THE SOLIDPHASE SYNTHESIS OF COBALT AND MANGANESE(II) CYCLOTETRAPHOSPHATES SOLID SOLUTION

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Work carried out in terms of expansion of assortment of anhydrous polymer phosphate with controlled composition and properties. They are basis of many modern inorganic materials such as catalysts in organic synthesis, corrosion-resistant coatings etc.

With the purpose of determination the conditions of solidphase synthesis of cobalt and manganese(II) cyclotetraphosphates solid solution the compositions of the products of partial and complete dehydration of $Co_{1-x}Mn_x(H_2PO_4)_2 \cdot 2H_2O$ ($0<x<1.0$) in a dynamic (speed of 2.5, 5, 10 deg/min., Q-1500D derivatograph, Al_2O_3 standart) and isothermal regimes of heating were investigated.

Results of termoanalytical researches have shown, that heating them to 160-190 °C (depending on cations) does not lead to condensing monophosphate anion. The formation of polyphosphates of general formula $(Co_{1-x}Mn_x)_{(n+2)/2}P_nO_{3n+1}$ with the linear structure of anion takes place for the increase of temperature to 210-290 °C.

The degree of polycondensation phosphate anion (n) depends on the temperature of heating and cationic composition of initial phosphate and varies from 2 to 9. At heating, for example, of dihydrogenphosphate of composition $Co_{0,5}Mn_{0,5}(H_2PO_4)_2 \cdot 2H_2O$ to 225 °C formed are linear polyphosphates containing a chain of up to six phosphorus atoms. The value of n increases to nine at the increase of temperature of heating to 255 °C.

Researches of phosphates that form on every stage of dehydration of initial crystallohydrates showed that in products them partial dehydration there is a selection of free phosphoric acids. They participate in formation of fully water-free phosphate. Heating of dihydrogenphosphates at 330-370 °C in the conditions of the dynamic (speed 2.5; 5.0; 10.0 hail/min) and isothermal regimes of heating leads to formation of the condensed phosphates of composition of $(Co_{1-x}Mn_x)_2P_4O_{12}$ ($0<x<1.0$) with the fundamentally different structure of anion – cyclic.

The solid-phase synthesis of anhydrous solid solution cyclotetraphosphates general formula $(Co_{1-x}Mn_x)_2P_4O_{12}$ ($0<x<1.0$) implemented in two parallel routes of process. The first of these supposes dehydration of acidic of low molecular of condensed phosphates. The second is the interaction of free polyphosphate acids with middle condensed phosphates. Quantitative ratio of process directions of determined by the nature of the cation. By increasing the Mn(II) content in the composition of solid solutions increases the number of phosphoric acids released. Proportion of their participation in the formation of anhydrous cyclotetraphosphate increases to 20-25 % (second route).

Anhydrouses cyclotetraphosphates composition of $(Co_{1-x}Mn_x)_2P_4O_{12}$ are crystalline compounds, the ratio of cations in the composition of which changes in the wide limits (CoO – 22.0-0,1 wt.%; MnO – 0.1-34 wt.%). They are crystallized in monoclinic (the space group C2/c, Z=4). Parameters of unit cells of the crystal lattices are changed according to law Veharda. This indicates the chemical nature $(Co_{1-x}Mn_x)_2P_4O_{12}$ as continuous solid solution, that composition is varied in the range $0<x<1.00$.

The temperature regimes of solidphase synthesis $(Co_{1-x}Mn_x)_2P_4O_{12}$ are 330-370 ºC. They are determined by the ratio of cations consisting of the original crystallohydrate and grow by 10-20 degrees with increasing content of Mn(II). The synthesized cyclotetraphosphates are stable when heated to 1000 ºC.