

Peculiarities of thermal solid-phase transformations of hydrogenphosphates Co(II)–Mn(II)

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Peculiarities of thermal solid-phase transformations of $\text{Co}_{1-x}\text{Mn}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ ($0 < x \leq 0.45$), which accompanying the formation of a final product of thermolysis — anhydrous diphosphate solid solution with composition $\beta\text{-(Co}_{1-x}\text{Mn}_x)_2\text{P}_2\text{O}_7$ ($0 < x \leq 0.45$) are established. It is shown that low-temperature α -modification of the diphosphate is the first formed during heat treatment of the hydrogenphosphates $\text{Co}_{1-x}\text{Mn}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ with $0 < x \leq 0.15$. Crystalline $\beta\text{-(Co}_{1-x}\text{Mn}_x)_2\text{P}_2\text{O}_7$ ($x \leq 0.15$) is formed only after the polymorphic transformation of the α -form into the β -form. The formation of $\beta\text{-(Co}_{1-x}\text{Mn}_x)_2\text{P}_2\text{O}_7$ with $0.15 < x \leq 0.45$ occurs bypassing the α -form. Free phosphoric acid during the heat treatment $\text{Co}_{1-x}\text{Mn}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ ($0 < x \leq 0.45$) are is not formed.

Keywords: hydrogenphosphates, solid solution, solid-phase transformations, dehydration.

Определены особенности термических твердофазных превращений $\text{Co}_{1-x}\text{Mn}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ ($0 < x \leq 0.45$), сопровождающие образование конечного продукта термолиза — твердого раствора безводных дифосфатов состава $\beta\text{-(Co}_{1-x}\text{Mn}_x)_2\text{P}_2\text{O}_7$ ($0 < x \leq 0.45$). Показано, что при термообработке гидрофосфатов с $0 < x \leq 0.15$ вначале образуется низкотемпературная α -модификация дифосфата. Кристаллические $\beta\text{-(Co}_{1-x}\text{Mn}_x)_2\text{P}_2\text{O}_7$ ($x \leq 0.15$) образуются лишь после полиморфного превращения α -формы в β -форму. Образование $\beta\text{-(Co}_{1-x}\text{Mn}_x)_2\text{P}_2\text{O}_7$ с $0.15 < x \leq 0.45$ происходит минуя α -форму. Свободные фосфорные кислоты при термообработке $\text{Co}_{1-x}\text{Mn}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ ($0 < x \leq 0.45$) не образуются.

Особливості термічних твердофазних перетворень гідрогенфосфатів Co(II)–Mn(II).
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Визначено особливості термічних твердофазних перетворень $\text{Co}_{1-x}\text{Mn}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ ($0 < x \leq 0.45$), що супроводжують утворення кінцевого продукту термолізу — твердого розчину безводних дифосфатів складу $\beta\text{-(Co}_{1-x}\text{Mn}_x)_2\text{P}_2\text{O}_7$ ($0 < x \leq 0.45$). Показано, що під час термообробки $\text{Co}_{1-x}\text{Mn}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ $0 < x \leq 0.15$ спочатку утворюється низькотемпературна α -модифікація дифосфату. Кристалічні $\beta\text{-(Co}_{1-x}\text{Mn}_x)_2\text{P}_2\text{O}_7$ ($x \leq 0.15$) утворюються лише після поліморфного перетворення α -форми на β -форму. Утворення $\beta\text{-(Co}_{1-x}\text{Mn}_x)_2\text{P}_2\text{O}_7$ з $0.15 < x \leq 0.45$ відбувається минуючи α -форму. Вільні фосфатні кислоти під час термообробки $\text{Co}_{1-x}\text{Mn}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ ($0 < x \leq 0.45$) не утворюються.

1. Introduction

Thermal treatment of crystalline hydrates is one of the most technologically advanced methods for preparing anhydrous salts and modern functional materials made of them [1–3]. To select the optimal conditions for obtaining products of partial and full dehydration of a given composition and controlled properties one needs to know the peculiarities of thermal transformations consistency accompanying their formation.

We have obtained such data regarding the solid solution of hydrogenphosphates of composition $Mn_{1-x}Co_xHPO_4 \cdot 3H_2O$ ($0 < x \leq 0.2$) with the structure of $MnHPO_4 \cdot 3H_2O$ [4]. It is shown that processes of anion condensation and release of free phosphoric acid in the products of partial dehydration accompany its heat treatment. Interaction of phosphoric acid with solid-phase intermediate products determines one of the parallel directions of the formation of anhydrous diphosphates.

Thermal dehydration of $CoHPO_4 \cdot 1.5H_2O$, which is a structural analogue of hydrogen phosphate $Co(II)$ – $Mn(II)$ is described [5]. Its heating is accompanied by condensation of the monophosphate anion that produces polymeric phosphates and oxides involved in the formation of the final thermolysis product — diphosphate $Co_2P_2O_7$. However, the methodology of this study do not include the determination of free phosphoric acid in the composition of dehydration products of $CoHPO_4 \cdot 1.5H_2O$ that may make significant changes in chemistry of the formation of anhydrous diphosphate.

Information on the systematic studies of thermolysis of $Co(II)$ – $Mn(II)$ hydrogenphosphates with concretization of composition and properties of its heat treatment products is absent for now in the literature.

The purpose of the present work is to study the thermal behavior of $Co(II)$ – $Mn(II)$ hydrogenphosphates of composition $Co_{1-x}Mn_xHPO_4 \cdot 1.5H_2O$ ($0 < x \leq 0.45$) and to determine the characteristics of solid-phase thermal transformations accompanying their heat treatment, to concretize the influence of cation nature.

2. Experimental

Hydrogenphosphates $Co_{1-x}Mn_xHPO_4 \cdot 1.5H_2O$ ($0 < x \leq 0.45$) were obtained by reacting of cobalt(II) and manganese(II) hydroxocarbonates in the ratio of $1.2 \leq K = Co/Mn$ (molar)

≤ 10.0 with 55 % solution of phosphoric acid at 50°C and pH 2.8, as described in [6].

The main object of the study was hydrogenphosphate with a maximum content of $Mn(II)$ – $Co_{0.55}Mn_{0.45}HPO_4 \cdot 1.5H_2O$, comprising, in wt. %: Co — 18.27, Mn — 13.91, P — 16.95, H_2O — 20.08. To clarify the influence of cation nature there were performed thermal and analytical studies of hydrogenphosphates with different content of cobalt(II) and manganese(II), which varied in the range of 31.29–18.27 wt. % of Co, and 1.05–13.91 wt. % of Mn. Selective analysis was performed to analytically determine free phosphoric acid in the intermediate products of $CoHPO_4 \cdot 1.5H_2O$ heat treatment — composition of the solid solution of $Co_{1-x}Mn_xHPO_4 \cdot 1.5H_2O$ with $x = 0$.

Heat treatment of hydrogenphosphates was performed outside in the range of 25–900°C in the conditions of dynamic (derivatograph Q-1500D, platinum crucibles with lid, standard sample — freshly calcined Al_2O_3 , the sample weighed — 0.300 g, heating rate — 2.5°/min, accuracy of temperature determination $\pm 5^\circ C$) and quasi-isothermal (the sample weighed — 0.100 g, heating rate is 3.0°/min, conical holder of the sample) modes.

The heat treatment products obtained similar to [7], at temperatures corresponding to thermal effects on the DTA curve, were studied by complex analysis methods: chemical, X-ray diffraction (powder diffractometer DRON-4-M, Fe K_α), IR spectroscopy (IR spectrometer Nexus-470, sample (0.05 wt. %) pressed into KBr tablets). In addition, IR spectra were recorded during the heating of hydrogen phosphates. The anionic composition was established by quantitative chromatography on a paper. Determination of free phosphoric acid was performed by quinolone molybdate gravimetric method after the acid extraction with dry acetone, as described in [8].

3. Results and discussion

Differential thermal analysis results showed that $Co_{0.55}Mn_{0.45}HPO_4 \cdot 1.5H_2O$ is stable when heated in air atmosphere at rate of 2.5°/min up to 150°C (Fig. 1). Increasing temperature in the range of 150–510°C is accompanied by the sample weight loss, which goes in two major stages recorded on the thermal gravimetry (TG) curve of two quite distinct stages corresponding to removal of 1.28 and 0.49 moles of H_2O . On the DTA and DTG curves there

Table. Anionic composition of heat treatment products of $\text{Co}_{0.55}\text{Mn}_{0.45}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ (heating rate $2.5^\circ/\text{min}$)

Temperature, $^\circ\text{C}$	Mass loss, mole H_2O	P_2O_5 , gen., wt. %	Phosphate content (P_2O_5 , wt. %) as					
			mono-	di-	tri-	tetra-	penta-	hexa-phosphate
25		39.38	39.4	0,0				
185	0.84	40.88	38.1	2.8	0.0			
200	1.14	44.99	36.9	6.7	1.4	0.0		
230	1.28	45.67	32.8	9.1	2.6	1.2	0.0	
275	1.77	48.07	13.3	28.4	4.1	2.3	0.0	
295	1.85	48.46	5.6	33.7	4.4	2.9	1.9	0.0
470	1.96	49.00	2.3	40.3	3.2	2.1	1.2	0.0
510	1.98	49.10	1.8	43.6	2.0	1.6	0.0	
540	2,00	49.31	2.1*	45.9	1.3*	0.0	0.0	

* Result of diphosphate hydrolysis during sample preparation to analysis.

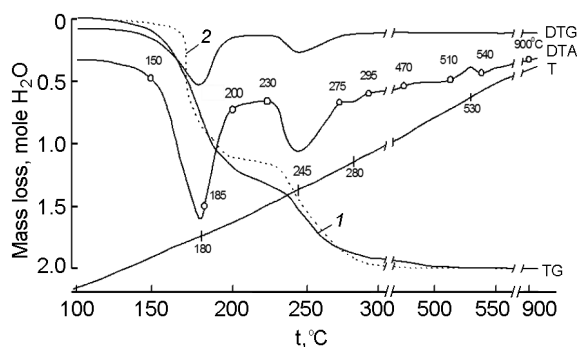


Fig. 1. Curves of thermal analysis of $\text{Co}_{0.55}\text{Mn}_{0.45}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ in dynamic (1) and quasi-isothermal (2) heating regimes, -o- place of sampling for analysis.

are two broad endothermic effects in the ranges of $150\text{--}200$ and $230\text{--}275^\circ\text{C}$. The subsequent removal of 0.21 mole of H_2O occurs in the range of $275\text{--}510^\circ\text{C}$, and it is described by the slight endothermic effect at $275\text{--}295^\circ\text{C}$ and a smooth mass loss curve.

When heated $\text{Co}_{0.55}\text{Mn}_{0.45}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ in the quasi-isothermal mode (partial pressure of water vapor above the sample reaches $0.7\text{--}0.8$ atm.), it's thermal resistance is increased up to 170°C . Dehydration under these conditions is also realized in two stages and finishes almost at 385°C (Fig. 1). On the TG curve, which describes the first stage of dehydration, two sections are distinguished with different patterns of water removal. The first corresponds to the removal of 0.70 mole of H_2O at a substantially constant temperature (170°C); 0.4 mole of the second section are removed in the range of $175\text{--}195^\circ\text{C}$ without tempera-

ture stabilization similarly to dehydration of the crystallohydrate on the second stage ($240\text{--}290^\circ\text{C}$). Such character of the TG curve shows, according to classification of the processes in isothermal conditions [9], the complication of the process of dehydration with polycondensation reactions.

Interpretation of the results of the complex study of heat treatment of the products obtained at each stage of the dehydration shows, that heating of $\text{Co}_{0.55}\text{Mn}_{0.45}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ up to 180°C is followed by removal of 0.76 mole of coordinatively bound water with formation of hydrogenphosphates of lesser degree of hydration of the composition $\text{Co}_{0.55}\text{Mn}_{0.45}\text{HPO}_4 \cdot m\text{H}_2\text{O}$ ($0.74 < m < 1.5$). The condensation processes of monophosphate anion start at 185°C and continue when heating $\text{Co}_{0.55}\text{Mn}_{0.45}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ up to $470\text{--}510^\circ\text{C}$ — the temperature of almost completely dehydrated phosphate formation (Table).

According to the chromatography quantitative analysis results, in composition of the partial dehydration products obtained at 185°C , in addition to monophosphate, diphosphate is also fixed (2.8 wt. % counting with P_2O_5). The composition of the heat treatment products of $\text{Co}_{0.55}\text{Mn}_{0.45}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ at 200°C is a mixture of condensed phosphates with a linear anion structure, in which, besides diphosphate, the number of which increases substantially in 2.5 times, triphosphate is formed, and at 230°C — tetraphosphate (see Table). The conversion of the monophos-

phate anion to polyphosphate at 230°C is 20–23 %.

Formation of the condensed phosphates occurs with destruction of the crystalline structure of the initial crystalhydrate. In the IR spectra the amorphization of the solid phase, obtained by heating of $\text{Co}_{0.55}\text{Mn}_{0.45}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ up to 185–230°C, is fixed with a change in spectral absorption pattern throughout the absorption range. In $\nu(\text{OH})$ area a decrease in the intensity, broadening and smoothing of bands at 3385 and 3180 cm^{-1} are fixed. The spectral curve is wide with low-intensity round of many disordered valence vibrations of OH groups. Absorption in the vibration area of the anion sublattice is of the nature of round spectra of several phases. One of them, considering the presence of bands in the spectrum $\delta(\text{H}_2\text{O})$ 1630 cm^{-1} and $\nu(\text{OH})$, which characterize the molecular vibrations of water as a unit, and 730 cm^{-1} band from HPO_4^{2-} anion in the initial crystalhydrate, is X-ray amorphous $\text{Co}_{0.55}\text{Mn}_{0.45}\text{HPO}_4 \cdot m\text{H}_2\text{O}$. The appearance of two strong bands (at 1080 and 555 cm^{-1}) with outlined shoulders (930, 530 cm^{-1}) and 420 cm^{-1} are characteristic vibration frequency bands of PO_3 and POP groups of $\text{P}_2\text{O}_7^{4-}$ anion, and this indicates that the second component of the heat treatment products is diphosphate.

Disordered state of the solid phase is retained upon the heat treatment of $\text{Co}_{0.55}\text{Mn}_{0.45}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ in the range of 275–295°C, promoting the formation of the condensed phosphates including pentaphosphate (Table). The degree of conversion of the monophosphate anion to polyphosphate reaches 86–88 %, characterizing the deepening of the anion condensation process. The greatest difficulty is anionic composition of the thermal treatment products obtained at 295°C. It is the multiphase mixture of oligo-phosphates with a degree of polycondensation of $n = 2-5$. Their formation in the IR spectra is fixed by a set of bands corresponding, according to [10], to vibrations of the diphosphate and polyphosphate anions: sh. 1145 cm^{-1} — ν_{qs} (PO_3); 1090 cm^{-1} — ν_s (PO_3); 960 cm^{-1} — ν_{as} (POP); 710 cm^{-1} — ν_s (POP); 565, 520, 420 cm^{-1} — δ (PO_3).

Accumulation in the heat treatment products of the X-ray amorphous condensed phosphates, composition and quantity of which vary in the process of dehydration of $\text{Co}_{0.55}\text{Mn}_{0.45}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$, complicates their

crystallization. The transition from the disordered amorphous state to the start of formation of the crystal lattice is recorded with the most intense diffraction reflections (d_{exp} , 0.305, 0.293, 0.258, 0.214, 0.207, 0.183 nm) at X-ray photograph of the samples obtained at 295°C. They include one identified crystalline phase — β - $(\text{Co}_{0.55}\text{Mn}_{0.45})_2\text{P}_2\text{O}_7$ diphosphate, X-ray metric and IR spectroscopic characteristics of which correspond to known for isostructural β -diphosphates of cobalt (II) and manganese (II) [10, 11]. The condensed phosphates with $\bar{n} = 3-5$ are the X-ray amorphous. Their presence becomes indirectly apparent in the overall diffusion of the X-ray diffraction patterns, broadening, and low intensity of the diffraction reflections.

Heating of $\text{Co}_{0.55}\text{Mn}_{0.45}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ up to 470°C — temperature at which the mass loss is mainly finished, does not introduce substantial changes in the material composition of the dehydrated phosphates. Qualitatively it remains constant, but the quantitative relations between the components of the mixture change: amount of the diphosphate increases (up to 40.3 % P_2O_5), and the high molecular condensed phosphate — reduces (Table).

Heat treatment of $\text{Co}_{0.55}\text{Mn}_{0.45}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ in the range of 470–510°C is accompanied by not only a content increase of the mixed diphosphate, but, considering the appearance on the diffraction patterns of the new intense reflections, known for β -diphosphates, by increase of the crystallinity degree as well. When increasing the temperature up to 510–540°C, anionic composition of the heat treatment product is simplified. Value \bar{n} at 510°C does not exceed 4, at 540°C — one crystalline phase is recorded — β - $(\text{Co}_{0.55}\text{Mn}_{0.45})_2\text{P}_2\text{O}_7$. Free phosphoric acid under the heating of $\text{Co}_{0.55}\text{Mn}_{0.45}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ is not allocated. In the composition of the products of thermolysis of $\text{CoHPO}_4 \cdot 1.5\text{H}_2\text{O}$ it is also absent.

Formation of the crystalline structure of β - $(\text{Co}_{0.55}\text{Mn}_{0.45})_2\text{P}_2\text{O}_7$ almost finishes at 540°C. The exothermic effect with a maximum of 530°C is the total effect of crystallization of diphosphate and being began earlier (about 470°C) solid phase reacting of the intermediate products of heat treatment of $\text{Co}_{0.55}\text{Mn}_{0.45}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$, which results in simplification of the anionic composition and diphosphate formation. With further increase in temperature up to 900°C in the IR spectrum of β - $(\text{Mn}_{0.59}\text{Co}_{0.41})_2\text{P}_2\text{O}_7$, the

broadening of absorption bands without changing the nature of the spectrum as a whole improves. The X-ray diffraction shows the intensity increase of diffraction reflections characterizing the crystalline structure improvement and the thermal stability of $\beta\text{-(Co}_{0.55}\text{Mn}_{0.45})_2\text{P}_2\text{O}_7$ in the range of 540–900°C. Formation of α -diphosphate of this composition, similar to $\alpha\text{-Co}_2\text{P}_2\text{O}_7$ as described in [5, 12], was not performed. Low-temperature α -modification of the anhydrous diphosphates is recorded only during the formation of $\beta\text{-(Co}_{1-x}\text{Mn}_x)_2\text{P}_2\text{O}_7$ with the value $x \leq 0.15$.

Thermal analysis studies of hydrogen phosphates $\text{Co}_{1-x}\text{Mn}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ ($0 < x \leq 0.45$) with different content of cobalt (II) and manganese (II), that were carried out to determine the peculiarities of solid state reactions accompanying their thermal treatment, showed, that formation of the crystalline structure of the high-temperature β -form of diphosphates $\beta\text{-(Co}_{1-x}\text{Mn}_x)_2\text{P}_2\text{O}_7$ ($0 < x \leq 0.45$) was determined by the composition of the initial crystallohydrates. During the heat treatment of $\text{Co}_{1-x}\text{Mn}_x\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ with $0 < x \leq 0.15$ (cobalt content — 40.4–34.8 wt. %, manganese — does not exceed 5.2 wt. %) the low-temperature α -modification of the diphosphate is formed at first (at 250–270°C). Crystalline β -diphosphates $\beta\text{-(Co}_{1-x}\text{Mn}_x)_2\text{P}_2\text{O}_7$ with $x \leq 0.15$ fixed on X-ray photograph only after polymorphic converting from α -form to β -form, ongoing at 290–310°C. The formation of $\beta\text{-(Co}_{1-x}\text{Mn}_x)_2\text{P}_2\text{O}_7$ with manganese content of 5.2–22.1 wt. % ($0.15 < x \leq 0.45$) occurs only when bypassing the α -form.

Setting such peculiarities of formation of the anhydrous β -diphosphates of this set became possible by analyzing IR spectra obtained during the heat treatment of $\text{Co}_{0.95}\text{Mn}_{0.05}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ and saturated solid solution — $\text{Co}_{0.55}\text{Mn}_{0.45}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ (Fig. 2). The IR spectrum of $\text{Co}_{0.95}\text{Mn}_{0.05}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ heated up to 200–230°C, in the area of anion sublattice vibrations consists of a structureless diffuse band at 1105 cm^{-1} with a weak shoulder 1065 cm^{-1} , and bands at 580 and 530 cm^{-1} . With increasing the heat treatment temperature up to 250–270°C a clear line with frequency of 535 cm^{-1} , and two broad triplet bands in the intervals of 550–600 and 1060–1200 cm^{-1} are fixed. In terms of the group frequencies, they correspond to ap-

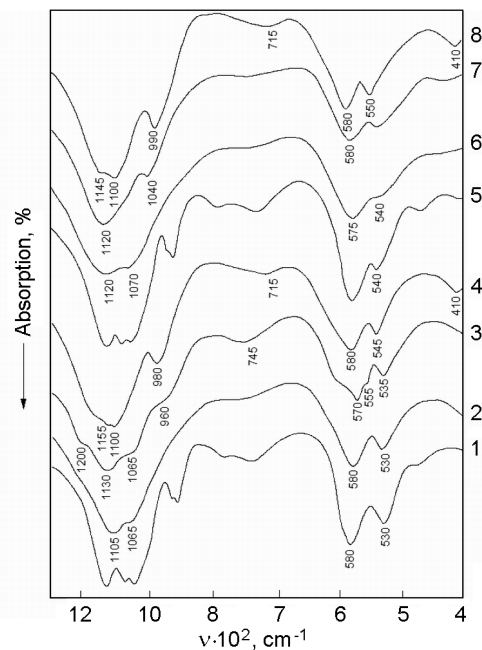


Fig. 2. IR spectrum of $\text{Co}_{0.95}\text{Mn}_{0.05}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ (1) and products of its heat treatment, recorded during the heating up to 200–230 (2), 250–270 (3), 290–340°C (4), and $\text{Co}_{0.55}\text{Mn}_{0.45}\text{HPO}_4 \cdot 1.5\text{H}_2\text{O}$ (5) to 190–225 (6), 240–260 (7), 270–310°C (8).

pearance of deformation and valence vibrations of PO_3 groups of $\text{P}_2\text{O}_7^{4-}$ anion: 535, 555, 595 cm^{-1} — $\delta(\text{PO}_3)$; 1065 cm^{-1} — $\nu_s(\text{PO}_3)$; 1130, 1200 cm^{-1} — $\nu_{as}(\text{PO}_3)$. The band at 745 and shoulder at 960 cm^{-1} — ν_s and ν_{as} groups POP respectively. High frequency and intensity of the band ν_s (POP), according to [13], suggests that the angle P–O–P in the formed diphosphate anion does not exceed 150–160°. Such a spectrum character allows to interpret it as a spectrum of $\alpha\text{-(Co}_{0.95}\text{Mn}_{0.05})_2\text{P}_2\text{O}_7$, which corresponds to known $\alpha\text{-Co}_2\text{P}_2\text{O}_7$ with anion noncentrally symmetric structure and the angle of P–O–P equal to 142.6° [10, 12]. At 290–340°C the spectral pattern is simplified: shoulder at 1155 cm^{-1} relates to the vibration of $\nu_{as}(\text{PO}_3)$; band at 1100 cm^{-1} — $\nu_s(\text{PO}_3)$; 580 cm^{-1} — $\delta(\text{PO}_3)$. It is registered that 535 and 960 cm^{-1} bands shift in the high frequency area of the spectrum up to 545 and 980 cm^{-1} , which, along with decreasing frequency of 745 cm^{-1} (down to 715 cm^{-1}), and significant decrease in its intensity, characterizes an increase in the angle P–O–P of diphosphate anion. The obtained spectral characteristics indicate a near-centrosymmetric configuration of

formed $P_2O_7^{4-}$ anion, known for β -diphosphate [10, 14].

Changes recorded in the IR spectrum of α - and β -forms of $(Co_{0.95}Mn_{0.05})_2P_2O_7$ are observed in the heat treatment products of $Co_{1-x}Mn_xHPO_4 \cdot 1.5H_2O$ with a value of x , which does not exceed 0.15. They are explained with the transition from curved to the straightened configuration of P–O–P bridge of $P_2O_7^{4-}$ anion. But considering the decrease in ν_s (POP) band intensity, the angle P–O–P does not reach 180° (Fig. 2). Described above behavior of the spectrum is preserved under the further heat treatment of the β -diphosphate up to $900^\circ C$, indicating its thermal stability.

With increasing content of manganese(II) in the composition of $Co_{1-x}Mn_xHPO_4 \cdot 1.5H_2O$ to the value of $0.15 < x \leq 0.45$, a sequence of thermal and structural transformations, fixed in the IR spectra, indicates the absence of polymorphic transition from the α -form diphosphate to the β -form. At 210 – $225^\circ C$ and above, the IR spectroscopic pattern of dehydration products of $Co_{0.55}Mn_{0.45}HPO_4 \cdot 1.5H_2O$ clearly shows the gradual formation of the crystalline motif corresponding only to the β -diphosphate variations (Fig. 2). Despite the overall diffuse of the pattern, its characteristic band is performed in the form of shoulders at 1070 and 540 cm^{-1} , resolution of which is increased by heating the crystallohydrate up to 240 – $260^\circ C$. In the IR spectrum, recorded at 270 – $310^\circ C$, a set of absorption bands and their intensity fully correspond to those of β - $(Co_{1-x}Mn_x)_2P_2O_7$ with $x \leq 0.15$, indicating the formation of the β -diphosphates with a similar composition $0.15 < x \leq 0.45$.

Thus, despite the differences in the process of formation of the crystalline structures of the β -diphosphates of various compositions, they actually are solid solutions of diphosphates with a general formula β - $(Co_{1-x}Mn_x)_2P_2O_7$ ($0 < x \leq 0.45$). They crystallize in the monoclinic crystal system (sp. gr. $C2/m$, $Z = 2$). The crystallographic parameters of the β -diphosphates are changing according to their composition and the values of the ion radii of Co(II) 0.088 nm , and Mn(II) 0.097 nm (Fig. 3). They form, including the parameters of β - $Co_2P_2O_7$, a linear concentration dependence characterizing the formation of the single substitutional solid solution.

Temperature intervals of formation of partial or full dehydration products of

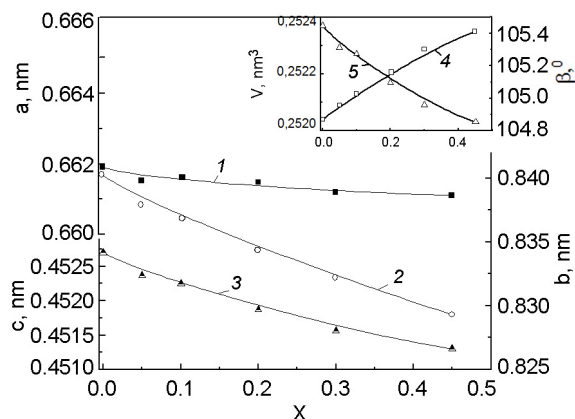


Fig. 3. Concentration dependences of crystallographic parameters of β - $(Co_{1-x}Mn_x)_2P_2O_7$, $0 < x \leq 0.45$.

$Co_{1-x}Mn_xHPO_4 \cdot 1.5H_2O$ ($0 < x \leq 0.45$) are also determined by the cation nature, and under other similar conditions are shifted upward to 25 – $30^\circ C$ if the hydrogenphosphate composition is changed from $x = 0.45$ to $x = 0$.

4. Conclusions

Special peculiarity of the thermal behavior of hydrogenphosphate $Co_{1-x}Mn_xHPO_4 \cdot 1.5H_2O$ ($0 < x \leq 0.45$) is the solid-phase sequence transformations accompanying the formation of the final product of thermolysis — the solid diphosphates anhydrous solution of composition β - $(Co_{1-x}Mn_x)_2P_2O_7$ ($0 < x \leq 0.45$). During the heat treatment of $Co_{1-x}Mn_xHPO_4 \cdot 1.5H_2O$ with $0 < x \leq 0.15$ the low temperature α -modification of diphosphate is formed at first. The crystalline β -diphosphates of composition β - $(Co_{1-x}Mn_x)_2P_2O_7$ ($x \leq 0.15$) are formed only after conversion of the polymorphic α -form to β -form. The formation of β - $(Co_{1-x}Mn_x)_2P_2O_7$ with $0.15 < x \leq 0.45$ occurs bypassing the α -form.

β - $(Co_{1-x}Mn_x)_2P_2O_7$, $0 < x \leq 0.45$ is formed along to two parallel ways. The first of them: up to 70 – 75% of β - $(Co_{1-x}Mn_x)_2P_2O_7$, is formed by rearrangement of the monophosphate anion; the second: 30 – 25% of β - $(Co_{1-x}Mn_x)_2P_2O_7$ is a result of the solid-phase interactions of the intermediate heat treatment products.

The temperature intervals formation and thermal stability of the heat treatment products of $Co_{1-x}Mn_xHPO_4 \cdot 1.5H_2O$ ($0 < x \leq 0.45$) are determined by the cation nature, and under other similar conditions are shifted upward to 25 – $30^\circ C$ if the composition of

the hydrogenphosphate is changed from $x = 0.45$ to $x = 0$. Free phosphoric acid in the heat treatment product isn't formed.

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