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# State of water and thermal properties of zinc and cobalt (II) phosphate solid solution

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It was established that the energy H-bonds and asymmetry of coordinationally connected of water molecules increases with elevation of cobalt content in the structure of $Zn_{3-x}Co_x(PO_4)2 \cdot 4H_2O$ ($0<x\leq1.00$). Thermal properties of phosphate solid solution are investigated. It was found that their thermal stability correlate with the energy state of water molecules and has maximum in the phosphate with composition $Zn_2Co(PO_4)_2 \cdot 4H_2O$. It was determined that the temperature ranges of formation and thermal stability of its partial and complete dehydration products at 30-40°C higher than in the phosphates, which has less cobalt content. The sequence of thermal solid phase transformations, which accompanying of $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$ dehydration is established.
**Keywords:** phosphate, solid solution, thermal properties, dehydration

Установлено, что энергия H-связей и асимметрия координационно связанных молекул воды возрастают с увеличением содержания кобальта в структуре $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$ ($0<x\leq1.00$). Исследованы термические свойства фосфатов твердого раствора, установлено, что их термическая устойчивость коррелирует с энергетическим состоянием молекул воды и максимальна в фосфате состава $Zn_2Co(PO_4)_2 \cdot 4H_2O$. Определено, что температурные интервалы образования и термической стабильности продуктов его частичного и полного обезвоживания на 30-40°C выше, чем в фосфатах с меньшим содержанием кобальта. Приведена последовательность термических твердофазных превращений, сопровождающих обезвоживания $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$.

**Стан води та термічні властивості твердого розчину цинк і кобальт(II) фосфатів.** *Н.М.Антрапцева, Н.В.Солод.*

Встановлено, що енергія H-зв'язків і асиметрія координаційно зв'язаних молекул води зростають зі збільшенням кобальту в структурі $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$ ($0<x\leq1.00$). Досліджено термічні властивості фосфатів твердого розчину, встановлено, що їх термічна стійкість корелює з енергетичним станом молекул води і максимальна у фосфата складу $Zn_2Co(PO_4)_2 \cdot 4H_2O$. Визначено, що температурні інтервали утворення і термічної стабільності продуктів його часткового та повного зневоднення на 30-40°C вищі, ніж у фосфатів з меншим вмістом кобальту. Наведено послідовність термічних твердофазних перетворень, що супроводжують зневоднення $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$.

## 1. Introduction

Solid solutions of hydrated phosphates of divalent metals, zinc and cobalt particularly, and products of their partial and complete dehydration is widely used as the basis of various inorganic materials: catalysts of the organic synthesis, pigments, thermophosphate decorative coverings, corrosion inhibitors, etc. [1–4]. To create on their basis the new materials with a given complex of operational characteristics need to know the composition, temperature ranges of formation and thermal stability of the products of their partial or complete dehydration. The thermal properties of hydrated salts are defined by the energy state of water molecules, which belong to their crystal lattice. Therefore the correct choice of conditions of the obtaining of dehydrated phosphate is possible only if to take into consideration the chemistry of dehydration [2, 3].

There are investigations devoted to the study of conditions of formation of zinc and cobalt (II) phosphate solid solution with composition $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$ [4, 5], it's chemical nature [6], structural features [4]. Concerning its properties, the authors [4, 7] describe some colorimetric properties of zinc phosphate modified by cobalt, and changes of its color when heated.

Information on the systematic study of water state and thermal properties of zinc and cobalt (II) phosphate solid solution in the literature is absent.

The purpose of the present work is to investigate the state of water and thermal properties of zinc and cobalt(II) phosphate solid solution with general formula $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$ $(0<x\leq1.00)$, and to determine composition, temperature ranges of formation and thermal stability of the products of partial and complete dehydration.

## 2. Experimental

Solid solution of middle phosphates $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$ $(0<x\leq1.00)$ and their deuterium analogues obtained by interaction of zinc and cobalt (II) hidrocarbonates with a phosphoric acid solution is similar to the one described in [5]. The saturated solid solution — $Zn_2Co(PO_4)_2 \cdot 4H_2O$ and phosphate of composition $Zn_{2.5}Co_{0.5}(PO_4)_2 \cdot 4H_2O$ were used as the main objects of the research.

IR spectra were recorded at 20°C and 190°C at the range of 400–4000 $cm^{-1}$ using spectrometer Nexus-470 with Fourier transformation and Omnic software. Samples were prepared by shifting of a fixed batch (0.05 wt.%) in KBr matrix. In addition, phosphate slurry in butyl alcohol was used, putting it on a neutral fluorite substrate.

Thermal properties were investigated in the temperature range of 25–900°C in dynamic (derivatograph Q-1500 D): platinum crucibles with lid, standard — heated $Al_2O_3$, batch sample — 300 mg, heating rate 2.5 degree/min., accuracy of the temperature determining ±5°C) and quasiisotermic (labyrinth crucible, heating rate of 3.0 degree/min.) regime of heating. Products of the heat treatment at the temperature corresponding to the thermal effects on DTA curve were identified similarly [8] using complex analysis methods: chemical, X-ray, IR spectroscopy.

## 3. Results and discussion

In the IR spectra of phosphate solid solutions $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$ $0<x\leq1.00$ of different composition, and their deuterium analogues, three types of vibrations of water molecules are observed: valence vibrations of OH-groups, deformation and libration vibrations of water molecules. At the room temperature two absorption bands of $\nu(OH)$ are recorded: one $\delta(H_2O)$ and one $\rho(H_20)$; the value of their absorption bands in the spectrum of phosphate $Zn_2Co(PO_4)_2 \cdot 4H_2O$ and their attribution is shown in Table 1. At the low temperatures (−190°C) multiplicity of the spectra increases and in the $\nu(OH)$ vibrations four absorption maxima (3500, 3345, 3230 and 3095 $cm^{-1}$) are observed, in the deformation vibrations their number is two (1635, 1630 $cm^{-1}$). Intensity of the individual bands slightly increases.

If to consider the vibrations of free water molecules (it symmetry $C_{2v}$), one can present a picture of splitting the internal vibrations of $H_2O$, based on their local symmetry, taking into account the change in its symmetry when entering the hydrate lattice. Phosphates of solid solution $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$ $(0<x\leq1.00)$ are isostructuraly, according to [6], with $Zn_3Co(PO_4)_2 \cdot 4H_2O$, and crystallized in the space group $D^{16}_{2h}$ $(Pnma)$. For this space group there is such a set of the local regulations: $C_1$ (8), $2C_1$ (4), $C_s$ (4). On the basis of atom position determined when identifying $Zn_3Co(PO_4)_2 \cdot 4H_2O$ [9], the water molecules in the phosphates $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$ occupy $C_s$ and $C_1$ sites. In the case of local symmetry $C_s$ in the IR spectra three vibrations $\nu_1(A^1)$, $\nu_2(A^1)$, $\nu_3(A^{II})$ at $C_1$ — $\nu_1(A)$, $\nu_2(A)$, $\nu_3(A)$ are active. That is, the two bands must correspond to every kind of water molecules in stretching frequency range, and the one band — in bending frequency range. This set of absorption bands is observed in the IR spectra of the solid phosphate solution at the low temperatures and in the deuterium analogue spectrum it is observed even at the room temperature (Table 1).

These data suggest the presence of $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$ in the structure of two types of non-equivalent water molecules of

Table 1. Wave number (cm$^{-1}$) peaks of absorption bands in IR spectra of $Zn_{3-x}Co_x(PO_4)_2·4H_2O$ ($0<x\leq1.00$)

| $Zn_2Co(PO_4)_2·4H_2O$ | | $Zn_2Co(PO_4)_2·4D_2O$ | | Attribution |
|---|---|---|---|---|
| 20°C | −190°C | 20°C | −190°C | |
| 3500 s. | 3500 s. | 3500 sh. | 3500 sh. | ν(OH)(OD) |
| – | – | 2580 s. | 2580 s. | |
| – | 3345 s. | 2480 sh. | 2480 sh. | |
| 3240 s.br. | 3230 s. | 3230 sh. | 3230 sh. | |
| – | – | 2400 s. | 2400 s. | |
| – | 3095 s. | 2280 s. | 2280 s. | |
| – | 1635 s. | – | – | $\delta(H_2O)$ |
| 1630 s. | 1630 s. | 1225 calculated | – | |
| – | 1130 sh | 1130 sh. | 1130 sh. | $\nu_3(PO_4)$ |
| 1095 s. | 1095 s. | 1095 s. | 1095 s. | |
| 1060 sh. | 1060 s. | 1060 sh. | 1060 s. | |
| 1015 sh. | 1020 s. | 1015 sh. | 1020 s. | |
| 1000 s. | 1005 s. | 1000 s. | 1005 s. | |
| 940 s. | 940 s. | 940 s. | 940 s. | $\nu_1(PO_4)$ |
| – | 930 sh. | 930 sh. | 930 sh. | |
| – | 860 sh. | – | 860 sh. | ρ(OH)(OD) |
| 750 sh. | 780 av. | 580 av. | 580 av. | |
| 625 s. | 630 s. | 480 av. | 480 s. | |
| 620 s. | 620 s. | 630 av. | 630 w. | $\nu_4(PO_4)$ |
| 570 w. | 580 s. | 570 av. | 570 av. | |
| 500 sh. | 490 av. | 500 sh. | 490 av. | $\nu_2(PO_4)$ |
| – | 450 sh. | – | – | |
| 420 w. | 420 s. | – | – | |
| – | 415 sh. | – | – | |

Comment: s. — strong, av. — average, w. — weak, sh. — shoulder, br. — broad.

the low symmetry. Their tough fixing, both in Oxygen and in Hydrogen, indicates absorption bands of libration vibrations of water molecules in the spectrum. In the spectrum of $Zn_2Co(PO_4)_2·4H_2O$ they include shoulder at 750 cm$^{-1}$ and peak at 625 cm$^{-1}$, in deuterium analogue — 580 and 480 cm$^{-1}$, respectively (isotope replacement ratio 1.33).

Character of configuration of the absorption bands ν(OH), their shape (expansion and low frequency vibrations as compared to free water molecules — 3700 cm$^{-1}$) indicates the existence of hydrogen bonds in the structure $Zn_{3-x}Co_x(PO_4)_2·4H_2O$. The difference in the values of the maxima bands ν(OH) reaches 254–260 cm$^{-1}$ (Table 2). The vibrations allow us to consider each of two OH-groups of the same water molecules as independent each from other, and to believe that they take part in formation of the different strength and directivity H-bonds. In addition to that, HOH angle in the molecules of water does not depend on the composition of phosphates, as indicates almost identical values of $\delta(H_2O)$. The absence of significant changes in $\delta(H_2O)$ in the spectra obtained at −190°C, and increased value of their frequency (1630 cm$^{-1}$ compared to the vibrations frequency of free water molecules — 1595 cm$^{-1}$) indicates the existence of the rigid system of hydrogen bonds in the structure of $Zn_{3-x}Co_x(PO_4)_2·4H_2O$. Some OH-groups (which corresponds to the maximum absorption of vibrations at the frequency range of 3270–3240 cm$^{-1}$) are involved in formation of the rather strong hydrogen bonds with phosphate anion — $[Me^{2+}–OH...OPO_3]$. Other OH-groups (absorption at the range of 3520–3500 cm$^{-1}$) are connected relatively weak within interactions between OH groups of different water molecules — $[Me^{2+}–OH_2...OH_2]$.

Analysis of the IR spectra of $Zn_{3-x}Co_x(PO_4)_2·4H_2O$ with different content of zinc and cobalt has shown that with increases of the cobalt content in the coordi-

Table 2. Wave number ($cm^{-1}$) peaks of absorption bands ν(OH) in IR spectra $Zn_{3-x}Co_x(PO_4)_2\cdot 4H_2O$ ($0<x\leq 1.00$) and characterization of H-bonds

| Phosphate composition | Wave number of maximums of the absorption band ν(OH), $cm^{-1}$ | | Characteristics of H-bonds | | |
|---|---|---|---|---|---|
| | | | *E*, kJ/bond | | $R_{O...O}$, nm $(PO_4)O...O(H_2O)$ |
| | | | $OH...OPO_3$ ÁÁM, | | |
| [illegible] $4H_2O$ | 3264 | 3518 | 29.35 | 12.48 | 0.274 |
| [illegible] $4H_2O$ | 3260 | 3515 | 29.41 | 12.51 | 0.274 |
| [illegible] $4H_2O$ | 3254 | 3510 | 29.50 | 12.60 | 0.274 |

nating polyhedron there is natural shift of the maxima of the absorption bands ν(OH) to the low-frequency region, as both in $M^{2+}$–$OH_2...OPO_3$, and $M^{2+}$–$OH_2...OH_2$ groups. It is clearly registered in the IR spectra of the samples deposited on $CaF_2$ (Fig. 1). The energy of hydrogen bonds is assessed according to [3] by this shift, increases at the transition from $Zn_{2.8}Co_{0.2}(PO_4)_2\cdot 4H_2O$ to $Zn_2Co(PO_4)_2\cdot 4H_2O$ (Table 2).

The given conclusion agrees completely with the thermal and analytical researches on phosphates of the solid solution $Zn_{3-x}Co_x(PO_4)_2\cdot 4H_2O$, which state that the highest thermal stability has phosphate, energy of H-bonds in the structure of which has the greatest value $Zn_2Co(PO_4)_2\cdot 4H_2O$. The temperature of the beginning of crystalline hydrate water removal increases with growth of the energy of H-bonds realized in the structure: from 80°C for $Zn_{2.8}Co_{0.2}(PO_4)_2\cdot 4H_2O$, up to 90°C for $Zn_{2.5}Co_{0.5}(PO_4)_2\cdot 4H_2O$, and 105°C for $Zn_2Co(PO_4)_2\cdot 4H_2O$ (Table 3).

The phosphates thermal stability can be significantly improved by using quasiisotermic heat treatment regime, in which the partial pressure of water vapor over the sample is close to the thermodynamic equilibrium one. Under these conditions, the weight loss for $Zn_2Co(PO_4)_2\cdot 4H_2O$, for example, starts when heating up to 180°C, for $Zn_{2.5}Co_{0.5}(PO_4)_2\cdot 4H_2O$ — up to 160°C (Fig. 2).

Dehydration of tetrahydrate $Zn_2Co(PO_4)_2\cdot 4H_2O$ is implemented in two stages, characterized by deep endothermic effects on DTA curves and DTG at the range of 105–240°C and 265–340°C (the first and the second stages of dehydration, respectively). The mass loss in each effect region corresponds to removing of two moles of water and, mostly, ends at 340°C.

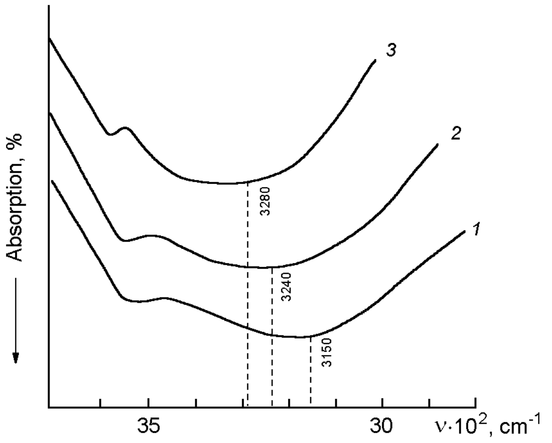

Fig. 1. IR spectra of $Zn_2Co(PO_4)_2\cdot 4H_2O$ (*1*), $Zn_{2.5}Co_{0.5}(PO_4)_2\cdot 4H_2O$ (*2*), $Zn_{2.8}Co_{0.2}(PO_4)_2\cdot 4H_2O$ (*3*) deposited on $CaF_2$.

The product formed at the first stage of dehydration is identified as dehydrate of composition $Zn_2Co(PO_4)_2\cdot 2H_2O$. Its X-ray and IR-spectroscopic characteristics correspond to known for isostructural $Zn_3(PO_4)_2\cdot 2H_2O$ [10]. The spectral pattern of $Zn_2Co(PO_4)_2\cdot 2H_2O$, obtained at 240°C ($Zn_{2.5}Co_{0.5}(PO_4)_2\cdot 2H_2O$ at 190°C) changes compared to the initial tetrahydrate at all frequency ranges (Fig. 3). The absorption band ν(OH) is asymmetrical with the maximum at 3400 $cm^{-1}$ and clearly contemplated shoulder 3180 $cm^{-1}$. In the characteristic frequencies of anions $PO_4^{3-}$ vibrations the narrowing of spectral interval absorption occurs and the maxima 1060 and 1015 $cm^{-1}$ disappear. This indicates restructuring of the bonds in the structure and, in particular, the reduction of the correlation field caused by the interaction of $PO_4$-tetrahe-

Table 3. Dependences of thermal properties of solid solution phosphates $Zn_{3-x}Co_x(PO_4)_2{\cdot}4H_2O$ ($0<x\leq1.00$) on their composition (heating rate 2.5 degree/min)

| Phosphate composition | The first stage of dehydration, °C | | | The second stage of dehydration, °C | | |
|---|---|---|---|---|---|---|
| | Start | Finish | Rate maximum | Start | Finish | Rate maximum |
| $_2$cdotБ% %А*рВБ@ЖФщ% %3щ7А3ТВА*3В®рВВ 4H$_2$O | 80 | 175 | 145 | 200 | 300 | 220 |
| $_2$cdotБ% %А*рВБ@ЖФщ% %3щ7А3ТВА*3В®рВВ 4H$_2$O | 95 | 190 | 175 | 225 | 320 | 245 |

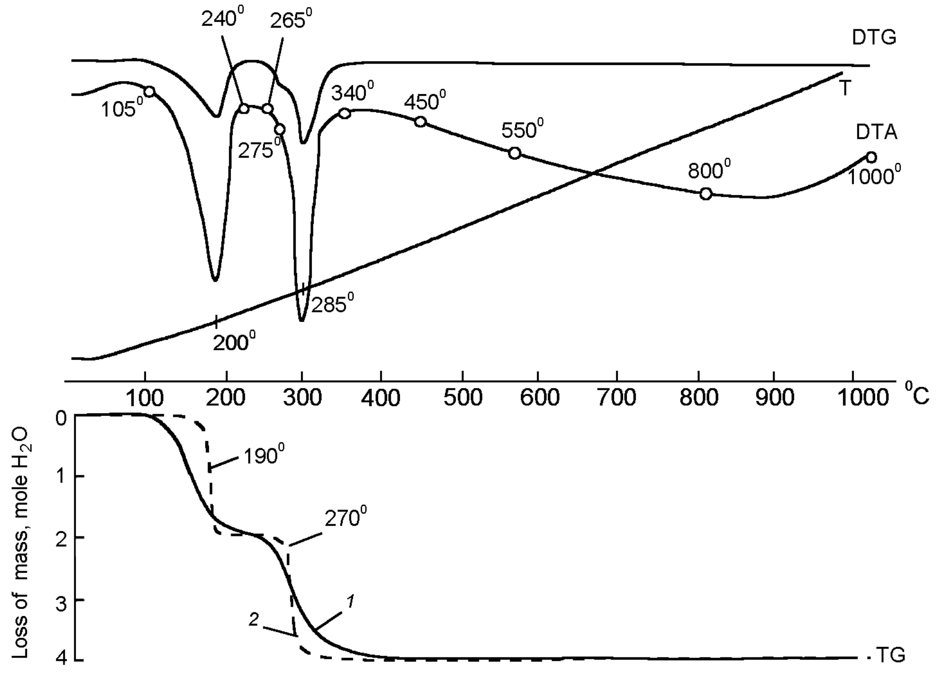

Fig. 2. Curves of differential thermal analysis of $Zn_2Co(PO_4)_2{\cdot}4H_2O$: *1* — in dynamic (heating rate 2.5 degree/min), *2* — quasiisotermic heating regime, -o- —place of sampling the sample for analysis.

dron together. As a result, splitting of the absorption bands is determined, mainly by the anion symmetry (effect of the static fields), which leads to decrease of the absorption bands number.

The spectrum of the sample obtained by $Zn_2Co(PO_4)_2{\cdot}4H_2O$ heating up to 265°C is quite similar to the previous one (Fig. 3). Two absorption maxima recorded at 20°C in the ν(OH) at −190°C are not separated. This shows that in the range of 105–240°C temperature at least two tightly bound water molecules remove, and this is accompanied by the restructuring of H-bonds in the crystalline structure. Dihydrate $Zn_2Co(PO_4)_2{\cdot}2H_2O$, which is formed, is stable when heated at the range of 240–265°C. Calculation of the energy of hydrogen bonds, that are formed in its structure indicates that two water molecules remaining are involved in formation of the system of the strong hydrogen bonds (about 20–35 kJ/mole), that are different from H-bonds in the structure of the initial tetrahydrate.

The subsequent heat treatment of $Zn_2Co(PO_4)_2{\cdot}2H_2O$ dihydrate in the range of 265–340°C (the second stage of dehydration) is registered on the DTA and DTG with endothermic effect, that has two nearly overlapping endothermic effects with the maximum speeds processes at 275 and 285°C. The total sample mass loss in this effect corresponds to removing of two water molecules. The dehydration of $Zn_2Co(PO_4)_2{\cdot}2H_2O$ in the quasiisotermic regime is also described by legible step of the mass loss at 270°C, that defines the joint removing of two $H_2O$ moles (Fig. 2).

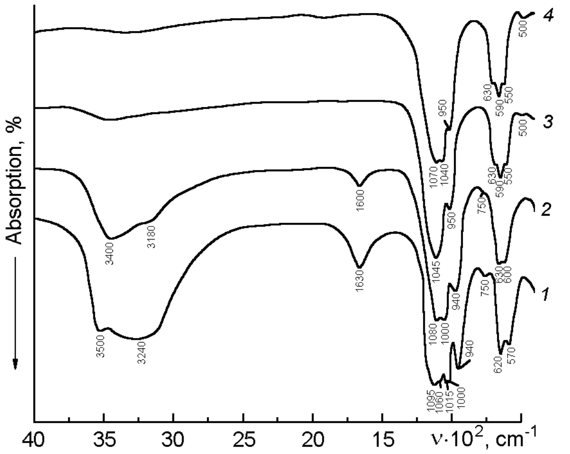

Fig. 3. IR spectra of $Zn_{2.0}Co(PO_4)_2{\cdot}4H_2O$ (*1*) and the products of its thermal dehydration obtained at 105°C (*1*) 240–265°C (*2*), 340–450°C (*3*), 900°C (*4*).

Explanation of the established fact follows from consideration of the structural features of $Zn_3(PO_4)_2{\cdot}4H_2O$ [9] and the solid solution on its bases with composition $Zn_{3-x}Co_x(PO_4)_2{\cdot}4H_2O$ [6]. In the structure of the tetrahydrates there are two crystal and graphical nonequivalent types of coordinational bounds of water molecules. Interatomic distances between the cation and Oxygen in the water molecules in the coordination polyhedron, considering the participation of OH-groups of the water molecules in formation of the hydrogen bonds formed in the structure, are different. They are 0.2099 nm ($H_2O$ — I) and 0.2116 nm ($H_2O$ — II) for the water molecules, that occupy opposite vertices in the octahedron (trans-position) and 0.2159 nm for molecules ($H_2O$ — III) located on the sharing edges of the octahedra (cis-position). Lengths of the ties between the two water molecules ($H_2O$ — III) with cation are 2–3 % bigger, than for $H_2O$ — I and $H_2O$ — II. This allows us to assume the fact that their separate pairs remove during the heating. And, above all, the most weakly bound to the cation water will be removed, that is two molecules of $H_2O$ — III. And this is observed at the first stage of dehydration of $Zn_2Co(PO_4)_2{\cdot}4H_2O$ in the range of 105–240°C.

The length of cation ties with molecules of $H_2O$ — I and $H_2O$ — II differs a little (at 0.78 %). In addition, the second stage of the dehydration is characterized by the dehydrate dehydration, the structure of which due to redistribution of the H-bonds after removal of the first two mole of $H_2O$, values of the bond lengths cation with $H_2O$ — I and $H_2O$ — II changed, and considering the IR spectra data became closer. This complicates the removal of each of the separate water molecules remaining and leads to almost complete overlaying of two endothermic effects, that characterize these processes in the second stage of dehydration of $Zn_2Co(PO_4)_2{\cdot}4H_2O$ (Fig. 2).

The mass loss in the tetrahydrate is almost finished in the case of heating above 300–340°C (Table 3). The slight changes associated with the removal of the final amount of water are observed when the sample is heated to 400–450°C. When further raising the temperature to 900°C, the mass loss on TG curve is not registered (Fig. 2).

In the IR spectra of the thermal transformations, that take place at the second stage of dehydration of $Zn_2Co(PO_4)_2{\cdot}4H_2O$ (265–340°C), it is observed the significant change in the whole spectral range (Fig. 3). Absorption bands that characterize the vibrations of water molecules are almost absent. Configuration of the absorption bands in the anion vibrations changes significantly. The spectral range of the fixed bands narrows, and appearance of the new intense band (550 $cm^{-1}$), referring to three degenerate antisymmetric deformational vibrations, indicates significant degree of deformation of the phosphate tetrahydra, whose interaction among themselves weakens due to absence of the hydrogen bonds (the correlation effect field is at minimum).

The IR spectrum of the dehydrated $Zn_2Co(PO_4)_2{\cdot}4H_2O$ at 900°C is similar to the spectrum of the sample obtained by heating up to 340°C. Strong absorption bands splitting and increasing of their intensity is the evidence of improved structure of the dehydrated phosphate. These data complement the results of X-ray analysis of the products of dehydration of $Zn_2Co(PO_4)_2{\cdot}4H_2O$, under which the completely dehydrated phosphate is identified as $\gamma$–$Zn_2Co(PO_4)_2$ (monoclinic system, sp.gr. $P2_1/n$). It is stable when heated at the range of 340-900°C.

Thus, the sequence of the thermal solid phase transformations, that accompany the dehydration of phosphate of $Zn_2Co(PO_4)_2{\cdot}4H_2O$ composition can be described as follows:

$$Zn_2CoPo_{42} \cdot 4H_2O \xrightarrow[-2H_2O]{105\text{–}240\,^{\circ}C}$$

$$\rightarrow Zn_2Co^1(PO_4)_2 \cdot 2H_2O \xrightarrow[-2H_2O]{265\text{–}340\,^{\circ}C} \gamma\text{–}Zn_2Co(PO_4)_2.$$

These correspond to the heat treatment temperature ranges of $Zn_2Co(PO_4)_2 \cdot 4H_2O$ in dynamic conditions with the heating rate of 2.5 degree/min. Changing of the heating rate leads to shift in the temperature ranges of formation and thermal stability of the products of partial and complete dehydration. So when the heating rate reaches 0.6 degree/min $Zn_2Co(PO_4)_2 \cdot 4H_2O$ is stable up to 80°C. In the range of 80–210°C (the first stage of water removal) formation of phosphate of lower hydration — $Zn_2Co(PO_4)_2 \cdot 4H_2O$ takes place. Received at 210°C dihydrate is stable even in the range of 210–235°C, but now it loses two water molecules to form the completely dehydrated $\gamma$-$Zn_2Co(PO_4)_2$ when heated up to 310°C. When heating rate is 10.0 degree/min formation of $Zn_2Co(PO_4)_2 \cdot 2H_2O$ and $\gamma$-$Zn_2Co(PO_4)_2$ is recorded at 120–255°C and 280–370°C, respectively. The common process patterns remain.

This scheme of dehydration of $Zn_2Co(PO_4)_2 \cdot 4H_2O$ is the same for phosphates of the solid solution of $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$ ($0<x\leq 1.00$) of different composition. The cation nature affects on the temperature ranges of resistance of the both initial crystalline hydrates and products of their partial and full dehydration. It was established, that the maximum for the phosphates of the solid solution $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$ ($0<x\leq 1.00$) with the larger content of cobalt is caused by the energy state of water molecules in their crystal structures.

## 4. Conclusions

In the structure of phosphate solid solution with composition $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$ ($0<x\leq 1.00$) there are two types of nonequivalent water molecules, OH-groups of which form the rigid system of different strength and directivity of hydrogen bonds. The energy of the H-bonds and the asymmetry of related water molecules increases with increasing of cobalt content in the composition of $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$.

Thermal stability of the crystalline hydrates of the solid solution of $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$ ($0<x\leq 1.00$) correlates with the energy state of water molecules in their structure and is at the maximum for phosphate of the composition $Zn_2Co(PO_4)_2 \cdot 4H_2O$. Temperature range of formation and thermal stability of the products of partial and complete dehydration is also at 30–40°C higher, than for the phosphates with the smaller cobalt content.

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