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Composition and the chemical nature of products of interaction in system $CoSO_4 – ZnSO_4 – K_4P_2O_7 – H_2O$

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Hydrated cobalt (II) and zinc diphosphates are used as a basis of of various modern materials: luminescent materials, catalysts of organic synthesis, pigments, heat-sensitive paints, corrosion-resistant coatings etc. Use for this solid solutions of cobalt (II) and zinc diphosphates, which contain both cations will create materials with a forecast complex of improved physico-chemical and production characteristics. For practical implementation synthesis of solid solution of hydrated cobalt (II) and zinc diphosphates of given composition necessary to know the correlation between the conditions of its preparation, composition and properties. There are any data on the interaction of the system $CoSO_4 – ZnSO_4 – K_4P_2O_7 – H_2O$ in literature. The purpose of this work - identify the chemical nature of the products of interaction in the system $CoSO_4 – ZnSO_4 – K_4P_2O_7 – H_2O$.

As parameters, providing a common deposition Co^{2+} and Zn^{2+} in the system $CoSO_4 – ZnSO_4 – K_4P_2O_7 – H_2O$, defined as follows: concentration of solutions - 0.1 mole/l; a ratio in composition of initial solutions $n = P_2O_7^{4-}/\sum Co^{2+}$, $Zn^{2+} = 0.2$; $4.00 \le K = Co^{2+}/Zn^{2+} \le 49.00$; duration of contact of a solidphase with a mother solution – on achievement of equilibrium; temperature - 293-298 K.

The results of chemical analysis of the equilibrium solid phase obtained for all values K of field $4.00 \le K \le 49.00$ including the case when Zn^{2+} as part of the initial solution is absent, indicate precipitation of diphosphates (atomic ratio $n_1 = P/\Sigma Co, Zn = 1.00$). They anionic composition at 98.7-99.2 %. presented diphosphate anion. Diphosphates cationic composition is determined by the K consisting of the initial solution and it is proportional to the content of Co^{2+} and Zn^{2+}. The water content of diphosphate obtained under conditions $9.00 \le K \le 49.00$ virtually unchanged and corresponds to the value set $Co_2P_2O_7 \cdot 6H_2O$ (incl substitution proportion of Co(II) to Zn). In diphosphate, which are deposited at $4.00 \le K < 9.00$, H_2O content of 5 - 6% lower compared with the first group diphosphate.

As a result of X-ray diffraction analysis diphosphate, which formed in the absence of Zn^{2+}, identified as cobalt(II) diphosphate hexahydrate. The diphosphates, which containing simultaneously two cations ($4.00 \le K < 9.00$), are divided into two different groups for the phase composition. The first of them belong diphosphates that are deposited under conditions of $9.00 \le K \le 49.0$, the second - $4.00 \le K < 9.00$. X-ray characteristics of the first group diphosphates are similar to each other and corresponds to $Co_2P_2O_7 \cdot 6H_2O$. X-rays of diphosphate obtained at K = 5.67 and 4.00, clearly recorded the presence of a second crystalline phase of structure $Zn_2P_2O_7 \cdot 5H_2O$. Any phase composition of the two groups diphosphates clearly reflected in their IR spectrums. Shapes of the curves, set the intensity maxima and absorption bands in the IR spectrums diphosphate obtained at $9.00 \le K \le 49.0$, identical to each other and correspond to a known individual $Co_2P_2O_7 \cdot 6H_2O$. IR spectrums of diphosphates of second group have certain features characteristic of a mechanical mixture of two phases with different structures - $Co_2P_2O_7 \cdot 6H_2O$ and $Zn_2P_2O_7 \cdot 5H_2O$.

Most clearly, they are recorded in the vibrations of water molecules, where the absorption curve looks like a total envelope of vibrations ν(OH) belonging diphosphates of different hydrated.

Using complex physical and chemical methods revealed that during the interaction in the system $CoSO_4 – ZnSO_4 – K_4P_2O_7 – H_2O$ formed limited solid solution substitution of general formula $Co_{2-x}Zn_xP_2O_7 \cdot 6H_2O$ ($0<x\leq0.39$) The composition of the saturated solid solution corresponds diphosphate $Co_{1.61}Zn_{0.39}P_2O_7 \cdot 6H_2O$. It is formed as a result of isomorphic substitution of Co(II) in the structure diphosphate-matrix - $Co_2P_2O_7 \cdot 6H_2O$ in Zn. Attempts to replace Zn over 6.31 mas.% of Co(II) lead to the deposition of a mechanical mixture of two crystalline phases - saturated solid solution substitution $Co_{1.61}Zn_{0.39}P_2O_7 \cdot 6H_2O$ and phase structure $Zn_2P_2O_7 \cdot 5H_2O$. $Co_{2-x}Zn_xP_2O_7 \cdot 6H_2O$ ($0<x\leq0.39$) crystallize in the monoclinic system (sp. gr. $P2_1/n$, Z=4). For saturated solid solution of composition $Co_{1.61}Zn_{0.39}P_2O_7 \cdot 6H_2O$ the unit cell parameters are, nm: a = 0.7199 (3), b = 1.8356 (4), c = 0.7680 (3), V = 1.0410 $нм^3$, β = 92.25^0 (5). In the IR spectrums of $Co_{2-x}Zn_xP_2O_7 \cdot 6H_2O$ ($0<x\leq0.39$) presence of isomorphous cations (Zn^{2+}) recorded a slight shift of the bands ν (OH) in the high-frequency region of the spectrum. Evaluation of H-bonds energy indicates the existence of a structure of diphosphates of solid solution the system rather strong H-bonds, which differ in energy (from 11.3 to 43.3 kJ/mole) and directivity. The three components of the band $\delta(H_2O)$ indicate the presence in the diphosphate structure of three types of crystallographical non-identical molecules of crystalline hydrate water. Number of absorption bands in the fluctuations groups of $P_2O_7^{4-}$ indicates low symmetry of diphosphate anion, which is characteristic curved bridge configuration P–O–P. POP angle is less than 160^0 and in diphosphates of solid solution $Co_{2-x}Zn_xP_2O_7 \cdot 6H_2O$ ($0<x\leq0.39$) of different composition does not change.