

Thermal solid-phase transformations of hydrated Zn-Co(II) diphosphates

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Dedicated to Evgen I. Gladyshevskii (1924-2012)

Received May 25, 2013; accepted June 26, 2014; available on-line November 10, 2014

The sequence of physico-chemical and structural transformations occurring during the thermolysis of the solid solution of diphosphates of composition $Zn_{2-x}Co_xP_2O_7 \cdot 5H_2O$ ($0 \leq x \leq 0.69$) has been established. The composition, temperature ranges of formation and the thermal stability of the products of partial and complete dewatering have been determined. The final thermolysis product, the solid solution of anhydrous diphosphates $\alpha-Zn_{2-x}Co_xP_2O_7$ ($0 \leq x \leq 0.69$), has been identified. It is shown that the formation proceeds via two routes. The first route consists in thermal dehydration of the original diphosphate (up to 57-63 %). Along the second route, up to 43-37 % $\alpha-Zn_{2-x}Co_xP_2O_7$ is formed by solid-phase reaction of partial dehydration products. A general scheme of the solid-phase thermal transformations of $Zn_{2-x}Co_xP_2O_7 \cdot 5H_2O$ ($0 \leq x \leq 0.69$) is proposed.

Thermolysis / Thermal dehydration / Destruction / Diphosphates

Introduction

Inorganic phosphate materials on the basis of anhydrous diphosphates are widely used as active catalysts, pigments, phosphate glasses, heat sensitive dyes, luminescent materials, etc. [1-3].

One way to obtain anhydrous salts is the thermal treatment of crystalline hydrates, accompanied by complex physico-chemical and structural transformations. To master the process and obtain products of given composition and quality requires knowledge about the sequence of thermal transformations that accompany the dehydration of the crystalline hydrates, composition, temperature ranges of formation and the thermal stability for partial and complete dehydration.

The thermal behavior of the parent $Zn_2P_2O_7 \cdot 5H_2O$ diphosphate matrix, on the basis of which the solid solution of the hydrated Zn-Co(II) diphosphate is formed, has been investigated earlier [4-6]. The thermal solid-phase transformations of diphosphates of the solid solution of $Zn_{2-x}Co_xP_2O_7 \cdot 5H_2O$ ($0 \leq x \leq 0.69$), which are largely dependent on the nature of the cation, have not yet been described in the literature.

The aim of this study was to determine the sequence of physico-chemical and structural transformations taking place during the thermolysis of hydrated solid solution Zn-Co(II) diphosphates, the composition and temperature ranges of formation and thermal stability of the products of partial or complete dehydration.

Experimental

Solid solutions of hydrated diphosphates $Zn_{2-x}Co_xP_2O_7 \cdot 5H_2O$ ($0 \leq x \leq 0.69$) were prepared by reacting aqueous solutions of the system $ZnSO_4-CoSO_4-K_4P_2O_7-H_2O$, as described in [7]. As main object of the study we used a saturated solid solution of $Zn_{1.31}Co_{0.69}P_2O_7 \cdot 5H_2O$.

The thermal transformations were studied in the temperature range 298-1273 K in dynamic (derivatograph Q-1500 D, platinum crucible with a lid, reference freshly burnt Al_2O_3 , sample weight 100-300 mg, heating rate 5 K/min, temperature uncertainty ± 5 K) and quasi-isothermal (conical holder samples, sample weight 200 mg, heating rate 3 K/min) heating mode.

The heat-treatment products obtained after reaching the temperatures of the peaks on the DTA and DTG curves, were identified using a combination of methods of analysis: chemical, X-ray powder diffraction (DRON 4G, connected to a computing system based on a computer IBM type PC/AT 486, Fe $K\alpha$, internal standard NaCl), and IR spectroscopy (Nexus-470; tableting fixed sample in a KBr matrix). The anionic products of partial and complete dehydration were determined by quantitative paper chromatography [2].

Results and discussion

The thermal analysis showed that the $Zn_{1.31}Co_{0.69}P_2O_7 \cdot 5H_2O$ compound is stable when heated in air to 333 K (heating rate 5 K/min.) Further increase of the temperature to 725 K was accompanied by weight loss, which occurred in three major stages (Fig. 1).

The first and second stages are almost unresolved on the TG curve under the conditions of heating used

here. On the DTA curve they are indicated by two partially superimposed endothermic effects (333-408 and 408-488 K).

At the third stage of dehydration of $Zn_{1.31}Co_{0.69}P_2O_7 \cdot 5H_2O$ (488-603 K), processes take place that are shown on the TG curve by a slope portion corresponding to the removal of 0.40 mole H_2O . Upon further heating to 628 K a relatively clear weight loss step (0.33 mol H_2O) appears. It corresponds to a broad endothermic effect on the DTA curve (628-725 K) with a maximum at 658 K. The last amount of water (0.1 mol) is removed by heating to 831 K.

The thermolysis of $Zn_{1.31}Co_{0.69}P_2O_7 \cdot 5H_2O$ under quasi-isothermal conditions, where the partial water vapor pressure above the sample increases from 20 kPa (platinum crucible with a lid) to 71-81 kPa (for conical sample holder), is different (Fig. 1, curve 2). Under these conditions, the first and second stages of dewatering occur separately. The result of the first step is the removal at a constant temperature (365 K) of 1.60 mole H_2O .

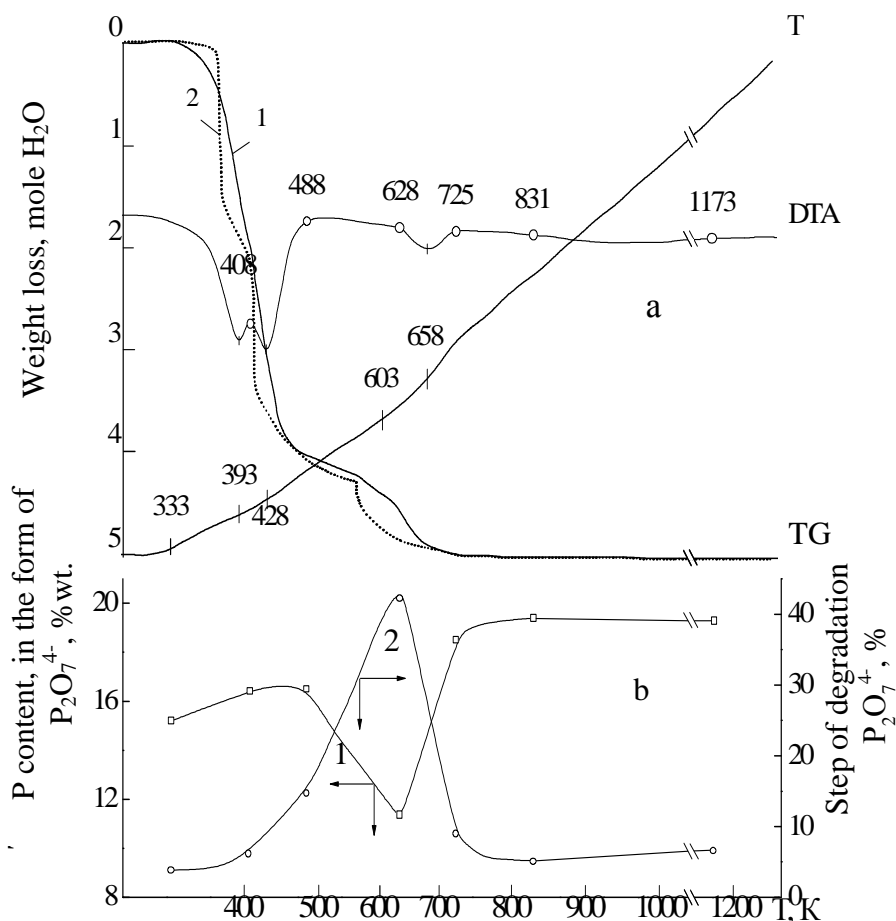


Fig. 1 Investigation of the thermolysis of $Zn_{1.31}Co_{0.69}P_2O_7 \cdot 5H_2O$ by differential thermal analysis (DTA) and thermogravimetry (TG):

a – thermal analysis curves in dynamic (1) and quasi-isothermal (2) heating mode,
b – temperature dependence of the content of diphosphate (1) and the degree of degradation (2) in the thermolysis products;

–o– – sampling points for the analysis.

The second stage is revealed by two different features on the TG curve, showing the nature of the weight loss. The first of these describes the removal at an approximately constant temperature (410 K) of another 1.40 mole H₂O. The second one is a kind of sloping curve, which corresponds to the removal of 0.89 mole H₂O over a fairly wide range of temperatures (410-545 K).

The TG curve describing the mass loss at the third stage (545-680 K) has a form that is characteristic of irreversible reactions [8]. Under these conditions, it may correspond to processes of thermal degradation. Overheating, established by prior removal of the last 0.71 mole H₂O in the range 550-680 K, illustrates the difficulty of crystallization of a new solid phase. This actually corresponds to an induction period before the start of the next thermal and structural transformations. According to the classification of processes under isothermal conditions [8] condensation reactions occur simultaneously with the crystallization of the final products of the thermolysis

of Zn_{1.31}Co_{0.69}P₂O₇·5H₂O. Dehydration is fully completed at 695 K.

Analysis of the products obtained at all the stages of the dehydration of Zn_{1.31}Co_{0.69}P₂O₇·5H₂O, showed that the removal of 2.05 mole H₂O (333-408 K) is accompanied by the formation of a mixture of diphosphates with lower water contents. These were identified, on the basis of X-ray diffraction patterns of the products of partial dehydration of parent Zn₂P₂O₇·5H₂O [5,6], as Zn_{1.31}Co_{0.69}P₂O₇·3H₂O and Zn_{1.31}Co_{0.69}P₂O₇·2H₂O (Table 1). The IR spectra of these diphosphates mainly differ in the vibrations of the water molecules (Fig. 2): decrease of the amount of absorption bands in the region of vibrations of ν(OH) (shoulder disappears at 3097 cm⁻¹) and δ(H₂O) (shoulder at 1642 cm⁻¹ and band at 1631 cm⁻¹ are combined into a strip at 1648 cm⁻¹).

This indicates the removal of one of the three types of non-identical water molecule. The character of the absorption corresponding to vibrations of the anionic sublattice is generally retained.

Table 1 X-ray diffraction characteristics (interplanar spacing *d*, relative intensity *I/I*₀) of the products of the thermolysis of Zn_{1.31}Co_{0.69}P₂O₇·5H₂O (dynamic mode, heating rate 5 K/min).

Zn _{1.31} Co _{0.69} P ₂ O ₇ ·5H ₂ O 333 K		408 K		488 K		725 K		Zn _{1.31} Co _{0.69} P ₂ O ₇ 831-1173 K	
<i>d</i> , nm	<i>I/I</i> ₀	<i>d</i> , nm	<i>I/I</i> ₀	<i>d</i> , nm	<i>I/I</i> ₀	<i>d</i> , nm	<i>I/I</i> ₀	<i>d</i> , nm	<i>I/I</i> ₀
1.272	100	1.085	100	0.909	100	0.398	20	0.508	5
0.793	6	0.749	15	0.740	55	0.353	10	0.436	5
0.636	28	0.615	17	0.502	32	0.301	100	0.382	4
0.594	10	0.537	26	0.415	13	0.254	30	0.333	4
0.553	15	0.469	19	0.384	20	0.210	27	0.301	100
0.502	19	0.407	9	0.314	10	0.1856	15	0.2834	5
0.456	9	0.355	50	0.2959	27	0.1572	10	0.2548	25
0.443	11	0.308	30	0.2855	27	0.1484	8	0.2309	5
0.431	10	0.2972	23	0.2659	26	0.1373	8	0.2161	8
0.415	8	0.2834	20	0.2543	13	0.1257	7	0.2106	20
0.371	12	0.2572	15	0.2307	15	–	–	0.2018	6
0.363	14	0.2350	19	0.1760	10	–	–	0.1856	8
0.350	22	0.2046	19	–	–	–	–	0.1701	4
0.326	13	0.1917	13	–	–	–	–	0.1613	8
0.316	30	0.1539	15	–	–	–	–	0.1578	11
0.306	15	–	–	–	–	–	–	0.1546	3
0.304	6	–	–	–	–	–	–	0.1478	7
0.2853	10	–	–	–	–	–	–	0.1388	4
0.2701	15	–	–	–	–	–	–	0.1323	4
0.2608	11	–	–	–	–	–	–	0.1259	3
0.2536	14	–	–	–	–	–	–	–	–
0.2372	8	–	–	–	–	–	–	–	–
0.2365	8	–	–	–	–	–	–	–	–
0.2156	12	–	–	–	–	–	–	–	–
0.2030	16	–	–	–	–	–	–	–	–
0.1955	10	–	–	–	–	–	–	–	–
0.1910	8	–	–	–	–	–	–	–	–
0.1751	10	–	–	–	–	–	–	–	–

With further increase of the temperature to 488 K (the second dehydration step), 1.98 mole H₂O are removed from the crystalline hydrates (the total mass loss reaches 4.03 moles H₂O). A solid phase, identified as the monohydrate Zn_{1.31}Co_{0.69}P₂O₇·H₂O, is formed. Its presence is shown by the appearance of X-ray diffraction reflections similar to those of the parent phosphate Zn₂P₂O₇·H₂O (Table 2). The low intensity of the reflections and the overall diffuse

X-ray spectrum indicate the formation of the crystalline phase together with an amorphous product. It was confirmed by electron microscopy studies that, at the first stage of dehydration of Zn_{1.31}Co_{0.69}P₂O₇·5H₂O, the crystal structure is preserved. The transition to an amorphous solid state at the second stage of dehydration was also observed on the micrographs, and intermediates in the electron dehydration.

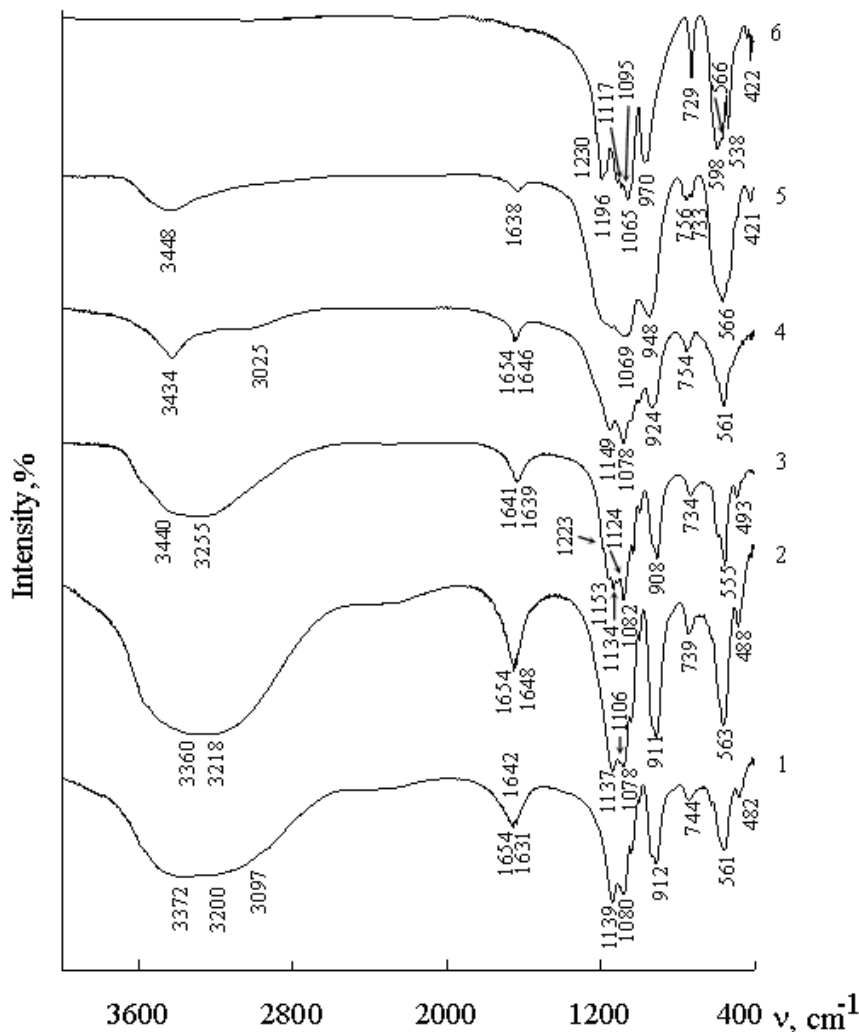


Fig. 2 IR spectra of the products of the thermolysis of Zn_{1.31}Co_{0.69}P₂O₇·5H₂O at 333 (1), 408 (2), 488 (3), 628 (4), 725 (5), and 831-1173 K (6).

Table 2 Anionic composition of the products of the thermolysis of Zn_{1.31}Co_{0.69}P₂O₇·5H₂O.

Temperature, K	Weight loss, mole H ₂ O	P _{total} , wt. %	Phosphorus content, wt.%, in the form of		
			mono-	di-	triphosphate
333	–	15.82	0.6 ^a	15.2	–
408	2.05	17.47	1.1 ^a	16.4	–
488	4.03	19.42	2.9	16.5	–
628	4.57	20.38	7.1	11.2	2.1
725	4.90	20.54	1.5	18.5	0.5
831	5.00	20.55	1.1 ^a	19.4	–

^a Hydrolysis of a diphosphate sample preparation for analysis.

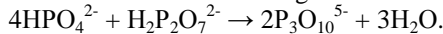
According to the results of the quantitative chromatography, the X-ray amorphous phase is a monophosphate, resulting from partial destruction of the structure of the initial diphosphate (Table 2). The amount of this phase among the dehydration products was 2.9 % by weight (14.9 % of the total phosphorus content).

The IR spectrum of this thermal transformation shows a reduction by more than half of the intensity of the absorption bands of vibration of water molecules.

Among the oscillations observed for the diphosphate anion, the band $\nu_{as}(\text{PO}_3)$ at 1137 cm^{-1} has split into two components with maxima at 1153 and 1134 cm^{-1} and the shoulder at 1106 cm^{-1} has become a band at 1124 cm^{-1} (Fig. 2). The lowering of symmetry describes the lowering of symmetry of the diphosphate anion. In the region of vibrations $\delta(\text{P-OH})$, there is a new absorption band with a maximum at 1223 cm^{-1} . It points to the formation of protonated anions of the types $\text{H}_2\text{P}_2\text{O}_7^{2-}$ and HPO_4^{2-} .

It is harder to remove water from the monohydrate $\text{Zn}_{1.31}\text{Co}_{0.69}\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$, formed as an intermediate product of the dehydration of $\text{Zn}_{1.31}\text{Co}_{0.69}\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ at 488 K . Heating up to 628 K leads to the removal of another portion of water (0.54 mol) from the crystalline hydrate and almost complete destruction of the structure of the diphosphate.

The amount of monophosphates, comprising the amorphous products of the thermolysis, reaches a maximum value of $7.1\text{ wt.}\%$ (Table 2). The degree of degradation of the anion diphosphate is increased to 42.7% . Simultaneously, the presence of amorphous solid triphosphate ($2.1\text{ wt.}\%$) indicates a process of anionic condensation according to:



Further heating of the amorphous mixture to 725 K leads to a simplification of the thermolysis products and the formation of a single crystalline phase: anhydrous diphosphate of composition $\text{Zn}_{1.31}\text{Co}_{0.69}\text{P}_2\text{O}_7$ (Table 2). The X-ray diffraction pattern of this compound is similar to that obtained for anhydrous $\text{Zn}_2\text{P}_2\text{O}_7$ in [6].

In the IR spectrum recorded at 725 K the absorption band corresponding to vibration of water molecules has low intensity. Among the oscillations characteristic of the diphosphate anion observed at the crystallization step, the diphosphate band $\nu_s(\text{POP})$ at 754 cm^{-1} is split into two peaks at 756 and 733 cm^{-1} . This indicates the formation of diphosphates with variable angle POP in the $\text{P}_2\text{O}_7^{4-}$ anions in the solid phase.

Heating of the thermolysis products obtained at 725 K is accompanied by complete dehydration of the diphosphate at 1173 K , improving the structure of the anhydrous crystalline diphosphate identified as $\alpha\text{-Zn}_{1.31}\text{Co}_{0.69}\text{P}_2\text{O}_7$ [9,10].

In IR spectra of $\alpha\text{-Zn}_{1.31}\text{Co}_{0.69}\text{P}_2\text{O}_7$ contain all the absorption bands characteristic of the non-centrosymmetric anion $\text{P}_2\text{O}_7^{4-}$: $\nu_{as}(\text{PO}_3) - 1230, 1196, 1117, 1095\text{ cm}^{-1}$, $\nu_s(\text{PO}_3) - 1065\text{ cm}^{-1}$, $\nu_{as}(\text{POP}) - 970\text{ cm}^{-1}$, $\nu_s(\text{POP}) - 729\text{ cm}^{-1}$, $\delta(\text{PO}) - 598, 566, 538, 422\text{ cm}^{-1}$. $\alpha\text{-Zn}_{1.31}\text{Co}_{0.69}\text{P}_2\text{O}_7$ crystallizes in the monoclinic system (space group $I2/a$, $Z = 12$). The refined unit-cell parameters are: $a = 2.0058(3)$, $b = 0.8259(4)$, $c = 0.9094(3)\text{ nm}$, $\beta = 106.3(9)^\circ$, $V = 1.446\text{ nm}^3$.

Summarizing the findings, the sequence of solid-phase transformations that accompany the thermolysis of $\text{Zn}_{2-x}\text{Co}_x\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ can, with some assumptions, be described by the scheme presented in Fig. 3.

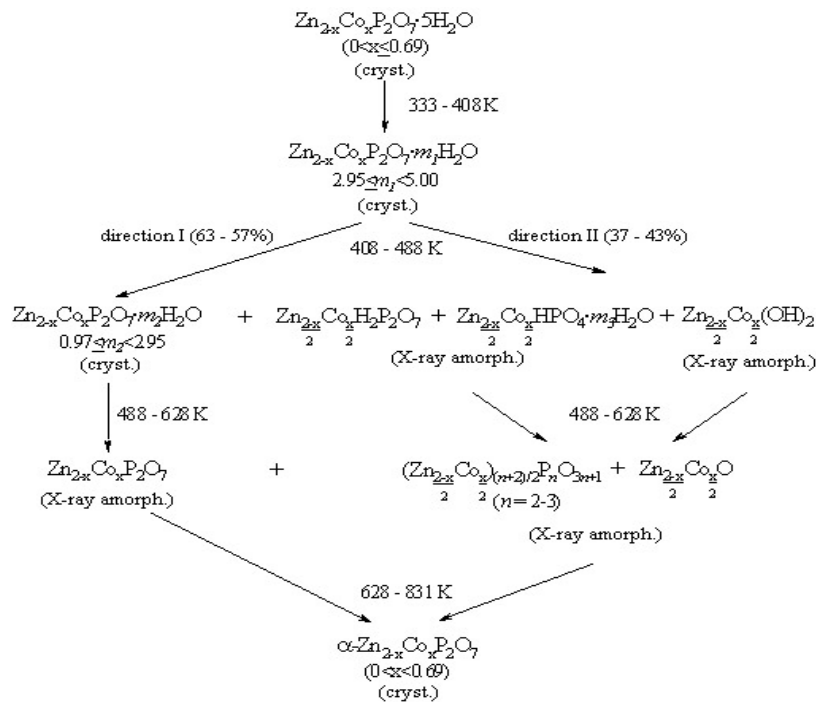


Fig. 3 Reaction scheme for the dehydration of $\text{Zn}_{1.31}\text{Co}_{0.69}\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$.

The proposed sequence of thermal solid-phase transformations is valid for all diphosphates of the solid solution $Zn_{2-x}Co_xP_2O_7 \cdot 5H_2O$ ($0 \leq x \leq 0.69$).

The influence of the nature of the cation is seen in the areas of process, conditions of formation and thermal stability of the products of partial and complete dehydration. In particular, for values of x increasing from 0 to 0.69 the temperatures of formation of the intermediates of the first and second steps of the thermolysis increased by 5-30 degrees, and at the third stage by 60-100 degrees.

Conclusions

The formation of the solid solution α - $Zn_{2-x}Co_xP_2O_7$ ($0 \leq x \leq 0.69$) by thermolysis of the pentahydrate proceeds simultaneously via two alternative routes. The first of these involves the formation of up to 57-63 % anhydrous diphosphates, due to thermal dehydration of the initial crystalline hydrate. The second one produces 43-37 % α - $Zn_{2-x}Co_xP_2O_7$, formed as the result of solid-phase reactions of intermediates in the thermolysis.

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