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Thermal properties of Zn and Co(II) dihydrogenphosphate solid solution

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The thermal properties of the solid solution $Zn_{1-x}Co_x(H_2PO_4)_2 \cdot 2H_2O$ ($0 < x < 1.00$) were investigated. It was found that the thermal stability of the dihydrogenphosphates correlates with the cationic composition and increases with increasing cobalt(II) content. The composition-dependent temperature range of formation and thermal stability of the products of partial and complete dehydration were determined. It was established that the final product of dehydration is a cyclotetraphosphate solid solution of composition $(Zn_{1-x}Co_x)_2P_4O_{12}$, $0 < x < 1.00$ (monoclinic, space group $C2/c$, $Z = 4$), which remains stable when heated to 900°C. A sequence of solid-phase transformations taking place during the heat treatment is proposed.

Phosphates / Solid solutions / Thermal properties

Introduction

Solid solutions of hydrated phosphates of divalent metals, including zinc and cobalt(II), and products of their partial and complete dehydration, are widely used as the basis for various modern inorganic materials: active catalysts for organic synthesis, pigments, decorative coatings, corrosion inhibitors, luminescent materials, phosphate glasses, *etc*. [1,2].

One of the most efficient methods for producing anhydrous solid solutions is the heat treatment of their crystalline hydrates. To control the process and design of new materials with a predefined set of improved performances requires knowledge about the thermal properties of the hydrated salts, and the composition and thermal stability of the products of their partial and complete dehydration.

The $Zn(H_2PO_4)_2 \cdot 2H_2O$ and $Co(H_2PO_4)_2 \cdot 2H_2O$ compounds are the limiting compositions of the solid solution $Zn_{1-x}Co_x(H_2PO_4)_2 \cdot 2H_2O$ ($0 < x < 1.00$). The sequence of thermal transformations and the structures and properties of the intermediate and final products have been established [3,4]. The compounds are isostructural, but the chemical reactions occurring during dehydration and the quantitative aspect of the individual stages are different. Removal of the two crystallization water molecules from $Co(H_2PO_4)_2 \cdot 2H_2O$ follows a molecular mechanism yielding $Co(H_2PO_4)_2$, whereas the process of $Zn(H_2PO_4)_2 \cdot 2H_2O$ thermolysis is more complicated. It comprises partial dissociation of crystallization water and formation of free phosphoric acid. $Zn(H_2PO_4)_2$ as an individual phase is not formed.

Information on systematic studies of the thermal behavior of mixed zinc and cobalt(II) dihydrogenphosphates, to a large extent dependent on the nature of the cation, is not available in the literature.

The purpose of the present work was to study the thermal properties of the solid solution of zinc and cobalt(II) dihydrogenphosphates with the general formula $Zn_{1-x}Co_x(H_2PO_4)_2 \cdot 2H_2O$ ($0 < x < 1.00$), to determine the composition, temperature range of formation and thermal stability of the products of thermal treatment, with quantitative assessment of the influence of the nature of the cation.

Experimental

As main objects of the studies dihydrogenphosphates of composition $Zn_{0.75}Co_{0.25}(H_2PO_4)_2 \cdot 2H_2O$, $Zn_{0.5}Co_{0.5}(H_2PO_4)_2 \cdot 2H_2O$ and $Zn_{0.25}Co_{0.75}(H_2PO_4)_2 \cdot 2H_2O$ were chosen. They had been prepared by reacting phosphoric acid (reagent grade, 64.13 wt.% P_2O_5; 180-200% of the stoichiometric amount) with a mechanical mixture of zinc and cobalt(II) hydroxocarbonates (reagent grade, 77.25 wt.% ZnO, 68.32 wt.% CoO, respectively) at 25°C; the molar Zn/Co ratios in the mixture were 3.2, 1.1, and 0.30, respectively. The resulting crystalline precipitate was isolated, washed with an organic solvent (acetone) and dried in air until a constant weight was reached, as described in [5,6]. The single-phase character of the solid solution $Zn_{1-x}Co_x(H_2PO_4)_2 \cdot 2H_2O$ was established through a set of physical and chemical methods of analysis: X-ray diffraction, IR- spectroscopy, crystal-optical studies.

The thermal properties were studied in the temperature range 25-900°C in dynamic (derivatograph Q-1500D, platinum crucible with a lid, reference freshly burnt Al_2O_3, sample weight 300 mg, heating rate 2.5 deg/min, temperature uncertainty ±5°C) and quasi-isothermal (labyrinth crucible, heating rate 3.0 deg/min) heating modes. The products of the heat treatment were obtained as described in [7] after having reached the temperatures corresponding to thermal effects on the DTA curve and were identified using X-ray diffraction (DRON-4M diffractometer, Fe *K*α radiation, internal standard NaCl) and infrared spectroscopy (spectrometer Nexus-470, range 400-4000 cm^{-1}, at 20°C and 190°C). The anionic composition of the dehydration products was determined by means of quantitative paper chromatography. The products were also analyzed for free phosphoric acid.

Results and discussion

Phase analysis of the synthesized samples showed that the homogeneity range of the solid solution $Zn_{1-x}Co_x(H_2PO_4)_2 \cdot 2H_2O$ is $0 < x < 1.00$. The concentration dependence of the unit cell parameters of the dihydrogenphosphates (including $Zn(H_2PO_4)_2 \cdot 2H_2O$ and $Co(H_2PO_4)_2 \cdot 2H_2O$) is in accordance with Vegard's law, clearly confirming their identity and chemical composition. The dihydrogenphosphates of the solid solution crystallize in the monoclinic system, space group $P2_1/n$, $Z = 2$. Isomorphic substitution of the cations in the structure of $Zn_{1-x}Co_x(H_2PO_4)_2 \cdot 2H_2O$ was further confirmed by the crystal-optical and IR spectroscopic characteristics, which are similar to those reported in [5].

According to the results of the differential thermal analysis, the behavior of the dihydrogenphosphate solid solution $Zn_{1-x}Co_x(H_2PO_4)_2 \cdot 2H_2O$ $(0 < x < 1.00)$ during heating depends on the cationic composition (Fig. 1). First of all, this concerns the thermal stability of the initial dihydrates and the products of their partial dehydration. When heated to 80°C at a rate of 2.5 deg/min, the composition and properties of $Zn_{0.5}Co_{0.5}(H_2PO_4)_2 \cdot 2H_2O$, for example, remain unchanged. The corresponding conditions are 75 and 85°C for the dihydrogenphosphates $Zn_{0.75}Co_{0.25}(H_2PO_4)_2 \cdot 2H_2O$ and $Zn_{0.25}Co_{0.75}(H_2PO_4)_2 \cdot 2H_2O$, respectively (Table 1). With further increase in temperature dehydration begins and proceeds in three principal steps. The separation of the thermal effects on the curves of DTA and DTG, and the TG-gradation curves (especially at the first stage of dehydration) varies according to the composition of the solid solution.

The character of the thermal curves for the dihydrogenphosphates where the value of *x* is $0 < x < 0.5$ (including $Zn_{0.75}Co_{0.25}(H_2PO_4)_2 \cdot 2H_2O$) is similar to the character of the curves obtained for the parent $Zn(H_2PO_4)_2 \cdot 2H_2O$: the first (75-180°C) and the second (180-230°C) dehydration steps are practically continuous. The process, according to the corresponding TGA curve, consists in the removal of two moles of H_2O, and is described on the DTA curve by a number of endothermic effects superimposed on each other. The same process for $Zn_{0.50}Co_{0.50}(H_2PO_4)_2 \cdot 2H_2O$, with equal amounts of cobalt and zinc atoms ($x = 0.5$; 10.08 wt.% Co), takes place at 80-185°C. It is described by three partially superimposed endothermic effects (peaks at 95, 135 and 150°C), which clearly distinguish the end of the first stage of dehydration and the beginning of the second stage (185-275°C). Further increase of the cobalt content (from 10.08 to 15.14 wt.%; *x* varies in the range $0.5 < x < 1.0$) produces noticeable changes in the character of all the thermal curves. The curves of $Zn_{0.25}Co_{0.75}(H_2PO_4)_2 \cdot 2H_2O$ are in many respects similar to those obtained for $Co(H_2PO_4)_2 \cdot 2H_2O$ [4]. They differ only in the less distinct gradation of the TG curve, and the temperature ranges corresponding to the implementation of the individual stages of the process are shifted by up to 10°C to lower temperatures.

The heat treatment of $Zn_{1-x}Co_x(H_2PO_4)_2 \cdot 2H_2O$ under quasi-isothermal heating conditions (Q-mode), when the partial pressure of water vapor above the sample corresponds to equilibrium, is accompanied by an increase of the thermal stability of the dihydrogenphosphates to 85, 90 and 95°C, respectively, and has an effect on the temperature ranges of the process steps. In most aspects the dehydration is similar to the process described above for the dynamic heat treatment and ends at a temperature of 360-380°C (Fig. 1).

The results of the thermoanalytical studies of the products of partial and complete dehydration of $Zn_{0.5}Co_{0.5}(H_2PO_4)_2 \cdot 2H_2O$ showed that, when it is heated in the range 80-185°C, a heterogeneous mixture of solids (salt component) and a liquid (free H_3PO_4) are formed. Their formation started at 95°C and continued while heating to 185°C (Table 2). The salt component and the free phosphoric acid are present as monophosphate anion in the sample heated to 95 and 110°C. Condensation of the anion in the composition of the salt component begins at 140°C with the formation of 8.2% diphosphate (calculated as P_2O_5). The presence of diphosphate acid in the composition of the free phosphoric acid

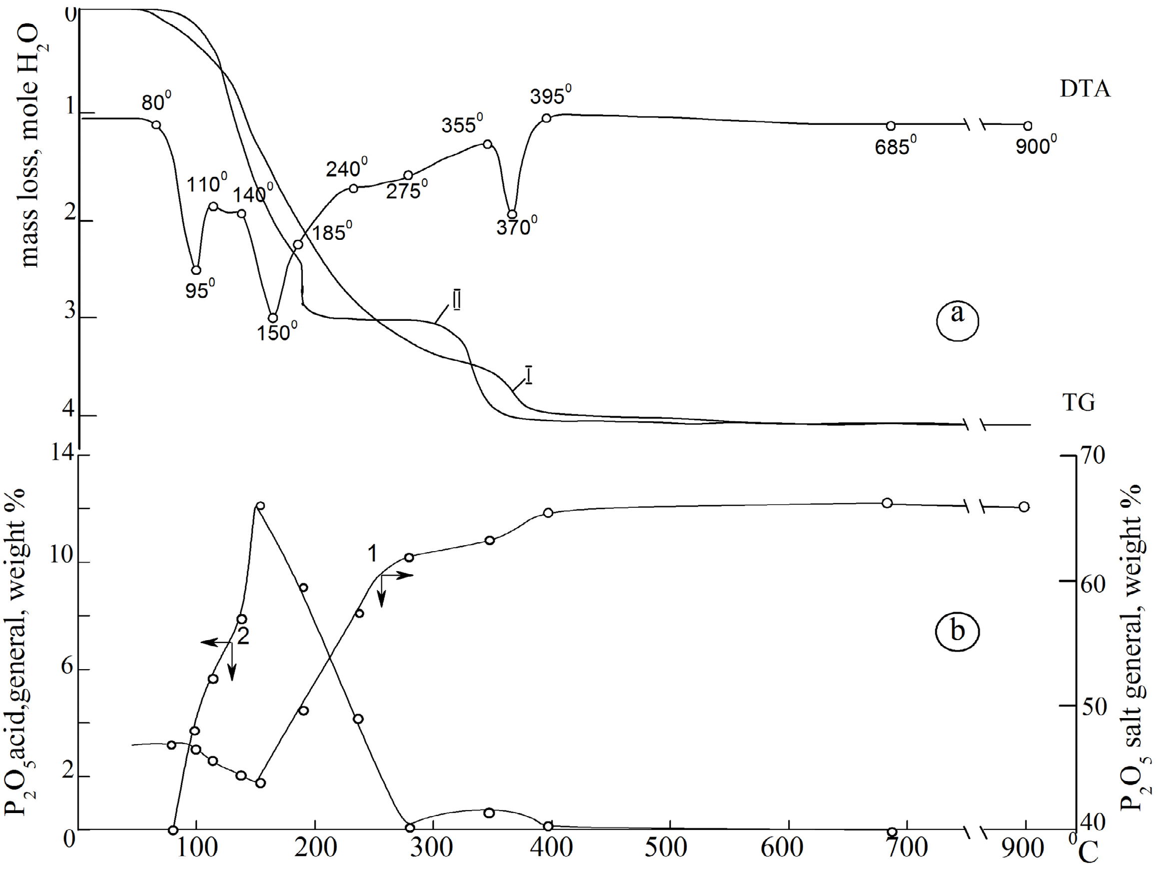

Fig. 1 Thermal properties of $Zn_{0.5}Co_{0.5}(H_2PO_4)_2 \cdot 2H_2O$: (a) curves of thermal analysis in dynamic (I) and quasi-isothermal (II) heating mode; (b) temperature dependence of the total content of salt component (1) and free phosphoric acids (2) in the heat treatment products; circles indicate sampling points for the analysis.

Table 1 Composition dependence of the thermal stability of dihydrogenphosphates $Zn_{1-x}Co_x(H_2PO_4)_2 \cdot 2H_2O$ ($0 < x < 1.00$) and products of their partial dehydration.

Composition of the dihydrogenphosphate	Dehydration temperature, °C		
	First stage	Second stage	Third stage
$Zn_{0.90}Co_{0.10}(H_2PO_4)_2 \cdot 2H_2O$	70	170	255
$Zn_{0.75}Co_{0.25}(H_2PO_4)_2 \cdot 2H_2O$	75	180	260
$Zn_{0.50}Co_{0.50}(H_2PO_4)_2 \cdot 2H_2O$	80	185	275
$Zn_{0.25}Co_{0.75}(H_2PO_4)_2 \cdot 2H_2O$	85	190	285
$Zn_{0.10}Co_{0.90}(H_2PO_4)_2 \cdot 2H_2O$	90	200	290

(0.8% in terms of P_2O_5) was observed at 150°C. The quantities of H_3PO_4 formed during the heat treatment of $Zn_{0.75}Co_{0.25}(H_2PO_4)_2 \cdot 2H_2O$ and $Zn_{0.25}Co_{0.75}(H_2PO_4)_2 \cdot 2H_2O$ differ: the more zinc in the solid solution, the more acid is formed during the heat treatment and below the onset temperature of its allocation.

Anhydrous dihydrogenphosphate of composition $Zn_{0.5}Co_{0.5}(H_2PO_4)_2$, the formation of which is clearly seen on the X-ray diffraction and IR spectra, is the main component of the solid phase at 95-140°C. The diffraction pattern (d = 1.23; 0.76 nm) indicates the presence of a second component, identified as a less protonated phosphate of composition $Zn_{0.5}Co_{0.5}HPO_4 \cdot mH_2O$ (Fig. 2).

During the heat treatment of $Zn_{0.5}Co_{0.5}(H_2PO_4)_2 \cdot 2H_2O$, removal of the constitutional water begins in the range 150-185°C and, as a result, deeper anionic condensation takes place. The degree of conversion of monophosphate anions to polyphosphates, including tri- and tetraphosphates, is 61% at 185°C (Table 2). Such changes in the products of partial dehydration are accompanied by the destruction of the structure and complete amorphization of the solid phase (Fig. 2).

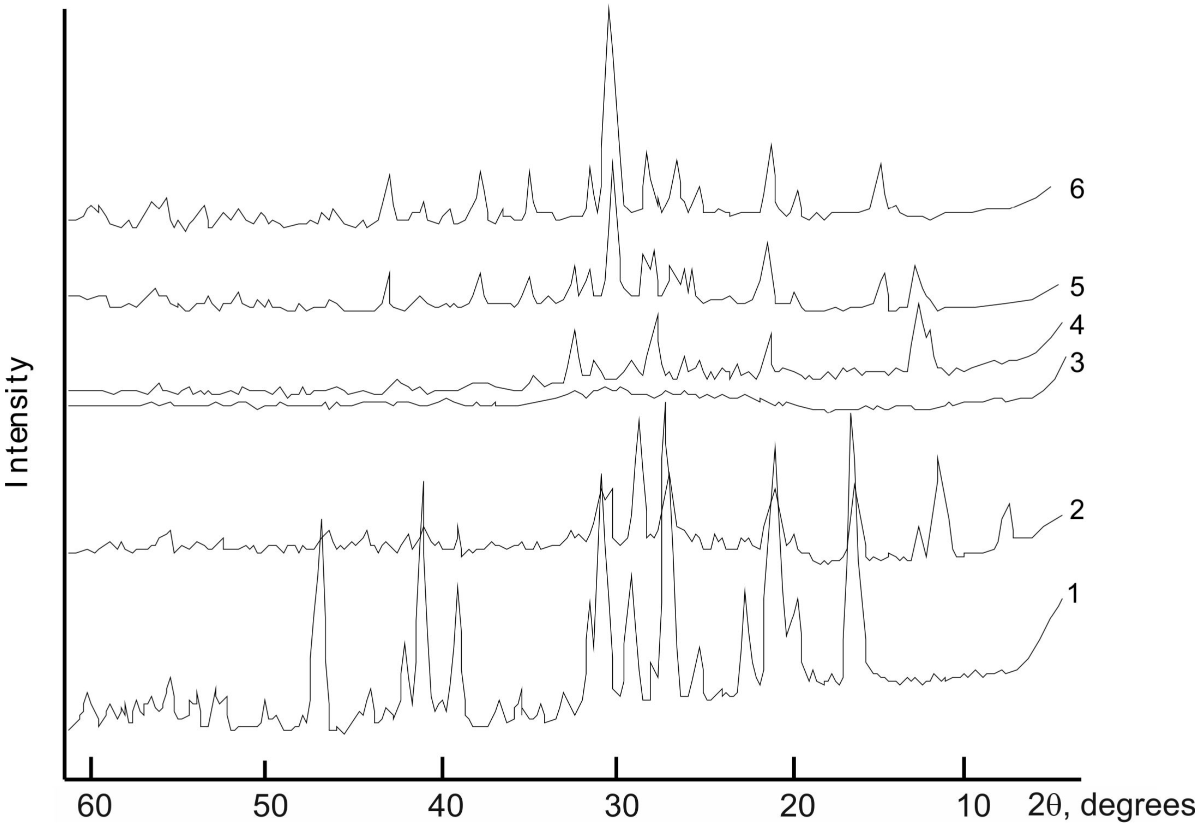

Fig. 2 X-ray diffraction of $Zn_{0.5}Co_{0.5}$ $(H_2PO_4)_2 \cdot 2H_2O$ (1) and its heat treatment product obtained at 95, 110, 140°C (2), 150, 185°C (3), 240, 275°C (4), 355°C (5), 395-900°C (6).

Table 2 Anionic composition of the heat treatment products of $Zn_{0,5}Co_{0,5}(H_2PO_4)_2 \cdot 2H_2O$ (heating rate 2.5 deg/min).

T, °C	Weight loss, mole H_2O	Total P_2O_5, wt.%	Phosphorus content (P_2O_5, wt.%) in the form of									
			mono-	di-	tri-	tetra-	cyclo-tetra-	penta-	hexa-	hepta-	octa-	unse-parated
95	0.16	47.02[a]	47.0									
		3.70	3.7									
110	0.24	45.45	45.4									
		5.60	5.6									
140	0.74	45.00	36.8	8.2								
		8.06	8.1	0.0								
150	1.42	43.70	27.5	16.2								
		12.14	11.3	0.8								
185	2.19	49.52	19.6	22.5	6.1	1.3						
		9.42	7.6	1.8	0.0	0.0						
240	2.81	58.23	9.9	34.5	10.7	2.9	0.0	0.2				
		3.49	1.8	1.4	0.3	0.0	0.0	0.0				
275	2.92	61.94	3.4	36.1	12.3	3.2	0.0	2.6	0.4	0.3	0.6	3.0
		0.10	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
355	3.46	63.30	2.1	21.4	15.3	4.9	19.6					
		0.82	0.5	0.3	0.0	0.0	0.0					
395	3.92	65.84	1.0	0.1	1.6	0.0	63.2					
		0.10	0.1	0.0	0.0	0.0	0.0					
685	4.00	66.29	1.9	1.2	0.8	0.0	62.4					
		0.00	0.0	0.0	0.0	0.0	0.0					

[a] In the enumerator, P_2O_5 in the salt component; in the denominator, P_2O_5 in the free phosphoric acid.

The formation of new crystalline compounds was observed by heating $Zn_{0.5}Co_{0.5}(H_2PO_4)_2 \cdot 2H_2O$ up to 240°C. Heated to this temperature, the sample contains a crystalline phase identified according to [8,9] as the protonated diphosphate $Zn_{0.5}Co_{0.5}H_2P_2O_7$, accompanied by $Zn_{0.5}Co_{0.5}P_2O_7$ (Fig. 2). The content of diphosphates as part of the heat treatment products represents 59.2% of the total P_2O_5 content. The polyphosphates, having a degree of polymerization $n = 3$-5, are X-ray amorphous. The quantity in the composition of the product of the heat treatment at 240°C is 13.8 wt.% and increases to 22.4 wt.% at 275°C. The quantity of diphosphates also increases, and reaches a maximum value of 36.1 wt.% (58.2% of the total P_2O_5 content) at 275°C.

The changes in the composition of the acid component are different. Continuous monophosphate acid condensation leads at 240°C to additional formation of diphosphate and triphosphate acids (0.3 wt.% P_2O_5). The quantitative composition of the released free mono- and polyphosphoric acids also changes. The maximum amount, registered at 150°C, decreases with increasing temperature to 240°C. When the sample is heated to 275°C free phosphoric acids are practically absent, but they reappear at 355°C (Table 2). These, on the one hand, are characterized by their direct involvement (primarily polyphosphoric acids as more active than H_3PO_4) in the formation of highly condensed phosphates, and on the other hand indicate different mechanisms of formation in the heat treatment product of $Zn_{0.5}Co_{0.5}(H_2PO_4)_2 \cdot 2H_2O$. During the first stage of the dehydration, free monophosphate acid is formed by intramolecular hydrolysis of dihydrogenphosphate reacting with crystalline water. During the second stage allocation of free phosphoric acids occurs when constitutional water is removed as a result of the reorganization of the protonated diphosphate anion.

When $Zn_{0.5}Co_{0.5}(H_2PO_4)_2 \cdot 2H_2O$ is heated to 275°C, condensed phosphates of complex anion composition are formed, namely polyphosphates with $n = 2$-8 and more; the degree of conversion of the monophosphate anions reaches 94-95% (Fig. 1, Table 2). The composition of the heat treatment products is simplified when the second constitutional water molecule is removed. Polyphosphates with $n = 5$-8 are absent at 355°C, and the content of diphosphate is decreased to 21.4 wt.% P_2O_5. Condensed phosphates with a cyclic anion with $n = 4$, cyclotetraphosphates (19.6 wt.% P_2O_5), are formed. Their presence was detected by XRD and IR spectroscopic analyzes, according to which the products (phosphates) obtained at 355°C represent a mixture of two crystalline phases: $Zn_{0.5}C_{0.5}H_2P_2O_7$ and the cyclotetraphosphate of composition $ZnCoP_4O_{12}$ (Fig. 2).

Heating of $Zn_{0.5}Co_{0.5}(H_2PO_4)_2 \cdot 2H_2O$ in the range 355-395°C is described by a deep endothermic minimum on the DTA curve (maximum process rate at 370°C), which corresponds to the abrupt removal of 0.46 mole H_2O. This process is accompanied by substantial restructuring and physico-chemical interactions that result in the formation of a single crystalline phase of the final product of the dehydration – the cyclotetraphosphate $ZnCoP_4O_{12}$. Formation of crystals was confirmed by a number of intense X-ray diffraction reflections (d_{exp} 0.615, 0.423, 0.299 nm). Identification of $ZnCoP_4O_{12}$ was made on the basis of the data known for $Zn_2P_4O_{12}$ and $Co_2P_4O_{12}$ [4,9,10], and indicates isotypism and crystallization of the cyclotetraphosphate in the monoclinic system (space group $C2/c$, $Z = 4$). The resulting cyclotetraphosphate remains stable when heated up to 900°C.

Having determined the sequence of the physico-chemical and structural transformations observed for $Zn_{0.5}Co_{0.5}(H_2PO_4)_2 \cdot 2H_2O$, the composition of the heat treatment products, modes of formation and thermal stability, there is enough information to properly describe the thermal behavior of the dihydrogenphosphate solid solution $Zn_{1-x}Co_x(H_2PO_4)_2 \cdot 2H_2O$ $(0 < x < 1.00)$ with different contents of zinc and cobalt(II). The nature of the cation has an influence both on the separate temperature intervals of the steps observed during the heat treatment, and on the dewatering process as a whole. For dihydrogenphosphates with high cobalt content, the intervals are moved to 10-20 degrees higher temperatures. The nature of the cation also influences the quantitative composition of the heat treatment product: with increasing zinc content in the dihydrogenphosphate the proportion of free phosphoric acids during the formation of the final heat treatment product increases. The final product, regardless of the composition of the dihydrogen solid solution $Zn_{1-x}Co_x(H_2PO_4)_2 \cdot 2H_2O$, is a solid solution of cyclotetraphosphates of general formula $(Zn_{1-x}Co_x)_2P_4O_{12}$ $(0 < x < 1.00)$.

Conclusions

The results of thermoanalytical studies and investigation of the physico-chemical solid-phase transformations accompanying the heat treatment of dihydrogenphosphates of the solid solution $Zn_{1-x}Co_x(H_2PO_4)_2 \cdot 2H_2O$ $(0 < x < 1.00)$, indicate that a solid solution of cyclotetraphosphates of composition $(Zn_{1-x}Co_x)_2P_4O_{12}$ $(0 < x < 1.00)$ is obtained simultaneously *via* two parallel routes. According to the first of these, up to 67-70% $(Zn_{1-x}Co_x)_2P_4O_{12}$ is formed by dehydration of protonated condensed phosphates with linear structure of the anion. The second way involves the formation of up to 33-30% cyclotetraphosphates as a result of the interaction of intermediately released free polyphosphoric acid and polyphosphates medium. The quantitative ratio of these two ways of formation of $(Zn_{1-x}Co_x)_2P_4O_{12}$ largely depends on the nature of the cation, namely, for high cobalt content in the solid solution the first way is favored, for high zinc content the second one.

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