

SYNTHESIS OF ZINC AND MANGANESE PHOSPHATES SOLID SOLUTION

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The phosphates of polyvalent metals, due to their chemical properties and thermal stability, are widely used to produce active catalysts for organic synthesis reactions. It has repeatedly stated that the complex salt have greater catalytic effect than the individual.

The purpose of this work is to synthesize solid solutions of hydrated zinc and manganese(II) phosphates.

The solid solution of zinc and manganese(II) dihydrogenphosphate were synthesized by crystallization at 25 °C from phosphate solutions. The solutions were prepared by the interaction of phosphoric acid (64.15 mas.% P₂O₅), taken in the amount of 180 % of the stoichiometric composition, with a mechanical mixture of zinc (77.25 mas.% ZnO) and manganese(II) (67.43 mas.% MnO) hydroxocarbonates. Ratio $K = \text{Zn}^{2+}/\text{MnO}^{2+}$ in this mixture ranged from 0 to 100 mole %. Identification of the synthesized phosphates was carried out using chemical, X-ray, IR spectroscopy. Raman spectrums were recorded on a modernized DFS-24.

Chemical analysis of phosphates obtained by interaction of Zn and Mn(II) hydroxocarbonates with phosphoric acid, showed that in their composition at the same time there are two cations – zinc and manganese. The ratio of $\text{P}/\sum\text{Zn,MnO}$ (atomic) is almost constant throughout the range of values of K ($0.05 < K < 10.00$) and corresponds to the calculated for dihydrogenphosphate (tabl.).

Table. Characteristics of zinc-manganese(II) dihydrogenphosphates dihydrates

Composition of initial reagents, $K = \text{Zn}/\text{Mn}$, atomic	Composition of solid phase					
	mas. %				Chemical	Phase
	Zn	Mn	P	H ₂ O		
-	22.03	-	20.97	24.37	$\text{Zn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	$\text{Zn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$
10.0	20.62	1.40	21.00	24.43	$\text{Zn}_{0.93}\text{Mn}_{0.07}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	Solid solution $\text{Zn}_{1-x}\text{Mn}_x(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, $0 < x < 1.0$ monoclinic system, sp. gr. $P2_1/n$, $Z=2$
9.00	19.98	1.99	21.03	24.42	$\text{Zn}_{0.90}\text{Mn}_{0.10}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	
2.00	17.95	3.82	21.01	24.45	$\text{Zn}_{0.81}\text{Mn}_{0.19}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	
1.00	10.92	10.19	21.06	24.70	$\text{Zn}_{0.49}\text{Mn}_{0.51}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	
0.25	5.85	15.01	21.12	24.80	$\text{Zn}_{0.26}\text{Mn}_{0.74}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	
0.13	4.24	16.22	21.10	24.91	$\text{Zn}_{0.19}\text{Mn}_{0.81}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	
0.10	2.82	18.35	21.16	24.93	$\text{Zn}_{0.09}\text{Mn}_{0.91}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	
0.05	1.30	19.18	21.14	24.91	$\text{Zn}_{0.06}\text{Mn}_{0.94}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	$\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$
-	-	20.00	21.45	24.93	$\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	

X-ray investigations established that they are the only crystalline phase. The general formula can be presented in the form of $\text{Zn}_{1-x}\text{Mn}_x(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. The values of x defined on results a chemical analysis change from 0 to 1.0, characterizing formation of continuous solid solution of substitution. $\text{Zn}_{1-x}\text{Mn}_x(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ($0 < x < 1.0$) is crystallized in monoclinic system (sp. gr. $P2_1/n$, $Z=2$). They of the same types on a structure with individual $\text{Zn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, that are the border representatives of solid solution with $x = 0$ and 1.0, accordingly.

Analysis of the IR and Raman spectrums of $\text{Zn}_{1-x}\text{Mn}_x(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ different composition showed that at retaining all types of vibrations the total spectral pattern changes, reflecting the influence of the cation nature.