

Influence of crystal hydrate water on the process and products of heat treatment of magnesium-manganese(II) dihydrogen phosphates

N.M.Antraptseva, N.V.Solod, O.O.Kravchenko

National University of Life and Environmental Sciences of Ukraine,
15 Geroev Oborony Str., 03041 Kyiv, Ukraine

Received March 19, 2020

It has been established that crystalline water affects the change in the quantitative composition of the products and the characteristics of the process as a whole during the heat treatment of $Mg_{1-x}Mn_x(H_2PO_4)_2 \cdot 4H_2O$ tetrahydrates. The maximum content of free mono- and polyphosphate acids, which are isolated in the composition of the intermediate heat treatment products during the thermolysis of tetrahydrates, is 1.6 times higher than in dihydrates with the same ratio of cations. The degree of conversion of the monophosphate anion to polyphosphate in the heat treatment products of tetrahydrates is 1.1–1.2 times greater than at the similar stages of the thermolysis of $Mg_{1-x}Mn_x(H_2PO_4)_2 \cdot 2H_2O$ dihydrates. The maximum degree of polycondensation is also higher for polyphosphates in the composition of the heat treatment products of tetrahydrates ($\bar{n} = 8$ for $Mg_{0.5}Mn_{0.5}(H_2PO_4)_2 \cdot 4H_2O$, $\bar{n} = 7$ for $Mg_{0.5}Mn_{0.5}(H_2PO_4)_2 \cdot 2H_2O$).

Keywords: dihydrogen phosphates, tetrahydrates, crystalline hydrate water, heat treatment.

Вплив кристалогідратної води на процес і продукти термообробки магнію-мангану(II) дигідрогенфосфатів. *Н.М.Антрапцева, Н.В.Солод, О.О.Кравченко*

Визначено, що під час термообробки тетрагідратів $Mg_{1-x}Mn_x(H_2PO_4)_2 \cdot 4H_2O$ кристалогідратна вода впливає на зміни кількісного складу продуктів і характеристики процесу в цілому. Максимальна кількість вмісту вільних моно- і поліфосфатних кислот, що виділяються у складі проміжних продуктів термообробки, при термолізі тетрагідратів в 1.6 рази більша, ніж у дигідратів з тим же співвідношенням катіонів. Ступінь перетворення монофосфатного аніона на поліфосфатний у продуктах термообробки тетрагідратів в 1.1–1.2 рази більший, ніж на аналогічних стадіях термолізу дигідратів $Mg_{1-x}Mn_x(H_2PO_4)_2 \cdot 2H_2O$. Максимальний ступінь поліконденсації також вищий у поліфосфатів у складі продуктів термообробки тетрагідратів ($\bar{n} = 8$ для $Mg_{0.5}Mn_{0.5}(H_2PO_4)_2 \cdot 4H_2O$, $\bar{n} = 7$ для $Mg_{0.5}Mn_{0.5}(H_2PO_4)_2 \cdot 2H_2O$).

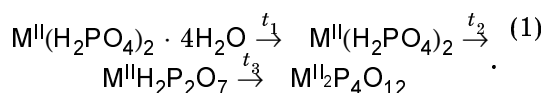
Определено, что при термообработке тетрагидратов $Mg_{1-x}Mn_x(H_2PO_4)_2 \cdot 4H_2O$ кристалогидратная вода влияет на изменение количественного состава продуктов и характеристики процесса в целом. Максимальное количество содержания свободных моно- и полифосфатных кислот, выделяющихся в составе промежуточных продуктов термообработки, при термолізе тетрагидратов в 1.6 раза больше, чем у дигидратов с тем же соотношением катионов. Степень превращения монофосфатного аниона в полифосфатный в продуктах термообработки тетрагидратов в 1.1–1.2 раза больше, чем на аналогичных стадиях термолізу дигидратов $Mg_{1-x}Mn_x(H_2PO_4)_2 \cdot 2H_2O$. Максимальная степень поликонденсации также выше у полифосфатов в составе продуктов термообработки тетрагидратов ($\bar{n} = 8$ for $Mg_{0.5}Mn_{0.5}(H_2PO_4)_2 \cdot 4H_2O$, $\bar{n} = 7$ для $Mg_{0.5}Mn_{0.5}(H_2PO_4)_2 \cdot 2H_2O$).

1. Introduction

Recently, a significant amount of work has been devoted to studying the solid solutions and double phosphates of divalent metals due to their ability to form compounds with technically valuable properties. Not only the conditions of their synthesis are studied, but their applied significance as well, various characteristics and properties, starting from structural features, IR spectroscopic, colorimetric, catalytic and other characteristics [1–5].

Much attention is paid to studying their thermal properties, since it is the dehydration of hydrated phosphates that makes it possible to obtain various functional materials with performance characteristics that can be controlled over a fairly wide range. It has been established, for example, that the thermal properties of hydrated phosphates depend on such basic factors as the structure, nature of the cation, and heat treatment conditions [6–10]. The hydration of the initial crystal hydrate significantly affects the formation of polymer products after heat treatment of phosphoric acid salts [8, 11, 12].

However, the effect of crystal hydrate water on the course of this complex process has been established only for some phosphates and requires further study. It is known, for example, that the composition of the products of dehydration of monohydrate $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ is much more complex than that of anhydrous $\text{Ca}(\text{H}_2\text{PO}_4)_2$ [11]. For solid solutions of dihydrogen phosphates, this effect could be assessed on the example of the described tetra-hydrate $\text{Mn}_{0.5}\text{Mg}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ [9] and dihydrate with the same ratio of cations — $\text{Mn}_{0.5}\text{Mg}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ [10]. However, in [9] the chemistry of tetra-hydrate dehydration is presented in the form of the following simplified scheme of thermal transformations:



This scheme does not take into account the actual process of thermolysis of dihydrogen phosphates, which, according to [10], is accompanied by complex solid-phase transformations, including complete amorphization of partial dehydration products, their anionic condensation together with forming a mixture of condensed phosphates, release of free phosphoric acid and subsequent interaction with the formation of anhydrous cyclotetraphosphate.

The purpose of this work is to investigate the thermal properties of solid solution

tetrahydrates of the general formula $\text{Mg}_{1-x}\text{Mn}_x(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ with specification of the anionic composition of polymer phosphates formed at all stages of dehydration, to evaluate the effect of crystal hydrate water on the process and heat treatment products.

2. Experimental

A solid solution of magnesium and manganese(II) of dihydrogen phosphate tetrahydrates consisting of $\text{Mg}_{1-x}\text{Mn}_x(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($0 < x \leq 1.00$) was obtained at 30–40°C by interaction of a mechanical mixture of magnesium and manganese(II) of hydroxycarbonates with a 60–80 % H_3PO_4 solution at fixed pH values in the range of 0.8–1.1. The composition of the starting reagents was varied in a given molar ratio, similar to that described in [13].

A tetrahydrate of the composition $\text{Mg}_{0.5}\text{Mn}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ was used as the main object of the study. For the integrity of the experiment and in order to eliminate the impact of heat treatment products on the composition, the techniques of research and the nature of the cation, we analyzed the dehydration products obtained by heating dihydrogen phosphate dihydrate with the same ratio of cations — $\text{Mg}_{0.5}\text{Mn}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ to reference temperatures. Differential thermal analysis was performed in the temperature range of 25–700°C under conditions of dynamic (Q-1500 D derivatograph, platinum crucibles with lid, standard — freshly calcined Al_2O_3 , sample weight is 100–300 mg, heating rate is 2.5 deg/min, accuracy of temperature determination is $\pm 5^\circ$) and quasi-isothermal (conical sample holder, sample weight is 200 mg, heating rate is 3 deg/min) heating modes.

Heat treatment products were obtained, similarly to [7], at temperatures corresponding to the thermal effects on the DTA curves. To identify them, a set of analysis techniques were used: chemical, X-ray diffraction (DRON-4M, connected to a calculating complex, FeK_α , internal standard NaCl), IR spectroscopy (spectrometer Nexus-470, range 400–4000 cm^{-1} , at 20°C and — 190°C, pressing a fixed portion of 0.05 % of the mass sample into the matrix KBr).

The anionic composition of the dehydration products was determined by paper chromatography with a quantitative assessment of each of the condensed anions, as described in [10]. The content of phosphate

acids was determined by gravimetric quino-line molybdate method after extraction with dried acetone.

3. Results and discussion

According to the results of the thermo-analytical experiment, $\text{Mg}_{0.5}\text{Mn}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ is stable when heated in air to 60°C , and $\text{Mg}_{0.5}\text{Mn}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ — up to 80°C . A further increase in temperature to 700°C is accompanied by a loss of mass, which occurs in four main stages in tetra- and in three — in dihydrate. On the DTA curve, the process of dehydrating $\text{Mg}_{0.5}\text{Mn}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ is described by a number of endothermic effects in the temperature range of $60\text{--}120^\circ$, $120\text{--}180^\circ$, $180\text{--}235^\circ$ and $290\text{--}345^\circ\text{C}$, for $\text{Mg}_{0.5}\text{Mn}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ — these are $80\text{--}155^\circ$, $185\text{--}260^\circ$ and $280\text{--}330^\circ\text{C}$ (Fig. 1).

A comprehensive analysis of products heat-treated at temperatures characteristic of these thermal effects and stages of mass loss of dihydrogen phosphates showed that the composition of all products of partial dehydration of tetrahydrate — $\text{Mg}_{0.5}\text{Mn}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, is heterophase, starting from 80°C and up to almost 345°C . The formation of a liquid phase, in addition to the solid one, free phosphoric acid, is registered almost simultaneously with the onset of dehydration of the tetrahydrate (0.89 % of mass in terms of P_2O_5 already during removal of 0.23 moles of crystal hydrate H_2O from $\text{Mg}_{0.5}\text{Mn}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ at 80°C). In the case of further heating its amount increases reaching a maximum value during the removal of 0.58 moles of H_2O constitutional water (25.87 % of mass of P_2O_5 acid at 210°C), then decreases. In the products of thermolysis with mass loss (Δm) more than 5.77 moles of H_2O , phosphate acids are not registered (Table 1).

The formation of free phosphate acid in the heat treatment products of $\text{Mg}_{0.5}\text{Mn}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ dihydrate proceeds differently. During the removal of two moles of crystal hydrate water (heated up to 155°C), phosphate acids are not registered. A small amount of them is formed with the beginning of the removal of constitutional water (about 0.7 % of mass of P_2O_5 acid at 185°C) and acquires a maximum value of 16.28 % of mass of P_2O_5 acid at 205°C during the removal of about 0.5 moles of constitutional water (Fig. 2, a).

In the case of heating $\text{Mg}_{0.5}\text{Mn}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ up to 180°C , and $\text{Mg}_{0.5}\text{Mn}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ — up to 185°C , the composition of the acid component of

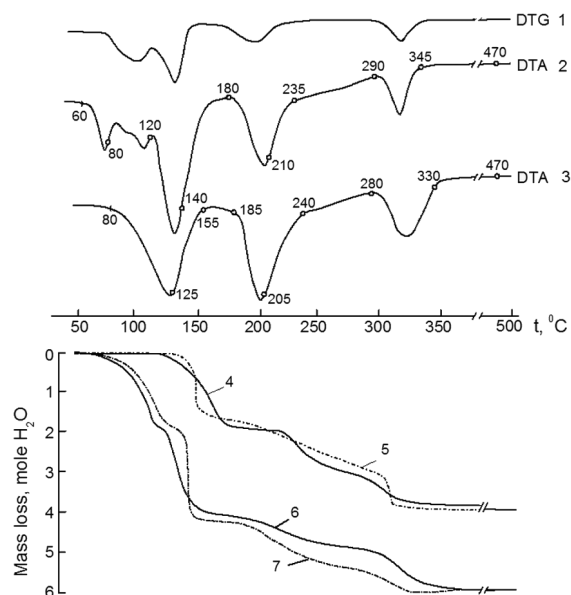


Fig. 1. Curves of thermal analysis of tetrahydrate $\text{Mg}_{0.5}\text{Mn}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ (1, 2, 6, 7) and dihydrate $\text{Mg}_{0.5}\text{Mn}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (3, 4, 5) in dynamic (4, 6) and quasi-isothermal (5, 7) heating regimes -o- — place of sampling for analysis.

the heat treatment products is represented only by monophosphate acid. Upon further heating, its condensation occurs with the formation of polyphosphate acids with the general formula $\text{H}_{n+2}\text{P}_n\text{O}_{3n+1}$. The degree of polycondensation (\bar{n}) at 210°C for tetra- and 205°C for dihydrate is $2 \leq \bar{n} \leq 4$ (Table 1). The maximum degree of polycondensation is achieved by polyphosphate acids, formed during the removal from the original tetrahydrate of 5.21 moles of H_2O ($\bar{n} = 7$ at 290°C). In heat treatment products, $\text{Mg}_{0.5}\text{Mn}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ polyphosphate acids with a maximum value $\bar{n} = 5$ are registered at 280°C (during removal of 3.24 moles of H_2O , 1.24 moles of which is constitutional water).

In the first two stages, the composition of solid-phase products of partial dehydration of $\text{Mg}_{0.5}\text{Mn}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ is associated with the removal of crystal hydrate water and is also represented only by monophosphate anions. In the case of heat treatment of $\text{Mg}_{0.5}\text{Mn}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ dihydrate, this occurs at the first stage of mass loss. The beginning of anionic condensation with the formation of a mixture of condensed phosphates of linear structure is observed at the third stage of $\text{Mg}_{0.5}\text{Mn}_{0.5}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ thermolysis during the removal of constitutional water in the range of $180\text{--}235^\circ\text{C}$. A

Table 1. Anionic composition of heat treatment products of $Mg_{0.5}Mn_{0.5}(H_2PO_4)_2 \cdot 4H_2O$

Temperature, °C	Mass loss, mole H_2O	P_2O_5 gan., wt. %	Phosphate content (P_2O_5 , wt. %) as										
			mono-	di-	tri-	tetra-	cyclo-tetra-	penta-	hexa-	hepta-	octa-	unresolved phosphates	
80	0.23	44.21*	44.0	0.0									
		0.89	0.9	0.0									
120	1.86	47.45	47.5	0.0									
		2.71	2.7	0.0									
140	3.74	55.61	55.6	0.0									
		3.21	3.2	0.0									
180	3.96	55.31	55.3	<0.1	0.0								
		3.83	3.8	0.0	0.0								
210	4.58	33.25	11.2	15.4	3.9	2.6	0.0	2.2	0.0				
		25.87	12.3	8.7	3.2	2.1	0.0	0.0	0.0	0.0			
235	4.70	38.48	5.5	20.2	4.7	3.1	0.0	2.5	1.7	0.8	0.0		
		22.37	4.3	9.4	1.9	2.8	0.0	2.0	1.4	0.0	0.0		
290	5.21	50.82	3.1	25.2	5.1	3.9	2.0	2.7	2.4	2.2	1.8	2.4	
		11.77	1.3	3.2	2.4	2.1	0.0	1.4	0.8	0.6	0.0	0.0	
345	5.77	64.17	1.7	1.2	0.8	0.0	60.5	0.0					
		0.18	0.2	0.0	0.0	0.0	0.0	0.0	0.0				
470	6.00	66.45	1.7	1.3	0.8	0.0	62.6	0.0					
		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0				

* The numerator shows the content of P_2O_5 in the salt component, in the denominator — in free phosphate acids.

small amount of diphosphate is registered in the heat treatment products at 180°C. With a further increase in temperature, the processes of anionic condensation deepen. The degree of polycondensation increases from $\bar{n} = 5$ for polyphosphates obtained at 210°C, to $\bar{n} = 7$ — at 235°C, to $\bar{n} = 8$ and more at 290°C — the temperature of forming the most complex mixture of macromolecular phosphates (Fig. 2, b). The increase in temperature up to 345°C is accompanied by the next, fourth stage of mass loss (Δm reaches 5.77 moles of H_2O) and almost complete cyclization of the polyphosphate anion. The composition of heat treatment products is simplified. It is represented by only one condensed phosphate with a cyclic structure of the anion — cyclotetraphosphate (Table 1).

The structural changes that accompany the heat treatment of $Mg_{0.5}Mn_{0.5}(H_2PO_4)_2 \cdot 4H_2O$, are registered immediately with the beginning of the removal of even a small amount of crystal hydrate water from the tetrahydrate. X-ray and IR spectra of partially dehydrated tetrahydrate at 80°C, despite the removal of only 0.23 moles of H_2O , clearly indicate the formation of another phase next

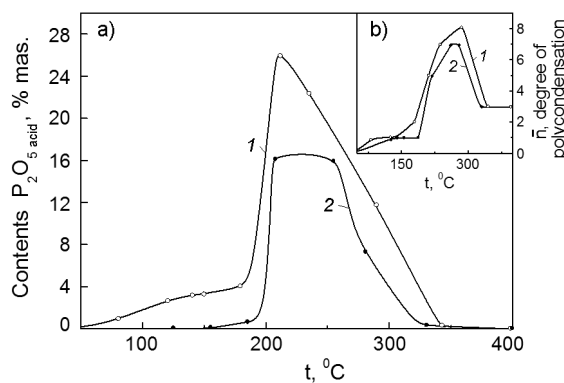


Fig. 2. Temperature dependences of: a — the amount of free phosphoric acid in the heat treatment products of $Mg_{0.5}Mn_{0.5}(H_2PO_4)_2 \cdot 4H_2O$ (1) and $Mg_{0.5}Mn_{0.5}(H_2PO_4)_2 \cdot 2H_2O$ (2); b — the degree of polycondensation of the phosphate anion in the salt component.

to the tetrahydrate — dihydrate (Fig. 3). Its composition, X-ray and IR spectroscopic characteristics are similar to those known for $Mg_{0.5}Mn_{0.5}(H_2PO_4)_2 \cdot 2H_2O$ synthesized by the interaction of hydroxycarbonates with phosphoric acid, as described in [10]. Quantitative ratios between tetra- and dihydrate

are shifted towards the latter with increasing temperature. When heated to 120°C, the mass loss of the tetrahydrate is close to two moles of H₂O (1.86) and the dihydrate is the main constituent part of the salt component.

The second crystalline phase is formed at the first stage of Mg_{0.5}Mn_{0.5}(H₂PO₄)₂·4H₂O dehydration and is identified as hydrogen phosphate of Mg_{0.5}Mn_{0.5}HPO₄·3H₂O composition. It is present in much smaller quantities and is recorded on X-ray diffraction patterns only as individual, inherent in it, diffraction reflections with intensity of not more than 10–15 %. The spectral curve, which is the total envelope of these two phases, describes mainly the fluctuations of the structural groups of dihydrogen phosphate. The absorption bands characteristic of the HPO₄²⁻ anion and three molecules of hydrogen hydrophosphate crystal hydrate almost completely overlap (Fig. 3).

The second stage (120–180°C) of Mg_{0.5}Mn_{0.5}(H₂PO₄)₂·4H₂O dehydration is characterized by formation of dihydrogen phosphate dihydrate and hydrogen phosphate as intermediates. According to the results of thermographic studies, it practically corresponds to the first stage of dehydration (removal of two moles of crystal hydrate water) of the synthesized dihydrate of Mg_{0.5}Mn_{0.5}(H₂PO₄)₂·2H₂O (Fig. 1).

The composition of partially dehydrated phosphates obtained by removal of crystal hydrate water from both tetra- and dihydrate is mainly represented by anhydrous dihydrogen phosphate Mg_{0.5}Mn_{0.5}(H₂PO₄)₂, identified on the basis of X-ray and IR spectroscopic characteristics. The composition of the second component of solid-phase dehydration products, which are present in much smaller quantities, is different: for dihydrate — it is hydrogen phosphate, for tetrahydrate — less protonated phosphate with the general formula (Mg_{0.5}Mn_{0.5})₅(PO₄)₂(HPO₄)₂·4H₂O, X-ray and IR spectroscopic parameters of which are similar to those known for the natural mineral composition of Mn₅(PO₄)₂(HPO₄)₂·4H₂O [14, 15].

Structural rearrangements occurring in the heat treatment products Mg_{0.5}Mn_{0.5}(H₂PO₄)₂·4H₂O during the removal of constitutional water (third and fourth stages of dehydration) are associated with the formation of polymer phosphates with a linear anion structure with 2 ≤ n ≤ 8 and their subsequent cyclization. They characterize the sequential formation of structures of two crystalline phases: dihydrogen diphosphate with an impurity of diphosphate

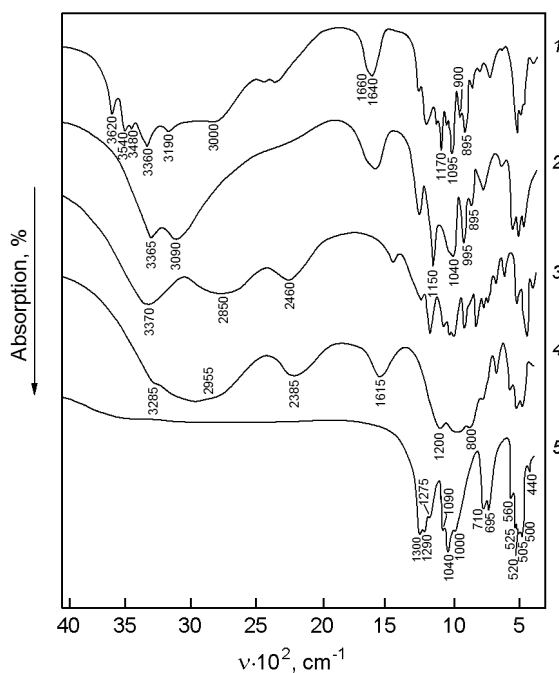


Fig. 3. IR absorption spectra of Mg_{0.5}Mn_{0.5}(H₂PO₄)₂·4H₂O (1) and its heat treatment products at 80–120° (2), 140–180° (3), 210–290° (4), 345–700°C (5).

(at 210–290°C) and cyclotetraphosphate (at 345–470°C). X-ray and IR spectroscopic characteristics of phosphates Mg_{0.5}Mn_{0.5}H₂P₂O₇, (Mg_{0.5}Mn_{0.5})₂P₂O₇ and (Mg_{0.5}Mn_{0.5})₂P₄O₁₂ are similar to those obtained during dehydration of dihydrate Mg_{0.5}Mn_{0.5}(H₂PO₄)₂·2H₂O, as well as individual MnH₂P₂O₇, Mn₂P₂O₇ and Mn₂P₄O₁₂ [10, 14, 15].

Condensed phosphates with 3 ≤ n ≤ 8 are X-ray amorphous. The formation of their crystal structures is limited by steric difficulties (large geometric parameters of anions, including protonated ones). The presence of highly condensed phosphates in the composition of the mixture of the salt component is indirectly revealed on X-ray diffraction and IR spectra by the general expansion of diffraction reflections and absorption bands and a decrease in their intensity. The diffuse nature of the IR spectrum clearly indicates the presence of a large number of amorphous phases, which, judging by the simplification of the spectral set of absorption bands, contain polymer chains with a degenerate pattern of oscillations (Fig. 3). The oscillations characterizing the presence of protonated di- and polyphosphate anions, as well as mono- and polyphosphate acids, are registered in the form of three broad bands in the region of ν(OH) band 1615 cm⁻¹ and the bands corresponding to the defor-

mation POH oscillations (planar — 1200 cm⁻¹ and extraplanar — 800 cm⁻¹).

During heating up to 345–470°C, the transition of a mixture of oligophosphates from the disordered state to the crystal structure takes place for the final heat treatment product of tetrahydrate — cyclotetraphosphate of (Mg_{0.5}Mn_{0.5})₂P₄O₁₂ composition: condensed phosphate with $\bar{n} = 4$ and a fundamentally different, annular structure of the anion occurs. The formation of cyclotetraphosphate is the result of complex structural and thermal rearrangements, which are realized simultaneously in two parallel directions. One of them involves the cyclization of the polyphosphate anion in the process of dehydration of protonated condensed phosphates (up to 63–65 % of cyclotetraphosphate). According to the second direction, 35–37 % of (Mg_{0.5}Mn_{0.5})₂P₄O₁₂ is formed due to the interaction of medium high molecular weight polyphosphates and free polyphosphate acids.

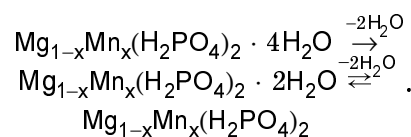
The end product of complete dehydration of the dihydrate, despite the structural differences and different content of crystal hydrate water, is also cyclotetraphosphate. It is formed in two similar directions, the quantitative ratios of which vary depending on the amount of crystal hydrate water, which determines the different content of free phosphate acids and, accordingly, their participation in the formation of cyclotetraphosphate.

Thermoanalytical studies of tetrahydrates Mg_{1-x}Mn_x(H₂PO₄)₂·4H₂O (0 < x ≤ 1.00) with different x values, have shown that the structure features revealed for Mg_{0.5}Mn_{0.5}(H₂PO₄)₂·4H₂O heat treatment products, quite correctly describe the dehydration of tetrahydrates with different contents of magnesium and manganese(II). Differences in some quantitative characteristics, temperature intervals of individual stages of dehydration and the process as a whole are determined by the cationic composition of the initial tetrahydrate: with an increase in magnesium content the amount of released phosphate acids decreases, temperature intervals of formation and stability of the heat treatment products are shifted by 15–20 degrees to the area of higher values.

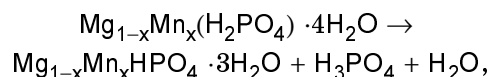
The generalization of the results obtained and their comparison with those for dihydrate makes it possible to determine the common and distinctive features of the products and the process of dehydration of tetra- and dihydrates (Table 2). Analysis of these data shows that the effect of crystal hydrate water on the process of heat treat-

ment of Mg_{0.5}Mn_{0.5}(H₂PO₄)₂·4H₂O tetrahydrate is detected mainly in the first two stages of dehydration, when about 4 moles of H₂O are removed from the crystal hydrate in the range of 60–180°C.

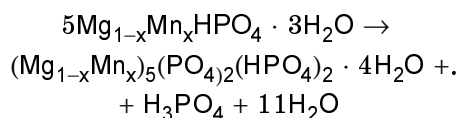
The chemistry of removing crystalline hydrate water with different energy states is different and is accompanied by the following processes: two water molecules bound in the structure of tetrahydrates by the least strong H-bonds, are removed as a molecular unit (molecular mechanism), with creating the corresponding dihydrate, followed by creation of anhydrous dihydrogen phosphate:



However, complete removal of 2 moles of H₂O does not occur (at 120°C, the mass loss is 1.8–1.9 moles). This creates conditions for partial implementation of the disproportionation process with the formation of less protonated salt and H₃PO₄. At the first stage of dehydration, this process occurs according to the scheme:



dihydrogen phosphate is involved; hydrogen phosphate is formed at the second stage:



The other two molecules of crystal hydrate water, bound in the structure of tetrahydrate by covalent bonds, are removed by a dissociative mechanism, participating in the implementation of solid-phase hydrolysis of the salt with the formation of hydrogen phosphate and free phosphoric acid.

Influence of crystalline water at III and IV stages of dehydrating tetrahydrates Mg_{1-x}Mn_x(H₂PO₄)₂·4H₂O, associated with the removal of constitutional water, is less significant (Table 2). There are no fundamental differences in the chemistry of the formation of free polyphosphate acids, as well as in the processes of anionic condensation, which are realized as a part of intermediate products of thermolysis of tetra- and dihydrates. The differences relate to the depth of realization of anionic condensation and the quantitative composition of high molecular weight polyphosphates, that are created.

Table 2. The main characteristics of the process and products of heat treatment of dihydrogen phosphates of tetra- and dihydrates

Indicators	$Mg_{0.5}Mn_{0.5}(H_2PO_4)_2 \cdot 4H_2O$	$Mg_{0.5}Mn_{0.5}(H_2PO_4)_2 \cdot 2H_2O$
Thermal stability, °C	60	80
The number of stages of the dehydration process	4	3
Temperature interval of crystal hydrate water removal, °C	60–180	80–185
Start of °C:		
— removal of constitutional water	180	185
— formation of free phosphoric acid	80	185
— amorphization of the solid phase	210	205
— anionic condensation of the salt component	210	205
The maximum amount of acid released, wt.% (in terms of P_2O_5)	25.87	16.28
The maximum degree of anionic condensation of dehydration products, n	8	7
The degree of conversion of monophosphate anion to polyphosphate (%) to:		
— 1 stage of dehydration;	0	0
— 2 stages;	0	75.0
— 3 stages;	87.0	96.3
— 4 stages	98.4	–

4. Conclusions

The effect of crystalline hydrate water on the process and products of heat treatment of magnesium-manganese(II) of dihydrogen phosphates consists in changing the quantitative characteristics of the process and, above all, in increasing the content of free mono- and polyphosphate acids released as part of intermediate products. The maximum amount of them in the thermolysis of tetrahydrates is 1.6 times greater than for dihydrates with the same ratio of cations. They catalyze the processes of anionic condensation and reduce the realization temperatures of both individual stages of dehydration and the process as a whole.

The degree of conversion of the monophosphate anion to polyphosphate in the products of dehydration of tetrahydrates is 1.1–1.2 times greater than for similar stages of thermolysis of dihydrates. The maximum degree of polycondensation is also higher in polyphosphates in the composition of heat treatment products of tetrahydrate ($\bar{n} = 8$ for $Mg_{0.5}Mn_{0.5}(H_2PO_4)_2 \cdot 4H_2O$, $\bar{n} = 7$ for $Mg_{0.5}Mn_{0.5}(H_2PO_4)_2 \cdot 2H_2O$).

The formation of completely dehydrated phosphates, which are cyclotetraphosphates with the general formula $(Mg_{1-x}Mn_x)_2P_4O_{12}$ in the thermolysis of both tetra- and dihydrates, is realized in two similar directions, the quantitative ratios of which for tetra- and dihydrates are different.

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