicinal ones.

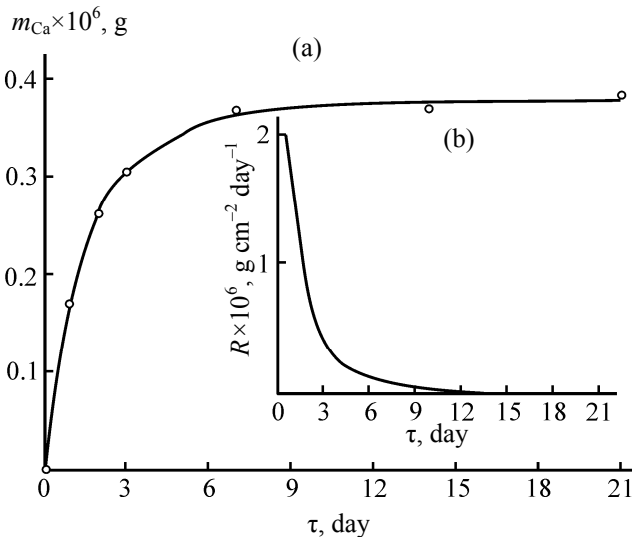
## EXPERIMENTAL

**Investigation methods.** Obtained samples were characterized and studied by differential thermal analysis, IR spectroscopy, X-ray phase analysis, atom force microscopy, and atom-absorption spectroscopy. For this purpose Setaram LabSys TG-DTA/DSC

**Table 4.** Bond angles in polyhedrons of  $\text{Ca}_{0.75}\text{Zr}_2(\text{PO}_4)_{2.5}(\text{SiO}_4)_{0.5}$  structure,  $\varphi$ -data of this work,  $\varphi'$ , reported data for  $\text{Ca}_{0.5}\text{Zr}_2(\text{PO}_4)_3$  [16]

Bond angle	$\varphi$	$\varphi'$	$\Delta\varphi = (\varphi - \varphi')$ , deg	$ \Delta\varphi /\varphi$ , %
$\text{O}^1\text{Zr}^1\text{O}^1 (\times 3)$	96.37(14)	92.9503(15)	3.42	3.5
$\text{O}^1\text{Zr}^1\text{O}^3 (\times 3)$	88.68(9)	91.1189(17)	–2.44	2.8
$\text{O}^1\text{Zr}^1\text{O}^{3*} (\times 3)$	93.26(12)	95.8139(15)	–2.55	2.7
$\text{O}^1\text{Zr}^1\text{O}^{3*} (\times 3)$	168.56(12)	170.13361(10)	–1.57	0.9
$\text{O}^3\text{Zr}^1\text{O}^3 (\times 3)$	80.76(8)	79.5228(18)	1.24	1.5
$\text{O}^2\text{Zr}^2\text{O}^2 (\times 3)$	89.52(9)	91.1513(15)	–1.63	1.8
$\text{O}^4\text{Zr}^2\text{O}^2 (\times 3)$	87.10(15)	88.8755(15)	–1.78	2.0
$\text{O}^4\text{Zr}^2\text{O}^2 (\times 3)$	87.25(17)	89.5668(15)	–2.32	2.7
$\text{O}^4\text{Zr}^2\text{O}^{2*} (\times 3)$	175.35(16)	179.2802	–3.93	2.2
$\text{O}^4\text{Zr}^2\text{O}^{4*} (\times 3)$	95.92(21)	90.4059(15)	5.51	5.7
$\text{O}^1\text{Si/PO}^4$	109.1(3)	108.51450(30)	0.59	0.5
$\text{O}^2\text{Si/PO}^1$	110.0(5)	110.8643(21)	–0.86	0.8
$\text{O}^2\text{Si/PO}^4$	108.6(2)	112.7338(9)	–4.13	3.8
$\text{O}^3\text{Si/PO}^1$	114.00(20)	108.6672(8)	5.33	4.7
$\text{O}^3\text{Si/PO}^2$	104.53(19)	106.70090(20)	–2.17	2.1
$\text{O}^3\text{Si/PO}^4$	110.48(18)	109.2728	1.21	1.1

thermoanalyzer, IR Prestige-21 Shimadzu IR Fourier spectrometer, Shimadzu LabX XRD-6000 (Bragg-Brentano geometry,  $\text{CuK}_\alpha$  filtered radiation,  $\lambda$  1.54178 Å) X-ray diffractometer, SOLVER Pro<sup>TM</sup> (NT-MDT, Russia) scanning atomic force microscope with the Smena-A scanning head and the system of optical observation, and Perkin-Elmer-603 atom-absorption spectrometer (atomic absorption by the calcium 422.7 nm line, detection limit  $0.08 \mu\text{g mL}^{-1}$ ) were used.

**Fig. 5.** Kinetic curve of migration of  $\text{Ca}^{2+}$  cations from  $\text{Ca}_{0.75}\text{Zr}_2(\text{PO}_4)_{2.5}(\text{SiO}_4)_{0.5}$  in the contact solution (a) and dependence of leaching rate on time (b).

### Method of investigation of phase formation.

Investigation of phase formation with the purpose of optimization of temperature and time regime of synthesis was carried out by means of differential thermal analysis together with the quantitative X-ray phase analysis [15] by an example of  $\text{Ca}_{0.75}\text{Zr}_2(\text{PO}_4)_{2.5} \cdot (\text{SiO}_4)_{0.5}$ . In the first stage processes preceding the formation of target NZP phase were analyzed. Temperature interval of occurrence of the solid phase reaction was evaluated by means of differential thermal analysis. After that reaction mixture was heated at  $T = 700$  and  $800^\circ\text{C}$ . Thermal treatment at each temperature was carried out step-by-step. The samples for analysis of solid phase were taken after each 0.5–1 h of stage-by-stage heating. For establishing the phase composition of samples in the course of their formation after each stage of isothermal annealing and for the control of sequence of phase transformations the quantitative version of X-ray phase analysis was used [15]. Recording of X-ray photographs was carried out in the angle range  $2\theta\ 10^\circ\text{--}50^\circ\text{C}$  with the step  $0.02^\circ\text{C}$  and time lag 2 s. Values of mass fraction of the target phase were obtained by treating of X-ray photographs by Rietveld method [16] with the help of RIETAN-97 program [17].

**Procedure of investigation of crystalline structure.** For the full profile structure analysis diffractogram of  $\text{Ca}_{0.75}\text{Zr}_2(\text{PO}_4)_{2.5}(\text{SiO}_4)_{0.5}$  sample was registered in the angle range  $2\theta\ 10^\circ\text{--}110^\circ$  with the step  $0.02^\circ$ , lag time in the point was 10 s. Treating of diffractogram and refining of structure of phosphosilicate were carried out by Rietveld method. The approximation of peak profiles was carried out using the modified Voit pseudo-function [15]. Refining of crystalline structure was carried out by gradual addition of refined parameters under constant graphic modeling of background until the stabilization of R-factor values. Atomic coordinates of phosphate  $\text{Ca}_{0.5}\text{Zr}_2(\text{PO}_4)_3$  within the frames of space group  $\bar{3}$  (NZP structural type) [13] were used as base analogs.

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