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Features of the synthesis of solid solutions of divalent metal phosphates with a newberyite structure

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

National University of Life and Environmental Sciences of Ukraine,
17 Heroiv Oborony Str., 03041 Kyiv, Ukraine

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The conditions for joint pair precipitation of isomorphic cations Mn^{2+} and Mg^{2+}, Mn^{2+} and Co^{2+}, Mn^{2+} and Zn^{2+} in the form of hydrogen phosphates are determined. Three solid solutions $Mn_{1-x}Mg_xHPO_4 \cdot 3H_2O$ $(0 < x < 1.00)$, $Mn_{1-x}Co_xHPO_4 \cdot 3H_2O$ $(0 < x \le 0.2)$ and $Mn_{1-x}Zn_xHPO_4 \cdot 3H_2O$ $(0 < x \le 0.07)$ with the newberyite structure are synthesized. It was shown that they are formed as a result of isomorphic substitution of the manganese(II) cation in the crystal lattice of the matrix hydrogen phosphate. The ranges of solid solution homogeneity vary widely: from continuous, as in $Mn_{1-x}Mg_xHPO_4 \cdot 3H_2O$ $(0 < x < 1.00)$, to limited by a narrow interval of homogeneity, as in $Mn_{1-x}Co_xHPO_4 \cdot 3H_2O$ $(0 < x \le 0.2)$ and $Mn_{1-x}Zn_xHPO_4 \cdot 3H_2O$ $(0 < x \le 0.07)$. The fact that different ranges of homogeneity are realized is substantiated using the characteristics of co-precipitated cations.

Keywords: solid solution, hydrogen phosphate, newberyite structure.

Особливості синтезу твердих розчинів фосфатів двовалентних металів із структурою ньюбериту. *Н.М.Антрапцева, Н.В.Солод, О.О.Кравченко*

Визначено умови спільного попарного осадження ізоморфних катіонів Mn^{2+} і Mg^{2+}, Mn^{2+} і Co^{2+}, Mn^{2+} і Zn^{2+} у вигляді гідрогенфосфатів. Синтезовано три тверді розчини із структурою ньюбериту складу: $Mn_{1-x}Mg_xHPO_4 \cdot 3H_2O$ $(0 < x < 1.00)$, $Mn_{1-x}Co_xHPO_4 \cdot 3H_2O$ $(0 < x \le 0.2)$ and $Mn_{1-x}Zn_xHPO_4 \cdot 3H_2O$ $(0 < x \le 0.07)$. Показано, що вони утворюються внаслідок ізоморфного заміщення катіону мангану(II) у кристалічній решітці гідрогенфосфату-матриці. Області гомогенності твердих розчинів змінюються у широких межах: від неперервних, як у $Mn_{1-x}Mg_xHPO_4 \cdot 3H_2O$ $(0 < x < 1.00)$, до обмежених вузьким інтервалом гомогенності, як у $Mn_{1-x}Co_xHPO_4 \cdot 3H_2O$ $(0 < x \le 0.2)$ і $Mn_{1-x}Zn_xHPO_4 \cdot 3H_2O$ $(0 < x \le 0.07)$. Факт існування різних меж гомогенності обгрунтований із застосуванням характеристик катіонів, що співосаджуються.

Определены условия совместного парного осаждения изоморфных катионов Mn^{2+} и Mg^{2+}, Mn^{2+} и Co^{2+}, Mn^{2+} и Zn^{2+} в виде гидрофосфатов. Синтезированы три твердые растворы со структурой ньюберита состава: $Mn_{1-x}Mg_xHPO_4 \cdot 3H_2O$ $(0 < x < 1.00)$, $Mn_{1-x}Co_xHPO_4 \cdot 3H_2O$ $(0 < x \le 0.2)$ и $Mn_{1-x}Zn_xHPO_4 \cdot 3H_2O$ $(0 < x \le 0.07)$. Показано, что они образуются в результате изоморфного замещения катиона марганца(II) в кристаллической решетке гидрофосфата-матрицы. Области гомогенности твердых растворов изменяются в широких пределах: от непрерывных, как у $Mn_{1-x}Mg_xHPO_4 \cdot 3H_2O$ $(0 < x\ 1.00)$, до ограниченных узким интервалом гомогенности как у $Mn_{1-x}Co_xHPO_4 \cdot 3H_2O$ $(0 \le x \le 0.2)$ и $Mn_{1-x}Zn_xHPO_4 \cdot 3H_2O$ $(0 < x \le 0.07)$. Факт реализации различных областей гомогенности обоснован с использованием характеристик соосаждающихся катионов.

1. Introduction

Phosphates of divalent metals are widely used for manufacturing various functional materials: thermo-sensitive coatings, luminophores, anticorrosive pigments, and catalysts for organic synthesis, etc. Technically, their valuable properties are improved by introducing an additional cation into their phosphate-matrix structure. This is achieved by synthesizing compounds that are chemically solid solutions or double salts. The most studied of various cationic phosphates are salts of monovalent and divalent metals $NaMnPO_4·2H_2O$, $KMnPO_4·H_2O$, $RbMnPO_4·6H_2O$, $CsMnPO_4·6H_2O$ [1–4].

Recently, work has intensified on the synthesis and study of various characteristics of solid solutions of inorganic phosphates, starting with structural features, IR spectroscopic, colorimetric, catalytic and other characteristics. This is due to the ability to regulate their composition within specified limits and, accordingly, physicochemical and operational properties. In particular, studies of isomorphic substitution of Cu(II) for Co, Ni or Zn in the structure of phosphates $CuHPO_4·H_2O$, $Cu_3(PO_4)_2·H_2O$, $Cu_2(OH)PO_4·xH_2O$ ($x = 0.1$–0.2) are well known [5]. Possibilities of obtaining Co(II) and Ni(II) phosphates with different degree of protonation, solid solutions of $M_{1-x}Ni_x(H_2PO_4)_2·2H_2O$, M = Mg, Mn, Co, Zn are considered in [6]. Some works are devoted to the synthesis of phosphates of the composition $Mn_{0.5}Fe_{0.5}(H_2PO_4)_2·xH_2O$ [7], $Mn_{0.5}Cu_{0.5}(H_2PO_4)_2·1.5H_2O$ [8], as well to the study of their properties.

There are very few data on solid solutions of Mg, Co(II), Zn phosphates based on the newberite structure in the literature. Systematic research in this area has not been performed.

The purpose of this work is to determine the conditions and specifics of obtaining solid solutions of phosphates of divalent metals (magnesium, manganese(II), cobalt(II), zinc) with the newberyite structure.

2. Experimental

Solid solutions were obtained by co-precipitation of Mn^{2+} and Mg^{2+} (Co^{2+} or Zn^{2+}) cations by the HPO_4^{2-} ion through the interaction of a mixture of the corresponding hydroxycarbonates with phosphoric acid at a fixed value of H^+ ion concentration in the range 2.6–3.3. The ratio of Mn(II) and Mg (Co(II), Zn) as part of a mixture of hydroxycarbonates ($K = Mn/M^{II}$) varied from 100 to 0 (in recalculation on molar content), concentration of H_3PO_4 — in the range of 30–87 %, the temperature — within 25–80°C.

For co-precipitation of cations, the conditions were chosen that ensure the formation of a crystal lattice of newberyite — $MnHPO_4·3H_2O$. For this purpose, in addition to the known data, additional series of experiments were carried out to clarify the conditions for obtaining individual hydrogen phosphates of manganese(II), magnesium, zinc, cobalt(II) in relation to the reaction applied. During the experiment, the dependence of the composition of the precipitated solid phase on the following main parameters was determined: pH, ratio $K = Mn/M^{II}$ (M^{II} = Mg, Co, Zn) in the composition of the starting reagents, H_3PO_4 concentration and temperature.

Identification and study of synthesized phosphates were carried out by the following methods: chemical analysis, XRD using FeK_α and CuK_α radiations with NaCl as an internal standard (DRON-4, equipped with an IBM PC/AT computer system); IR absorption spectroscopy in the range of 400–4000 cm^{-1}, at 20°C and −190°C, using a fixed portion of 0.05 % of the sample weight pressed into a KBr matrix (Nexus-470 spectrometer); Raman spectroscopy (modernized DSF-24, providing mathematical processing of spectra); electron microscopy (scanning electron microscope JSM-35, microscope TESLA BS 513A) and optical microscopy (MIN-8, MBS-1).

3. Results and discussion

Experimental data obtained to determine the conditions of co-precipitation of manganese(II) and magnesium cations in the form of hydrogen phosphates indicate that the hydrogen-phosphate matrix — $MnHPO_4·3H_2O$ — newberyite is formed in the pH range of 2.2 to 3.2. The composition of the precipitate is determined by the temperature regime of precipitation, and at temperatures above 50°C, along with $MnHPO_4·3H_2O$, phosphates of the composition $MnHPO_4·1.5H_2O$ are formed. The concentration of H_3PO_4 (from 30 to 87 %) has almost no effect on the composition of $MnHPO_4·3H_2O$.

The precipitation of $MgHPO_4·3H_2O$ during the interaction of magnesium hydroxycarbonate with H_3PO_4 occurs in the pH range of 2.8–3.4. The precipitation at pH

Table 1. Characteristics of manganese(II) and magnesium hydrogen phosphate solid solutions (pH 2.8; 45°C; 55 % H_3PO_4 solution)

K = Mn/Mg, molar units	The solid phase composition, wt.%				Chemical composition	Phase composition (according to the results of X-ray diffraction and IR spectroscopy)
	Mn	Mg	P	H_2O		
–	26.96	–	14.86	30.57	$MnHPO_4$*cdotБ*% % %*Ал*$3H_2O$	$MnHPO_4 \cdot 3H_2O$
	26.81*		15.12	30.75		
75.0	26.28	1.04	14.90	30.68	$Mn_{0.97}Mg_{0.03}HPO_4 \cdot 3H_2O$	Solid solution with the general formula $Mn_{1-x}Mg_xHPO_4 \cdot 3H_2O$
20.0	24.57	1.61	15.06	30.82	$Mn_{0.9}Mg_{0.1}HPO_4 \cdot 3H_2O$	
1.4	20.94	2.80	15.80	31.75	$Mn_{0.75}Mg_{0.25}HPO_4 \cdot 3H_2O$.	
1.0	19.38	4.02	16.19	32.30	$Mn_{0.7}Mg_{0.3}HPO_4 \cdot 3H_2O$.	
0.33	14.90	6.71	16.61	33.39	$Mn_{0.5}Mg_{0.5}HPO_4 \cdot 3H_2O$.	
0.2	8.30	9.91	17.04	34.09	$Mn_{0.25}Mg_{0.75}HPO_4 \cdot 3H_2O$.	
0.01	2.83	13.00	17.40	35.45	$Mn_{0.1}Mg_{0.9}HPO_4 \cdot 3H_2O$.	
–	–	13.76	17.79	35.96	$MgHPO_4$*cdotБ*% % %*Ал*$3H_2O$	$MgHPO_4 \cdot 3H_2O$

below 2.8 is accompanied by the formation an impurity phase of $Mg(H_2PO_4)_2 \cdot 2H_2O$. Increasing the pH is impractical, since it reduces the rate of interaction of the starting reagents. The precipitation temperature has almost no effect on the composition of the solid phase and affects only the duration of the process.

Based on the results obtained, co-precipitation of manganese (II) and magnesium hydrogen phosphates was carried out under the following conditions: pH 2.8; temperature 45°C; H_3PO_4 solution — 55 %. The ratio of manganese(II) and magnesium in the mixture of starting hydroxycarbonates varied from 100 to 0 (in terms of molar content). The results of the analysis of phosphates obtained under these conditions are given in Table 1.

Analysis of the solid phase obtained by co-precipitation of manganese(II) and magnesium hydrogen phosphates has showed that, regardless of the content of manganese(II) and magnesium in the starting reagents (K = Mn/Mg), only one crystalline phase is formed. Both manganese and magnesium ions take part in the formation of the crystal lattice of this phase, their content varying depending on the composition of the hydroxycarbonate mixture. The contents of phosphorus and water corresponding to values calculated for hydrogen phosphates, depends on it as well (Table 1).

The diffraction patterns of all the obtained compounds ions completely coincide with the diffraction patterns of individual isostructural hydrogen phosphates $MnHPO_4 \cdot 3H_2O$ and $MgHPO_4 \cdot 3H_2O$ in terms of the position of the reflections; the differences are only in the redistribution of the intensities of individual reflections [9]. The regular change in the values of interplanar distances characterizes hydrogen phosphates as a continuous solid solution of substitution of the general formula $Mn_{1-x}Mg_xHPO_4 \cdot 3H_2O$, structurally identical to newberyite. The values of x are determined by the composition of the original hydroxycarbonates and varies from 0 for $MnHPO_4 \cdot 3H_2O$ to 1.00 for $MgHPO_4 \cdot 3H_2O$, which are the limiting compositions of the synthesized solid solution.

The presence of a structural relationship between solid hydrogen phosphates and newberyite is clearly detected in the analysis of IR spectra. Complete identity of IR spectrum configurations of $Mn_{1-x}Mg_xHPO_4 \cdot 3H_2O$, recorded at 20°C and −190°C, with $MnHPO_4 \cdot 3H_2O$ spectra testifies in favor of their isostructurality (Fig. 1). The uniform displacement of the absorption bands, in particular, the ν(OH) and δ(H_2O) bands, of the OH-groups of the protonated anion characterizes the effect of the nature of the cation on the strength of the H-bonds realized in the $Mn_{1-x}Mg_xHPO_4 \cdot 3H_2O$ structure.

The unit cell parameters of polycrystalline $Mn_{1-x}Mg_xHPO_4 \cdot 3H_2O$ ($0 < x < 1.00$) in the whole range of compositions change in proportion to the content of manganese(II)

Table 2. Parameters (nm) of the unit cell of a solid solution with the structure of newberyite, (orthorhombic crystal system, space group *Pbca*, $Z = 8$)

Composition of hydrogen phosphates	R cation, nm	a	b	c	V, nm^3
$MnHPO_4 \cdot 3H_2O$	0.097	1.0440(3)	1.0872(3)	1.0223(2)	1.16035
$Mn_{0.9}Mg_{0.1}HPO_4 \cdot 3H_2O$	–	1.0422(2)	1.0843(3)	1.0200(1)	1.15380
$Mn_{0.75}Mg_{0.25}HPO_4 \cdot 3H_2O$	–	$1.0383(^{+1}{}_{-2})$	$1.0822(^{-1}{}_{+1})$	1.0170(0)	1.14344
$Mn_{0.5}Mg_{0.5}HPO_4 \cdot 3H_2O$	–	1.0328(1)	1.0775(2)	1.0117(1)	1.12632
$Mn_{0.25}Mg_{0.75}HPO_4 \cdot 3H_2O$	–	$1.0267(^{+1}{}_{-2})$	$1.0733(^{+1}{}_{-2})$	1.0066(0)	1.10937
$Mn_{0.1}Mg_{0.9}HPO_4 \cdot 3H_2O$	–	1.0237(2)	1.0701(2)	1.0034(2)	1.09928
$MgHPO_4 \cdot 3H_2O$	0.086	$1.0214(^{+2}{}_{-3})$	1.0682(2)	1.0016(2)	1.09281

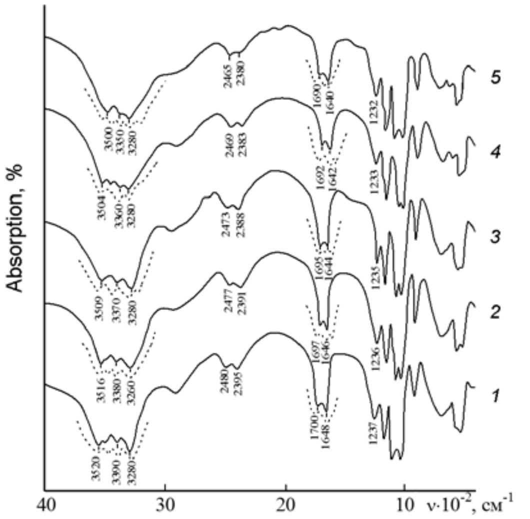

Fig. 1. IR absorption spectra of $Mn_{1-x}Mg_xHPO_4 \cdot 3H_2O$ solid solutions with $x = 1.0$ (*1*), 0.75 (*2*), 0.50 (*3*), 0.25 (*4*), 0 (*5*) at 20°C and −190°C (----).

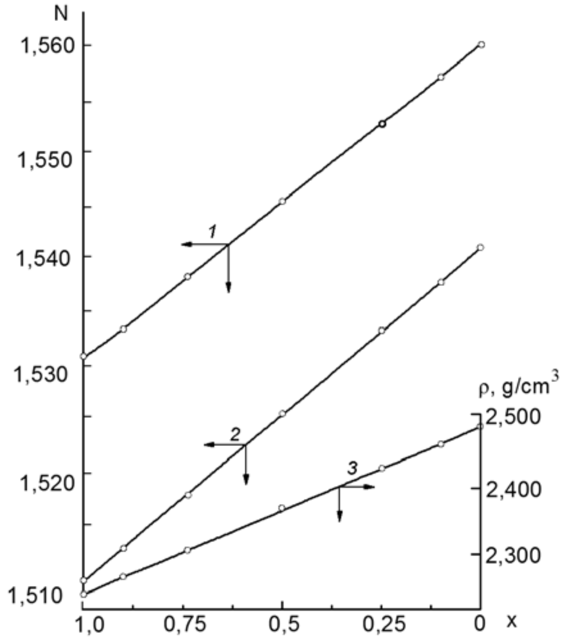

Fig. 2. Refractive indices (*1* — Ng, *2* — Np) and density (*3*) of hydrogen phosphates for the $Mn_{1-x}Mg_xHPO_4 \cdot 3H_2O$ solid solutions ($0 < x < 1.00$).

and magnesium and in accordance with the values of their ionic radii (0.086 nm for Mg^{2+} and 0.097 nm for Mn^{2+}). The dependence of the geometric dimensions of the crystal lattice of hydrophosphates on their composition is linear (Table 2). According to Vegard's law, this indicates the formation of a continuous solid solution of substitution. Hydrogen phosphates of the solid solution $Mn_{1-x}Mg_xHPO_4 \cdot 3H_2O$ ($0 < x < 1.00$) are crystals of regular shape in the form of truncated hexagonal bipyramids up to 0.6–0.8 cm in size. Their refractive indices and the density of crystals are determined by the composition and are linearly dependent on the content of manganese(II) and magnesium (Fig. 2).

Thus, under the conditions of coprecipitation of Mn^{2+} and Mg^{2+} in the form of hydrogen phosphates, as a result of isomorphic substitution of manganese (II) for magnesium in the structure $MnHPO_4 \cdot 3H_2O$, a continuous solid solution of substitution is formed containing $Mn_{1-x}Mg_xHPO_4 \cdot 3H_2O$ ($0 < x < 1.00$). The synthesized hydrogen phosphates crystallize in an orthorhombic crystal system (spatial group *Pbsa*, $Z = 8$) and are structurally identical to newberyite.

Substitution of manganese(II) for cobalt(II) in the structure of newberyite was investigated under conditions of pH = 2.8, temperature 40°C, 55 % aqueous solution of H_3PO_4. The content of manganese(II) and cobalt(II) in the original hydroxycarbonates (K = Mn/Co, in molar units) varied from 10.0 to 0.10.

The results of chemical analysis of the solid phase indicate that the ratio of $P/\sum Mn,Co$ at all values of K corresponds to the calculated value for hydrogen phosphates (1.00). However, according to the nature of changes in the content of Mn, Co, P, and H_2O in their composition, the formed hydrogen phosphates can be divided into two groups (Fig. 3). The first group consists of hydrophosphates obtained at $0.82 \le K \le 10.0$. The content of Mn(II) and Co(II) in them regularly changes depending on the composition of the mixture of hydroxycarbonates (26.17–21.44 wt.% of Mn; 0.62–5.35 wt.% of Co at $K = 10$ and $K = 0.82$, respectively). The composition of hydrogen phosphates formed under conditions of $0.10 \le K \le 0.80$ (second group) differs significantly: the content of manganese(II) is 13.91–1.05 wt.%, cobalt(II) — 18.27–31.29 wt.%. Quite sharp changes also concern the content of P and H_2O when going from $K = 0.82$ to $K = 0.80$ (Fig. 3).

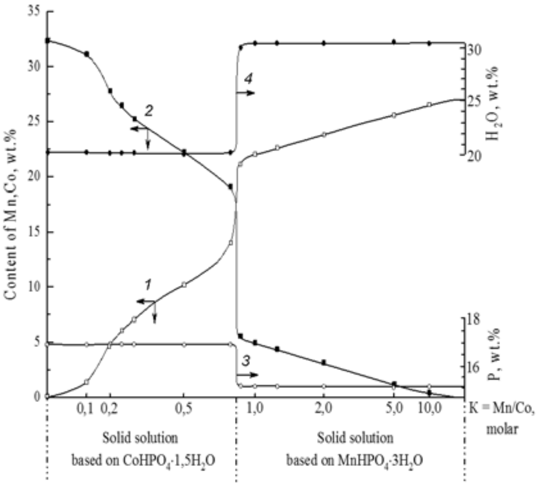

Fig. 3. Dependence of the content (wt.%) of Mn — *1*; Co — *2*; P — *3*; H_2O — *4* in the composition of hydrogen phosphates on the ratio K = Mn/Co (molar units), in the initial hydroxycarbonates.

Hydrogen phosphates precipitated under the conditions of $0.82 \le K \le 10.0$ are a crystalline phase, the X-ray characteristics of which correspond to those known for $MnHPO_4 \cdot 3H_2O$ [9]. The regular shift and redistribution of intensities of individual diffraction reflections on diffraction patterns of hydrogen phosphates with different content of Mn(II) and Co(II) characterizes the homogeneity of their crystalline structures and indicates the formation of a limited solid solution of general formula $Mn_{1-x}Co_xHPO_4 \cdot 3H_2O$ with the structure of newberyite. The values of x determined by the results of chemical analysis vary within $0 < x \le 0.2$. The saturated solid solution is hydrogen phosphate of the composition $Mn_{0.8}Co_{0.2}HPO_4 \cdot 3H_2O$.

The homogeneity of the structures of the synthesized hydrogen phosphates and newberyite is evidenced by the results of IR spectroscopic studies. The general form of absorption curves in the region of oscillations of the anionic sub-lattice (400–1500 cm^{-1}) is almost identical. In the range of frequency of valence oscillations of water crystallization molecules (2300–3600 cm^{-1}), a shift of absorption bands is observed, which reflects the influence of the nature of the cation on the state of water in hydrogen phosphates with different manganese(II) and cobalt(II) content.

A decrease in the values of K only by 0.02 (precipitation at $K = 0.80$) is accompanied by significant changes not only in the chemical but also in the phase composition of hydrogen phosphates. The formation of a solid solution of hydrogen phosphates of composition $Co_{1-x}Mn_xHPO_4 \cdot 1.5H_2O$ with the structure of $CoHPO_4 \cdot 1.5H_2O$ under conditions $0.10 \le K \le 0.80$ was found [10, 11].

The absorption curves in the IR spectra of hydrogen phosphates obtained at K = 0.82 and 0.80 differ significantly both in the region of oscillations of the molecules of crystallization water and in the low-frequency range of the spectrum corresponding to the oscillations of the anionic sublattice. In the Raman spectra, the difference in the structures of these phases mainly affects the oscillations of the P–OH bonds (Fig. 4).

The regions of existence of solid solutions based on the structures of isodimorphic individual hydrogen phosphates are different. Solid solutions of the composition $Mn_{1-x}Co_xHPO_4 \cdot 3H_2O$ ($0 < x \le 0.2$) are formed due to substitution of some manganese(II) atoms for isomorphic cobalt(II) in the struc-

Table 3. Characteristics of manganese(II) and zinc hydrogen phosphate solid solutions (pH 1.5; 40°C; 55 % H_3PO_4 solution)

IK = Mn/Zn, molar units	The solid phase composition, mas.%				Chemical composition	Phase composition (according to the results of X-ray diffraction and IR spectroscopy)
	Mn	Zn	P	H_2O		
–	26.96	–	14.86	30.57	MnHPO$_4$*cdotБ% % %A л*3H$_2$O	$MnHPO_4 \cdot 3H_2O$
	26.81*	–	15.12	30.75		
50.0	26.36	0.48	15.11	30.66	$Mn_{0.99}Zn_{0.01}HPO_4 \cdot 3H_2O$	Solid solution with the general formula $Mn_{1-x}Zn_xPO_4 \cdot 3H_2O$
30.0	26.26	0.61	15.10	30.54	$Mn_{0.98}Zn_{0.02}HPO_4 \cdot 3H_2O$	
15.0	25.29	1.59	15.10	30.61	$Mn_{0.95}Zn_{0.05}HPO_4 \cdot 3H_2O$	
5.5	25.05	1.90	15.10	30.68	$Mn_{0.94}Zn_{0.06}HPO_4 \cdot 3H_2O$	
1.5	24.83	2.14	15.09	30.67	$Mn_{0.93}Zn_{0.07}HPO_4 \cdot 3H_2O$	
1.2	24.44	4.87	14.72	20.08	$Mn_{0.93}Zn_{0.07}HPO_4 \cdot 3H_2O$ + $Zn_2Mn(PO_4)_2 \cdot 4H_2O$	Mixture of phases $MnHPO_4 \cdot 3H_2O$ and $Zn_3(PO_4)_2 \cdot 4H_2O$
1.0	24.32	5.21	14.44	19.12		

* Calculated values

ture of newberyite. They exist in the range of cobalt(II) concentrations from 0.62 to 5.35 mas.%. An attempt to replace more than 5.35 % of manganese(II) with cobalt(II) in the structure of $MnHPO_4 \cdot 3H_2O$ leads to an abrupt isodimorphic phase transition and the formation of solid solutions of hydrogen phosphates with the structure of $CoHPO_4 \cdot 1.5H_2O$ (a monoclinic crystal system) and composition $Co_{1-y}Mn_yHPO_4 \cdot 1.5H_2O$), $0 < y \leq 0.45$ (cobalt content is 18.27–31.6 wt.%). Concentration limits of manganese(II) are 0.7–13.9 wt.%.

Isomorphic substitution of manganese(II) for zinc in the structure of newberyite was investigated using co-precipitation of Mn^{2+} and Zn^{2+} cations under the following conditions: pH 1.5, temperature 40°C, 55 % aqueous solution of H_3PO_4. The content of manganese(II) and zinc in the original hydroxycarbonates (K = Mn/Zn, molar units) was varied from 50.0 to 1.0.

The results of a comprehensive analysis of the solid phase indicate that under these conditions, hydrogen phosphates are deposited in the range of K values from 50.0 to 1.5. In the absence of zinc in the starting reagents, the precipitate is represented by individual $MnHPO_4 \cdot 3H_2O$; its X-ray diffraction and IR spectroscopic characteristics coincide with the known ones [9, 11]. In the case of the presence of the starting reagents of manganese(II) and zinc ($1.5 \leq K \leq 50.0$) in the composition, the zinc content in hydrogen phosphates regularly increases from 0.48 wt.% at K = 50.0 to 2.14 wt.% at K = 1.5; the manganese(II) content is adequately reduced (Table 3). The precipitation under conditions of $K < 1.5$ (1.2 and 1.0) is accompanied by a significant change in the content, especially zinc, phosphorus, water, which indicates changes in the phase composition of the precipitate.

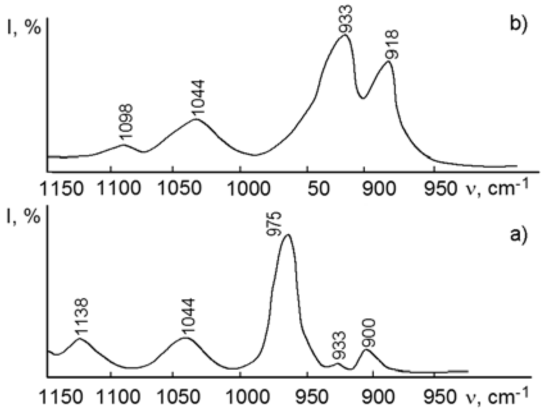

Fig. 4. Raman spectra of the $Mn_{0.8}Co_{0.2}HPO_4 \cdot 3H_2O$ solid solution with newberyite structure (a) and $Co_{0.55}Mn_{0.45}HPO_4 \cdot 1.5H_2O$ (b).

On the diffraction patterns of hydrogen phosphates obtained at $1.5 \leq K \leq 50.0$, there are diffraction reflections and absorption bands characteristic of one crystalline phase, identified as $MnHPO_4{\cdot}3H_2O$ [9]. Analysis of the set of diffraction reflections, their intensities and values of interplanar distances indicates the complete identity of their structures with the structure of matrix hydrogen phosphate — newberyite.

This conclusion is in full accordance with the results of IR spectroscopic studies, since not only the general view of the spectrum, but also the characteristic absorption bands in the spectra of synthesized trihydrates are similar to the spectral data known for $MnHPO_4{\cdot}3H_2O$ [11].

Interpretation of the obtained data testifies to the isomorphic incorporation of zinc into the structure of newberyite and characterizes the hydrogen phosphates obtained at $1.5 \le K \le 50.0$ as a solid substitution solution of the general formula $Mn_{1-x}Zn_xHPO_4{\cdot}3H_2O$. The values of x determined by the results of chemical analysis vary within $0 < x \le 0.07$, indicating the region of homogeneity of the limited solid solution. The composition of phosphate, which is a saturated solid solution, corresponds to the formula $Mn_{0.93}Zn_{0.07}HPO_4{\cdot}3H_2O$. In the composition of hydrogen phosphates formed at $K > 1.5$, along with the solid solution, an impurity phase is fixed — medium zinc phosphate tetrahydrate.

The ability of cobalt(II) and zinc to isomorphic substitution of manganese(II) in the structure of newberyite was assessed using the dimensional criterion (Δr_i) and differences in the nature of the bonds they form ($\Delta\chi$); the widest range of homogeneity is expected for co-precipitation of Mn^{2+} and Zn^{2+} (Δr_i for this pair is 8.99 %, $\Delta\chi = 0.2$, for the pair Mn^{2+} and Co^{2+} $\Delta r_i = 10.22$ %, $\Delta\chi = 0.4$). The obtained experimental data indicate that when the chemical properties (primarily solubility) of individual precipitated phosphates are different, a theoretical assessment of the homogeneity regions of limited solid solutions is impossible, because the contribution of this very factor is decisive for them.

4. Conclusions

The conditions of co-precipitation of isomorphic cations Mn^{2+} and Mg^{2+}, Mn2+ and Co^{2+}, Mn^{2+} and Zn^{2+} in the form of hydrogen phosphates are determined. Three solid solutions with the newberyite structure of the compositions: $Mn_{1-x}Mg_xHPO_4{\cdot}3H_2O$ ($0 < x < 1.00$), $Mn_{1-x}Co_xHPO_4{\cdot}3H_2O$ ($0 < x \le 0.2$) and $Mn_{1-x}Zn_xHPO_4{\cdot}3H_2O$ ($0 < x \le 0.07$), have been synthesized.

It has been shown that these solid solutions are formed due to the isomorphic substitution of the manganese(II) cation in the crystal lattice of the hydrogen phosphates matrix. The regions of homogeneity of the solid solutions vary widely: from continuous, as in $Mn_{1-x}Mg_xHPO_4{\cdot}3H_2O$ ($0 < x < 1.00$), to limited by a narrow range of homogeneity as in $Mn_{1-x}Co_xHPO_4{\cdot}3H_2O$ ($0 < x \le 0.2$) and $Mn_{1-x}Zn_xHPO_4{\cdot}3H_2O$ ($0 < x \le 0.07$).

The formation of solid solutions occurs both on the basis of the structure of one of the individual phosphates that co-precipitated (for example, $Mn_{1-x}Zn_xHPO_4{\cdot}3H_2O$) and isodimorphic salts. An example of the implementation of this interaction is the precipitation of Mn^{2+} and Co^{2+} cations in the form of hydrogen phosphates with the general formulas $Mn_{1-x}Co_xHPO_4{\cdot}3H_2O$ ($0 < x \le 0.2$), $Co_{1-y}Mn_yHPO_4{\cdot}1.5H_2O$ ($0 < y \le 0.45$). The fact that there are different limits of homogeneity is confirmed by the characteristics of the co-precipitated cations.

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