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Thermal solidphase transformations of hexahydrates Co(II)-Zn diphosphates

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The inorganic phosphatic materials obtained on the basis of anhydrous salts are widely used as active catalysts, pigments, luminescent materials, phosphate glasses etc. There are the literature data for obtaining solid solutions of anhydrous diphosphates by solidphase interaction of individual salts. They can also be obtained by thermal treatment of the corresponding crystallohydrates. The knowledge of the sequence of the thermal transformations, which accompany dehydration of crystallohydrates, is necessary both for controlling this process and for obtaining the products of the given composition. There are no literature data on hydrated solid solutions of Co (II) and Zn mono- and diphosphates.

The purpose of the present work is to establish the sequence of solid thermal transformation, composition, temperature ranges formation and thermal stability of the partial and complete dehydration products of diphosphate of solid solution $Co_{2-x}Zn_xP_2O_7 \cdot 6H_2O$ ($0<x\leq 0.39$).

The saturated solid solution of composition $Co_{1.61}Zn_{0.39}P_2O_7 \cdot 6H_2O$ was used as the main object of study. $Co_{1.61}Zn_{0.39}P_2O_7 \cdot 6H_2O$ stable when it heated in air at 5 °/min to 358 K according to the termoanalytical research. A further increase in temperature is accompanied by mass loss, which is recorded on the TG curve of two distinct steps in the interval 358 - 513 K and 558 – 698 K. Comprehensive analysis of the dehydration product obtained by heating of $Co_{1.61}Zn_{0.39}P_2O_7 \cdot 6H_2O$ to 463 and 513 K (the first stage of dehydration), shows that the removal of 3.95 and 0.28 mole H_2O, respectively, accompanied by the formation of a mixture of diphosphates. One of them is identified by X-ray and IR spectroscopic characteristics as dihydrate with structure $Co_{1.61}Zn_{0.39}P_2O_7 \cdot 2H_2O$. Second - as a starting hexahydrate $Co_{1.61}Zn_{0.39}P_2O_7 \cdot 6H_2O$. The quantitative correlations between of them with increase of temperature from 463 to 513 K are changing for the dihydrate. Installed adjustment indicate that crystalline-hydrated water removed in the form of molecular units when heated $Co_{1.61}Zn_{0.39}P_2O_7 \cdot 6H_2O$ in the range of 358 - 513 K. The results of the chromatographic analysis of the thermolysis products of $Co_{1.61}Zn_{0.39}P_2O_7 \cdot 6H_2O$, obtained at 558 and 633 K (the second stage of dehydration, total removal of water is 1.50 mole) indicate the realization of two simultaneous processes: destruction of dyphosphate anion and anionic condensation. In the course of the first of theme indicates an increase in their composition monophosphate content (from 1.5 to 6.8 mas. %) and reduction of diphosphate (from 17.2 to 11.6 mas.%.); diphosphate degree of conversion is 32%. The presence of polyphosphates with degree of polycondensation ($\bar{n}$) equal to 7 indicates to anionic condensation process. Established transformation indicate that the water in the range 513 - 633 K removed by dissociative mechanism, and participating in intramolecular salt hydrolysis. Mono- and polyphosphates which formed as a result of its implementation are X-ray amorphous. For further removal of water (total mass loss at 698 K are 5.86 mole H_2O) anionic composition of thermolysis products is simplified, and on the X-ray

diffractions and IR spectrums recorded beginning formation of the crystal structure of anhydrous α-$Co_{1.61}Zn_{0.39}P_2O_7$. The crystallization of α-$Co_{1.61}Zn_{0.39}P_2O_7$ completed at 843 K (temperature of complete dehydration of hexahydrate $Co_{1.61}Zn_{0.39}P_2O_7 \cdot 6H_2O$). Further its heating to 1273 K leads to an increase in intensity of reflections on X-ray diffractions of α-diphosphate, which characterizing improving its structure and thermal stability in the range of 843 - 1273 K. α-$Co_{1.61}Zn_{0.39}P_2O_7$ crystallizes in monoclinic system (sp. gr. $P2_1/c$, Z = 2) with unit cell parameters, nm: a = 0.6999 (2), b = 0.8337 (4), c = 0.9003 (3), β = 111.7° (14), V = 0.4813 (5) $нм^3$.

The cation nature influences the temperature regimes of formation of partial and full anhydrous diphosphates (with other things being equal of dehydration). So, for the diphosphates $Co_{2-x}Zn_xP_2O_7 \cdot 6H_2O$ with decrease of the *x* value from 0 up to 0.39 the intervals of all stages of process are displaced by 5 - 25 degree in area of the lower temperatures.

So, thermolysis of diphosphates of solid solution $Co_{2-x}Zn_xP_2O_7 \cdot 6H_2O$ ($0<x\leq0.39$) occurs simultaneously in two directions, which leading to the formation of solid solution of anhydrous diphosphates α- $Co_{2-x}Zn_xP_2O_7$ ($0<x\leq0.39$) as the final product. The first direction is realized by 69 - 62% and provides for the formation of α- $Co_{2-x}Zn_xP_2O_7$ due to the molecular mechanism of removal of crystalline-hydrated water. Under the second, the contribution of which is 31 - 38%, the formation of α- $Co_{2-x}Zn_xP_2O_7$ occurs as a result of solid-phase interaction of intermediates products of dehydration of $Co_{2-x}Zn_xP_2O_7 \cdot 6H_2O$ by dissociative mechanism.