

## The behavior of $\text{Co}_{3-x}\text{M}_x^{\text{II}}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ( $\text{M}^{\text{II}} = \text{Mg, Mn, Zn}$ ) solid solutions at elevated temperatures

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It has been determined that heating of solid solutions of hydrated medium phosphates of the composition  $\text{Co}_{3-x}\text{M}_x^{\text{II}}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  ( $\text{M}^{\text{II}} = \text{Mg, Mn, Zn}$ ) is accompanied by dehydration processes with the formation of lower hydration phosphates with the composition  $\text{Co}_{3-x}\text{M}_x^{\text{II}}(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ , where  $1.0 \leq n \leq 7.0$ . Further dehydration leads to the realization of the processes of amorphization and condensation of the phosphate anion. It has been shown that the content of condensed phosphates, depending on the cationic composition of the solid solution, is 7.2–9.6 rel. %  $\text{P}_2\text{O}_5^{\text{gen}}$ . The anionic composition of the heating products is simplified with the beginning of crystallization of the solid phase. Anhydrous crystalline phosphate identified as  $\text{Co}_{3-x}\text{M}_x^{\text{II}}(\text{PO}_4)_2$  ( $\text{M}^{\text{II}} = \text{Mg, Mn, Zn}$ ) is thermally stable when heated to 900°C. It has been determined that the cation nature affects not only the change of thermal stability of octahydrates, but also the temperature intervals of realization of all stages of the process of their dehydration. The most sensitive to the cationic composition of solid solutions was the depth of implementation of anionic condensation processes, which, judging by the number of condensed phosphates, occurs more fully in the heat treatment products of manganese-containing phosphates –  $\text{Co}_{3-x}\text{Mn}_x(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ . It has been shown that an increase in the heating rate of  $\text{Co}_{3-x}\text{M}_x^{\text{II}}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  ( $\text{M}^{\text{II}} = \text{Mg, Mn, Zn}$ ) from 1.3 deg/min to 10.0 deg/min leads to a shift of temperatures of realization of dehydration, amorphization, anion condensation and crystallization of anhydrous phosphates towards higher temperatures.

**Keywords:** solid solutions, hydrated phosphates, condensation, cation nature, thermal properties

**Поведінка твердих розчинів  $\text{Co}_{3-x}\text{M}_x^{\text{II}}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  ( $\text{M}^{\text{II}} = \text{Mg, Mn, Zn}$ ) в умовах підвищених температур.** *Н.М. Антрапцева, О.Д. Кочкодан, Н.В. Солад, О.О. Кравченко*

Визначено, що нагрівання твердих розчинів гідратованих середніх фосфатів складу  $\text{Co}_{3-x}\text{M}_x^{\text{II}}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  ( $\text{M}^{\text{II}} = \text{Mg, Mn, Zn}$ ) супроводжується процесами дегідратації з утворенням фосфатів меншої гідратності складу  $\text{Co}_{3-x}\text{M}_x^{\text{II}}(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ , де  $1.0 \leq n \leq 7.0$ . Подальше зневоднення призводить до реалізації процесів аморфізації і конденсації фосфатного аніону. Показано, що вміст конденсованих фосфатів залежно від катіонного складу твердого розчину становить 7.2–9.6 % відн.  $\text{P}_2\text{O}_5^{\text{зар}}$ . З початком кристалізації твердої фази аніонний склад продуктів нагрівання спрощується. Безводний кристалічний фосфат, ідентифікований як  $\text{Co}_{3-x}\text{M}_x^{\text{II}}(\text{PO}_4)_2$  ( $\text{M}^{\text{II}} = \text{Mg, Mn, Zn}$ ), термічно стійкий при нагріванні до 900°C. Визначено, що природа катіона впливає не лише на зміну термічної стійкості октагідратів, але й температурні інтервали реалізації всіх стадій процесу їх зневоднення. Найчутливішою до катіонного складу твердих розчинів виявилася глибина перебігу процесів аніонної конденсації, яка, судячи за кількістю конденсованих фосфатів, повніше відбувається в продуктах термообробки манганвмісних фосфатів –  $\text{Co}_{3-x}\text{Mn}_x(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ . Показано, що збільшення швидкості нагрівання  $\text{Co}_{3-x}\text{M}_x^{\text{II}}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  ( $\text{M}^{\text{II}} = \text{Mg, Mn, Zn}$ ) від 1.3 град/хв до 10.0 град/хв призводить до зсуву температур реалізації процесів дегідратації, аморфізації, аніонної конденсації і кристалізації безводних фосфатів у бік більш високих температур.

## 1. Introduction

Solid solutions of divalent metal phosphates are widely used to produce many functional materials for various fields of science and technology: active catalysts, thermosensitive coatings, pigments, ceramic and laser materials, etc. [1-4]. To determine the conditions for their rational operation and increase their service life at elevated temperatures, it is necessary to know their behavior during heating.

Modern data about the thermolysis of individual phosphates are summarized in monographs [1, 2]. It was shown, in particular, that classical simplified schemes of the sequence of thermal transformations, which do not include the formation of condensed phosphates, are becoming less common. According to [2, 5, 6], the actual thermolysis process is a set of complex physicochemical and structural transformations, including intramolecular salt hydrolysis, disproportionation and anionic condensation reactions. The final product formed by thermolysis, fully dehydrated phosphate, is often the result of several parallel processing steps. The priority of one or another direction of thermal reorganization is determined mainly by the state of water in the initial crystal hydrate and the nature of the transformation of the hydrogen bond system during its dehydration. It also depends on factors such as the degree of protonation and hydration of phosphate, its structure, the nature of the cation, and the heat treatment conditions.

The data on the thermal behavior of the individual phosphate-matrix  $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , as well as the energy state of water molecules in solid solutions of phosphates [2, 7], gave reason to assume that the heat treatment of solid solutions of the general formula  $\text{Co}_{3-x}\text{M}^{\text{II}}_x(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  ( $\text{M}^{\text{II}} = \text{Mg}, \text{Mn}, \text{Zn}$ ) is complicated by anionic condensation reactions.

However, the state of water in the initial crystal hydrates determines only the beginning of its removal. The further course of thermal behavior depends on the direction of the rearrangement of the bonds of proton-containing groups in the intermediate products of thermolysis. This, along with the influence of the second cation, makes it impossible to unambiguously predict the thermal and structural transformations accompanying the dehydration of solid phosphate solutions and requires experimental confirmation of the assumptions made.

In addition, the use of the results obtained during the study of individual salts with different crystal structures imposes significant restrictions on the establishment of general laws of the influence of the nature of the cation

on the behavior of crystalline hydrates at elevated temperatures. The lack of experimental data for a correct assessment of the influence of this parameter can largely be supplemented by the using solid solutions with similar structures and controlled cation content as objects of study.

The available experimental data on the thermal behavior of solid solutions of hydrated phosphates with the general formula  $\text{Co}_{3-x}\text{M}^{\text{II}}_x(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  ( $\text{M}^{\text{II}} = \text{Mg}, \text{Mn}, \text{Zn}$ ) are extremely insufficient. Solving these issues requires further systematic research.

The aim of this paper is to study the behavior of solid solutions of cobalt(II) and magnesium (manganese, zinc) hydrated phosphates at elevated temperatures to specify the composition, temperature intervals of formation and thermal stability of phosphates formed during heat treatment.

## 2. Experimental

Solid solutions of hydrated phosphates of cobalt(II) and magnesium (manganese, zinc) with the general formula  $\text{Co}_{3-x}\text{M}^{\text{II}}_x(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  ( $\text{M}^{\text{II}} = \text{Mg}, \text{Mn}, \text{Zn}$ ) were obtained by joint pairwise precipitation of the corresponding cations from aqueous solutions of chlorides or nitrates. As precipitants, a solution of potassium phosphate or its mixture with potassium hydrogen phosphate, were taken in the ratio  $\text{K}_3\text{PO}_4 : \text{K}_2\text{HPO}_4 = 1:1$ , as described in [8]. The synthesized solid solutions have homogeneity regions varying from 0 to 1.00 for the phosphates  $\text{Co}_{3-x}\text{Mg}_x(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  and  $\text{Co}_{3-x}\text{Mn}_x(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ; for  $\text{Co}_{3-x}\text{Zn}_x(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  – from 0 to 0.10. Their crystal structure is similar to the individual cobalt(II) phosphate octahydrate, which is a phosphate matrix.

Saturated solid solutions -  $\text{Co}_2\text{Mg}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{Co}_2\text{Mn}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{Co}_{2.9}\text{Zn}_{0.1}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  – were used as the main objects of study. Phosphates of different cationic compositions were studied to determine the effect of the nature of the cation on their thermal behavior:  $\text{Co}_{2.5}\text{Mg}_{0.5}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{Co}_{2.5}\text{Mn}_{0.5}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ . Taking into account the dependence of the results of differential thermal analysis on the methodological execution of the experiment, the studies of all phosphates were carried out under the same conditions, similar to those for  $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ .

Differential thermal analysis (DTA) was performed using a Q-1500 D derivatograph, with changing the heating rate in a dynamic mode from 1.3 to 10.0 deg/min. The products of partial and complete dehydration were obtained at temperatures determined from thermal curves. Their identification and anionic composition were determined using a set of physical and

chemical methods. The methodological implementation of this part of the study is similar to that given in [5].

### 3. Results and discussion

The analysis of the DTA results of a saturated solid solution of the composition  $\text{Co}_2\text{Mg}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  and a phosphate matrix –  $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  – shows that their behavior upon heating is influenced by the nature of the cation (Fig. 1). Removing 8 moles of cation-coordinated water, the energy state of the OH-groups of which is different, is a complex process. The thermal curves describe this process in two main stages. The first of them corresponds to the loss of about 7 mole of  $\text{H}_2\text{O}$ . It is registered by a complex endothermic effect in the range 135–290°C for  $\text{Co}_2\text{Mg}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  and 160–340°C for  $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ . On the thermal curves of  $\text{Co}_2\text{Mg}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , it consists of two practically superimposed endothermic effects with maximum process rates at 210 and 230°C (Fig. 1, b). For  $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , four superimposed endothermic effects with maxima at 195, 230, 255, and 270°C are recorded in this region (Fig. 1, a).

The phosphates formed under these conditions have the composition  $\text{Co}_2\text{Mg}(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ , where  $n$ , according to the mass loss, varies from 7 to 1. Reducing the number of water molecules leads to a decrease in the intensity and blurring of diffraction reflections on X-ray diffraction patterns, which are largely identical.

The second stage of dehydration of  $\text{Co}_2\text{Mg}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  characterizes the removal of the last 1 mole of  $\text{H}_2\text{O}$  and occurs in the range of 290–490°C without visible thermal effects (Fig. 1, b). The dehydration products are almost completely amorphous when heated above 290°C. In their IR spectra in the region of 740–755  $\text{cm}^{-1}$ , there are bands of symmetrical valence vibration ( $\nu_s$ ) of the P–O–P groups, which are a diagnostic sign of the presence of polymeric phosphates. According to the data of quantitative paper chromatography, they are formed up to 7.2 rel. % of the total phosphorus content (in terms of  $\text{P}_2\text{O}_5$ ) –  $\text{P}_2\text{O}_{5\text{gen}}$ . The maximum amount of diphosphate was determined in the products of heating the crystalline hydrate to 490°C. Phosphates obtained under these conditions have the most complex anionic composition; in addition to diphosphates, triphosphates are also found (up to 1.6 rel. %  $\text{P}_2\text{O}_{5\text{gen}}$ ). The total amount of condensed phosphate reaches a maximum when the last amounts of water are removed, after which amorphous anhydrous phosphate crystallizes.

The crystallization of the amorphous phase is recorded by the exothermic effect on the ther-

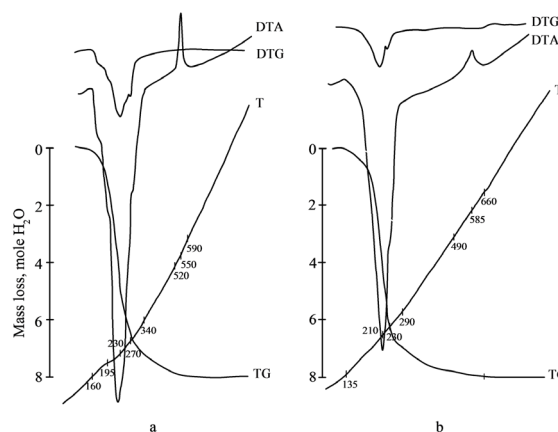


Fig. 1. The results of differential thermal analysis of  $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  (a) and  $\text{Co}_2\text{Mg}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  (b). Heating rate 5.0 degrees/min, weight – 0.3 g, platinum crucibles with lids

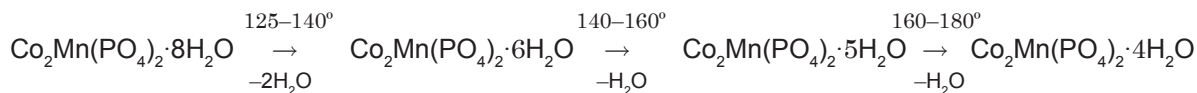
mal curves of  $\text{Co}_2\text{Mg}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  in the range 490–660°C with a process maximum at 585°C (Fig. 1, b). The anionic composition of the thermolysis products is simplified. Fully dehydrated phosphate, identified as  $\text{Co}_2\text{Mg}(\text{PO}_4)_2$ , is stable when further heated to 900°C.

The change in the cationic composition of  $\text{Co}_{3-x}\text{Mg}_x(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  within the established homogeneity region ( $0 < x \leq 1.00$ ) determines certain features in the thermal behavior of phosphates: an increase in the magnesium content leads to a decrease by 10–15 degrees in the temperature ranges of formation and stability of intermediate products and anhydrous phosphates.

The thermal behavior of a solid solution of the composition  $\text{Co}_{3-x}\text{Mn}_x(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  was studied at a heating rate of 1.3 deg/min. The choice of the thermography mode is due to the fact that in the case of dehydration of  $\text{Co}_2\text{Mg}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  at a heating rate of 5.0 deg/min, a total endothermic effect is recorded on the thermal curves, containing several superimposed endothermic effects. According to [1, 2], a decrease in the heating rate of crystal hydrates leads to a partial or even complete separation of the complex thermal effects.

The results of the DTA of  $\text{Co}_2\text{Mn}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  indicate that all thermal effects on the thermal curves become clearer, but the complete separation of endothermic effects under these conditions does not yet occur (Fig. 2). The general behavior of  $\text{Co}_2\text{Mn}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  during heating has much in common with a solid solution of cobalt(II)-magnesium phosphates. The differences caused by the influence of the nature of the cation are associated with the quantitative composition, formation temperatures, and thermal stability of its partial and complete dehydration products.

Scheme 1.



When analyzing the results of a comprehensive study of the heating products of  $\text{Co}_2\text{Mn}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , obtained at temperatures corresponding to the thermal effects on the thermal curves, a sequence of processes was established. Thus, the first stage of dehydration of  $\text{Co}_2\text{Mn}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , which ends at  $180^\circ\text{C}$  and corresponds to the removal of 4 mole of water, can be described by the following transformations (Scheme 1).

Further heating of  $\text{Co}_2\text{Mn}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  to  $245^\circ\text{C}$  is accompanied by the removal of about 2 mole of  $\text{H}_2\text{O}$ , which leads to the rearrangement and destruction of its crystal structure. Phosphates obtained in the range of  $245-545^\circ\text{C}$  undergo amorphization and condensation of the phosphate anion. Amorphous phosphates at  $245^\circ\text{C}$  contain up to 2.5 rel. %  $\text{P}_2\text{O}_{5\text{gen}}$  in the form of diphosphate. At  $545^\circ\text{C}$ , the degree of polycondensation increases, not only diphosphates (5.4 rel. %  $\text{P}_2\text{O}_{5\text{gen}}$ ), but also triphosphates (up to 1.7 rel. %  $\text{P}_2\text{O}_{5\text{gen}}$ ) are recorded.

The anionic composition of the  $\text{Co}_2\text{Mn}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  heating products is simplified at temperatures corresponding to the onset of solid phase crystallization. This process on the DTA curve corresponds to an exothermic effect in the range of  $545-595^\circ\text{C}$ , which is recorded after the final removal of water at  $545^\circ\text{C}$  (Fig. 2). The resulting crystalline phosphate was identified as a solid solution of the composition  $\text{Co}_2\text{Mn}(\text{PO}_4)_2$ . Its crystalline structure does not change during further heating to  $900^\circ\text{C}$  (Fig. 3).

An increase in the heating rate of  $\text{Co}_2\text{Mn}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  from 1.3 deg/min to 10.0 deg/min leads to a shift in the temperatures of the dehydration and crystallization processes of anhydrous  $\text{Co}_2\text{Mn}(\text{PO}_4)_2$  towards higher temperatures. In the general scheme of the behavior of  $\text{Co}_2\text{Mn}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  at elevated temperatures (except for the quantitative characterization of condensation processes), the accompanying solid-phase transformations, and the qualitative composition of partially and completely anhydrous phosphate do not depend on the heating rate.

The results of studying the thermal behavior of phosphates in the  $\text{Co}_{3-x}\text{Zn}_x(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  ( $0 < x \leq 0.10$ ) solid solution correlate well with the data obtained by IR spectroscopy, which is recognized as the most informative for the case of changes in the state of water in crystalline hydrates.

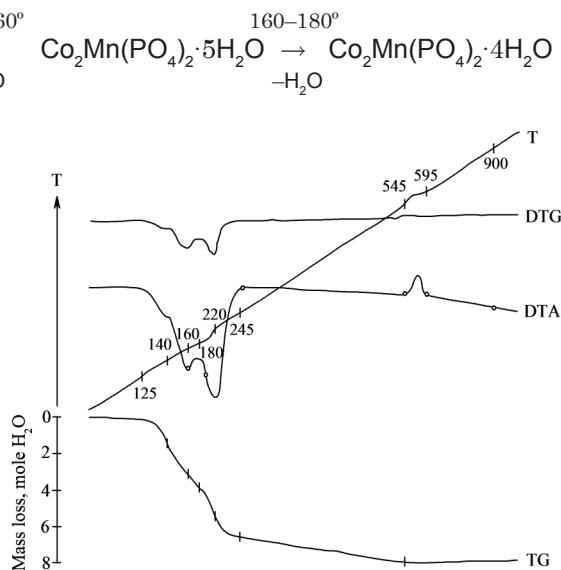


Fig. 2. The results of differential thermal analysis of  $\text{Co}_2\text{Mn}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  —o— place of sampling for analysis.

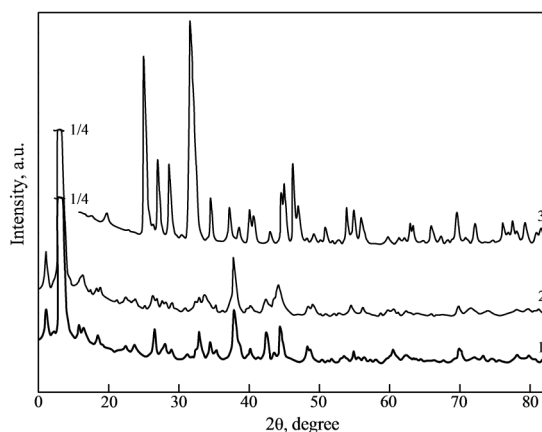


Fig. 3. X-ray diffraction patterns of  $\text{Co}_2\text{Mn}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  (1) and the products of its heating to  $140-180^\circ\text{C}$  (2) and  $595-900^\circ\text{C}$  (3)

For example, the analysis of the IR spectra of phosphate with the maximum zinc content,  $\text{Co}_{2.9}\text{Zn}_{0.1}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , indicates its thermal stability up to  $145^\circ\text{C}$  when heated at a rate of 1.3 deg/min. When the temperature is further increased to  $215^\circ\text{C}$ , the IR spectra show a decrease in the absorption bands of valence vibrations of OH-groups and deformation vibrations of water molecules. Such a change in the spectral curve indicates the removal of water with the formation of crystal hydrates of lower hydration (Table 1).

The removal of most of the water (about 7 mole according to thermal curves), when heating  $\text{Co}_{2.9}\text{Zn}_{0.1}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  to  $290^\circ\text{C}$ , leads to a significant change in the nature of absorption.



Table 1. Wave numbers (cm<sup>-1</sup>) of absorption band maxima in IR spectra of Co<sub>2.9</sub>Zn<sub>0.1</sub>(PO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O and its heat treatment products (heating rate 1.3 deg/min)

20–145°	215°	290°	530°	605–900°	Assignment of absorption bands
3450 s. 3180 s. 3060 m.	3450 m. – 3100 m.wd.	3160 wk.	–	–	v (OH)
1623 m. 1590 sh.	1630 wk. –	1626 wk. –	–	–	δ (H <sub>2</sub> O)
– 1068 wk. 1059 s.sh. 1035 s.	– – – 1030 s.	– – – 1024 s.wd.	– – – 1020 s.wd.	1090 s.sh. – 1050 s. 1010 s.	v <sub>3</sub> (PO <sub>4</sub> )
975 s. 938 s.	– –	– –	– –	960 s. –	v <sub>1</sub> (PO <sub>4</sub> <sup>-</sup> )
853 s.	852 m.sh.	–	–	–	v (P–O) a <sub>60</sub> ρ (H <sub>2</sub> O)
–	–	750 wk.sh.	750 m.	–	v <sub>s</sub> (P–O–P)
– – 582 s. 547 s.	– 625 m.sh. 590 s. 575 s.	– – 580 s. –	670 sh. 630 sh. 590 s. 563 s.	– 637 s. 608 s. 563 s.	v <sub>4</sub> (PO <sub>4</sub> )
– 477 wk.sh. –	– – –	– – –	– – –	515 m. 457 wk. 410 wk.	v <sub>2</sub> (PO <sub>4</sub> )

Notations: s. – strong band, m. – band of medium intensity, wk. – weak, wd. – wide, sh. – shoulder

In addition to the weak absorption bands at 3160 cm<sup>-1</sup> and 1626 cm<sup>-1</sup>, the spectra of the partial dehydration products contain only two broad intense bands with maxima at 1024 and 580 cm<sup>-1</sup>, which belong to the main vibrational frequencies v<sub>3</sub> and v<sub>4</sub> of the PO<sub>4</sub><sup>3-</sup> ion (Table 1). The diffuse nature of the spectrum is due to the loss of individual characteristics of the original octahydrate due to the restructuring of its structure and the beginning of the formation of amorphous phosphates.

The amorphization processes are deepened during the heat treatment of Co<sub>2.9</sub>Zn<sub>0.1</sub>(PO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O in the range of 290–530°C. At the same time, the IR spectra show the processes of anionic condensation of the phosphate anion. The formation of polymeric phosphates is evidenced by the absorption with a maximum of 750 cm<sup>-1</sup>, which, according to [9], refer to the symmetrical valence vibration (v<sub>s</sub>) of the P–O–P groups of the diphosphate anion. According to the results of quantitative paper chromatography, diphosphates (up to 5.5 rel. % P<sub>2</sub>O<sub>5 gen.</sub>) and triphosphates (up to 1.6 rel. % P<sub>2</sub>O<sub>5 gen.</sub>) are present in the composition of polymeric phosphates at 530°C.

The crystallization of amorphous dehydration products of Co<sub>2.9</sub>Zn<sub>0.1</sub>(PO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O begins when heated above 530°C and is completed at

605°C. This causes a decrease in the symmetry of the PO<sub>4</sub> tetrahedron, which leads to the splitting of the triply degenerate vibrations v<sub>3</sub>, v<sub>4</sub> in the IR spectra and the appearance of two groups of absorption bands: 1090, 1050, 1010 cm<sup>-1</sup> and 637, 608, 563 cm<sup>-1</sup> (Table 1). The infrared spectrum also shows the usually inactive absorption band v<sub>1</sub> with a frequency of 960 cm<sup>-1</sup> and the bands 457 and 410 cm<sup>-1</sup>, which, according to [9], belong to the doubly split degenerate frequency v<sub>2</sub> of the PO<sub>4</sub> tetrahedron. This assignment allows us to predict a decrease in the symmetry of the original tetrahedra to C<sub>2v</sub> or even lower. The distortion of PO<sub>4</sub> tetrahedra and, accordingly, the decrease in their symmetry in crystalline anhydrous phosphate, identified as Co<sub>2.9</sub>Zn<sub>0.1</sub>(PO<sub>4</sub>)<sub>2</sub>, may be due to the strong deformability of cobalt(II).

Solid-phase transformations, qualitative composition of phosphates, characteristic of the behavior of Co<sub>2.9</sub>Zn<sub>0.1</sub>(PO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O at elevated temperatures, quite correctly describe the behavior of phosphates when heating a solid solution of Co<sub>3-x</sub>Zn<sub>x</sub>(PO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O (0 < x ≤ 0.10) with different cationic composition.

To evaluate the influence of the nature of the cation on the behavior of solid solutions of hydrated phosphates of the general formula Co<sub>3-x</sub>M<sub>x</sub><sup>II</sup>(PO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O (Mg, Mn, Zn) at elevated

Table 2. Comparative characteristics of the behavior of  $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  and solid solutions based on it at elevated temperatures (5.0 deg/min, platinum sample holders with a lid)

Characteristic process and heat treatment products	Phosphates			
	$\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	$\text{Co}_2\text{Mg}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	$\text{Co}_2\text{Mn}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	$\text{Co}_{2.9}\text{Zn}_{0.1}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$
Beginning dehydration, °C	160	135	155 125 at 1.3	150 at 1.3
Removal of 7 mole of $\text{H}_2\text{O}$ (formation of phosphates of lower hydration), °C	160–340	135–290	155–310	150–305
Amorphization of heat treatment products, °C	340–520	290–490	310–555	305–535
Beginning of anionic condensation, °C	340	290	310	305
The most complex anionic composition, °C	520	490	555	535
The content of condensed phosphates, rel. % $\text{P}_2\text{O}_{5 \text{ gen.}}$ :				
- diphosphate	8.0	7.2	9.6	7.7
- triphosphate	6.7	5.6	7.4	5.9
	1.3	1.6	2.2	1.8
Complete dehydration, °C	520	490	555	535
Simplification of the anionic composition, °C	520–590	490–660	555–630	535–610
Crystallization of anhydrous phosphate, °C	520–590	490–660	555–630	535–610
Thermal stability of anhydrous phosphate, °C	590–900	660–900	630–900	610–900

temperatures, Table 2 summarizes the characteristics of the process and products of their heat treatment.

The cumulative analysis of the data shows that, depending on the cationic composition of the solid solution, the thermal stability of octahydrates and the temperature intervals of all stages of their dehydration process change. The most sensitive to the cationic composition was the depth of implementation of anionic condensation processes, which, judging by the amount of condensed phosphates, is more complete in the products of heat treatment of manganese-containing salts. This conclusion correlates with the state of water molecules: the value of the H-bonding energy of the OH-groups of water molecules in the structure of phosphates in the  $\text{Co}_{3-x}\text{Mn}_x(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  solid solution is higher than in the  $\text{Co}_{3-x}\text{Zn}_x(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  and  $\text{Co}_{3-x}\text{Mg}_x(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  structures.

#### 4. Conclusions

It was established that the behavior of solid solutions of hydrated phosphates of the composition  $\text{Co}_{3-x}\text{M}_x^{II}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  ( $\text{M}^{II} = \text{Mg}, \text{Mn}, \text{Zn}$ ) at elevated temperatures is associated with the removal of crystal hydrate water from their structure and accompanying complex structural and solid-phase transformations.

At the first stage of dehydration of  $\text{Co}_{3-x}\text{M}_x^{II}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  ( $\text{M}^{II} = \text{Mg}, \text{Mn}, \text{Zn}$ ), phosphates of lower hydration of the composition  $\text{Co}_{3-x}\text{M}_x^{II}(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ , where  $1.0 \leq n \leq 7.0$  occur. Removal of the next 1 mole of water leads to the restructuring and destruction of their crystal structure. Phosphates undergo amorphization and condensation of the phosphate anion. The content of condensed phosphates of 2-3 degrees of polycondensation is 7.2–9.6 rel. %  $\text{P}_2\text{O}_{5 \text{ gen.}}$  (depending on the cationic composition of the solid solution).

The anionic composition of the heating products of  $\text{Co}_{3-x}\text{M}_x^{II}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  ( $\text{M}^{II} = \text{Mg}, \text{Mn}, \text{Zn}$ ) is simplified at temperatures corresponding to the onset of solid phase crystallization, which begins after the final removal of water. The anhydrous crystalline phosphate, identified as  $\text{Co}_{3-x}\text{M}_x^{II}(\text{PO}_4)_2$  ( $\text{M}^{II} = \text{Mg}, \text{Mn}, \text{Zn}$ ), is thermally stable when heated to 900°C.

The influence of the nature of the cation in the composition of  $\text{Co}_{3-x}\text{M}_x^{II}(\text{PO}_4)_2$  ( $\text{M}^{II} = \text{Mg}, \text{Mn}, \text{Zn}$ ) solid solutions is manifested in changes in the thermal stability of octahydrates and the temperature intervals of all stages of the dehydration process. The most sensitive to the cationic composition was the depth of implementation of anionic condensation processes, which, judging by the amount of condensed phosphates, is more complete in the products of heat treatment of manganese-containing phosphates –  $\text{Co}_{3-x}\text{Mn}_x(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ .

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