ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 7, pp. 1153−1159. © Pleiades Publishing, Ltd., 2009.
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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Synthesis and Thermal Properties of $Co_2P_2O_7 \cdot 6H_2O$

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Received May 26, 2008

Abstract—The dependence of solid phase composition on the main parameters of the interaction in the $CoSO_4$–$K_4P_2O_7$–H_2O system was studied. The synthesis conditions were determined and a crystalline cobalt(II) diphosphate of the composition $Co_2P_2O_7 \cdot 6H_2O$ was synthesized. Its thermal properties were studied. The composition and the intervals, wherein the thermally stable products of partial and complete dehydration of $Co_2P_2O_7 \cdot 6H_2O$ are formed, were specified. The final heat treatment product, anhydrous α-$Co_2P_2O_7$, was identified and a sequence of the solid phase thermal transformations accompanying its formation was established.

DOI: 10.1134/S1070427209070015

Hydrated cobalt(II) diphosphates and products of their partial and complete dehydration are inorganic materials widely used as high quality pigments, catalysts of organic synthesis, and thermophosphate decorative coatings [1–3]. Development on their basis of new materials with controllable exploitation characteristics needs knowledge of the synthesis conditions of hydrated salts, their thermal properties, and the composition and temperature intervals, wherein the thermally stable intermediate and final heat treatment products are formed.

Only few studies concerning the synthesis conditions of hydrated cobalt(II) diphosphate are available [4–7]. The authors of [4, 5] gave much attention to the synthesis conditions of double salts, alkali metal and cobalt diphosphates. For example, amorphous diphosphate of composition $Co_2P_2O_7 \cdot 5H_2O$ was obtained in a study of the interaction of cobalt(II) nitrate with potassium diphosphate to establish the conditions for precipitation of double potassium–cobalt(II) phosphates [4]. According to [4], $Co_2P_2O_7 \cdot 5H_2O$ precipitates to form amorphous phase at the ratio $n = P_2O_7^{4-} : Co^{2+} = 0.05–0.54$ of the initial reagents (solutions' concentration 0.5 M, temperature 293 K). Amorphous diphosphate crystallizes during 80 days of contact with a mother solution.

In addition, the preparative data on the synthesis of crystal hydrates of the general formula $Co_2P_2O_7 \cdot xH_2O$ (x = 2, 4, 5, 6, 8) are available [6, 7]. $Co_2P_2O_7 \cdot 6H_2O$ precipitates as amorphous phase upon the interaction of $CoCl_2$ and $Na_4P_2O_7$ solutions [6]. Preparation of crystalline diphosphate hexahydrate needs prolonged (8–18 h) recrystallization from weakly acid solutions at elevated temperatures. In view of the tendency of polymeric phosphate anions to hydrolytic decomposition, the described conditions of $Co_2P_2O_7 \cdot 6H_2O$ synthesis must be refined, because the anionic composition in [6, 7] was not reported.

Data on the systematic study of the conditions of $Co_2P_2O_7 \cdot 6H_2O$ synthesis are lacking from the literature.

In [8], the thermal properties of $Co_2P_2O_7 \cdot 6H_2O$ were described and the dehydration and phase transformations of hexahydrate were presented by a simplified scheme:

$$Co_2P_2O_7 \cdot 6H_2O \xrightarrow{336–388°C} Co_2P_2O_7 \cdot 2H_2O$$

$$\xrightarrow{388–550°C} Co_2P_2O_7 \text{ (amorphous)}$$

$$\xrightarrow{575–624°C} 6\ \alpha\text{-}Co_2P_2O_7 \text{ (crystalline).}$$

However, the above scheme does not take into account the actual process and the composition of intermediate dehydration products, which, as shown by results obtained in studying the hydrated diphosphates in [9], is more complex and accompanied by the formation of a mixture of condensed phosphates.

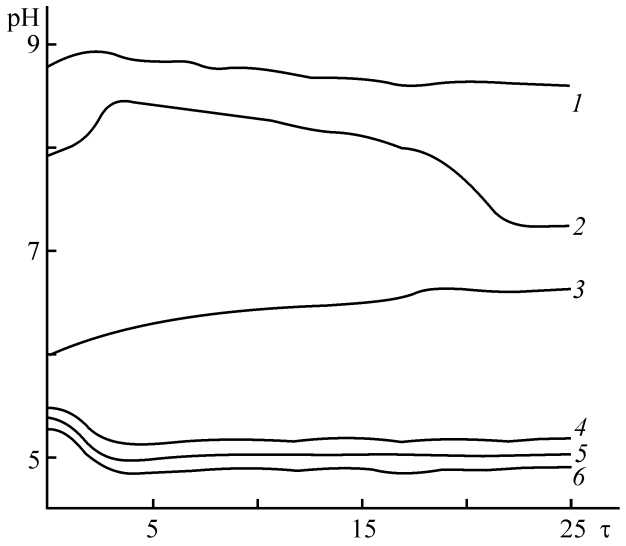


Fig. 1. pH of the mother solutions in the $CoSO_4$–$K_4P_2O_7$–H_2O system vs. the interaction time τ (day) (isomolar series of 0.1 M solutions) at different ratios of the starting solutions. (n = $P_2O_7^{4-}/Co^{2+}$): (*1*) 0.6, (*2*) 0.5, (*3*) 0.4, (*4*) 0.3, (*5*) 0.2, and (*6*) 0.1.

In this study, the conditions for synthesis of crystalline $Co_2P_2O_7 \cdot 6H_2O$ were determined, its thermal properties were studied, and the intervals, wherein the thermally stable heat–treatment products are formed, were specified.

EXPERIMENTAL

We used aqueous solutions of $CoSO_4 \cdot 7H_2O$ and $K_4P_2O_7$ (both analytical purity grade) as starting reagents. For obtaining reliable data on the conditions of the $Co_2P_2O_7 \cdot 6H_2O$ formation by the interaction in the $CoSO_4$–$K_4P_2O_7$–H_2O system, the dependence of the solid phase composition on the main parameters of the process was determined in some experiments [10]. The ratio $n = P_2O_7^{4-}:Co^{2+}$ of the starting solutions was varied within 0.10–0.60 and the concentration of solutions, within 0.05–0.50 M. The time of contact of the solid phase with a mother solution was established till attaining the equilibrium**.** The interaction was performed within 293–298 K. While choosing the recrystallization conditions, we controlled anionic composition.

The content of phosphorus in diphosphate was determined by the gravimetric quinoline molybdate method [11]. The Co^{2+} content was determined specrometrically (SF–46 spectrophotometer), as in [12]. The content of water was calculated from the mass loss after heating to 1073 K.

The composition of the solid phase was identified by the X–ray phase analysis (DRON–4–M diffractometer, $Fe_{K\alpha}$ radiation, NaCl inner standard) and IR spectroscopy (Nexus–470 spectrometer, frequency range 400–4000 cm^{-1}, 0.05% samples pressed into potassium bromide pellets).

The thermal properties of $Co_2P_2O_7 \cdot 6H_2O$ within the temperature range 298–1268 K were studied. Samples (300 mg) were heated in the dynamic mode at a rate of 5 deg min^{-1}. We used a Q–1500D derivatograph and platinum crucibles with a lid; reference was freshly calcined Al_2O_3. The temperature was measured to within 5 deg min^{-1}.

The heat treatment products obtained at temperatures corresponding to the thermal effects on the DTA curve were analyzed by a complex of methods, including chemical, X–ray diffraction, and IR spectroscopic analyses. The anionic composition of hydrated diphosphates and dehydration products was determined by quantitative paper chromatography [13].

The analysis of the curves describing variations of pH of the mother solution at different n ratios shows that the interactions at $0.1 \le n \le 0.3$ have many similar features (Fig. 1). On passing to $n = 0.4$ and especially, to $n = 0.5$ and 0.6, the curve character, pH values, and time of its stabilization upon the interaction of solutions change sharply. A fundamentally distinct character is also observed for variations of pH of the mother solution during its contact with a solid phase.

According to the results of the chemical analysis, the content of cobalt, phosphorus, and water in samples obtained at $0.1 \le n \le 0.3$ is virtually the same and corresponds to calculated values for diphosphate $Co_2P_2O_7 \cdot 5H_2O$. The n_1 = P/Co atomic ratio in the solid phase is 1.00, which confirms precipitation of diphosphates. The diphosphates obtained at $n > 0.3$ contain potassium, whose content at $n = 0.4$ is 0.23 wt % and increases to 0.60 wt % at $n = 0.6$.

The XPA of diphosphates obtained at all n revealed X–ray amorphous solid phase. This phase, contrary to the data of [4], is not crystallized even after 80 days of contact with a mother solution.

To determine the conditions for synthesis of crystalline $Co_2P_2O_7 \cdot 5H_2O$, amorphous diphosphate obtained from 0.1 M starting solutions at $n = 0.2$ within 293–298 K, was recrystallized in weakly acid solutions, as in [6].

According to the chemical analysis, the diphosphate obtained by recrystallization is a hexahydrate containing

Table 1. X–ray characterization of $Co_2P_2O_7 \cdot 6H_2O$ and heat treatment products obtained in the dynamic mode at a heating rate of 5 deg min^{-1}

$Co_2P_2O_7 \cdot 6H_2O$ 298–378 K		482 K		583 K		672 K		α–$Co_2P_2O_7$ 825–1268 K	
d, nm	I/I_0	*d*, nm	I/I_0	*d*, nm	I/I_0	*d*, nm	I/I_0	*d*, nm	I/I_0
0.923	10	0.646 [a]	9	0.646	25	0.508	9	0.640	3
0.671	12	0.580 [a]	5	0.529	100	0.437	9	0.586	1
0.569	47	0.531 [a]	100	0.496	70	0.333	5	0.509	7
0.517	83	0.496	57	0.491	70	0.301	100	0.435	7
0.496	50	0.491 [a]	61	0.381	50	0.296	48	0.413	5
0.387	18	0.380 [a]	42	0.303	10	0.254	21	0.381	7
0.384	7	0.323	7	0.299	45	0.211	14	0.369	4
0.360	8	0.303 [a]	6	0.297	12			0.351	5
0.354	31	0.299 [a]	32	0.280	30			0.332	3
0.349	9	0.297 [a]	14	0.269	10			0.327	2
0.335	26	0.283	13	0.238	8			0.301	100
0.322	18	0.281 [a]	27	0.235	10			0.298	49
0.313	18	0.264 [a]	17	0.220	8			0.282	5
0.307	9	0.249	9	0.205	7			0.268	3
0.2990	11	0.238 [a]	7					0.261	4
0.2945	100	0.234 [a]	13					0.255	16
0.2832	9	0.220 [a]	5					0.254	19
0.2753	6	0.212	5					0.231	3
0.2575	17	0.207	8					0.224	3
0.2510	10	0.204	10					0.215	7
0.2383	8	0.1982 [a]	6					0.211	18
0.2267	26							0.207	4
0.2119	9							0.202	5
0.2070	8							0.185	6
0.2030	15							0.1743	4
0.1967	27							0.1710	4
0.1919	10							0.1621	11
0.1882	17							0.1582	10

[a] Phase isostructural to $Co_2P_2O_7 \cdot 2H_2O$.

(wt %): Co 29.51, P 15.27, and H_2O 27.41. The calculated values for $Co_2P_2O_7 \cdot 6H_2O$ are (wt %): Co 29.47, P 15.49, and H_2O 27.03. By data of the quantitative chromatography, the diphosphate contains 98.3 rel% of diphosphate anion.

The synthesized crystalline diphosphate $Co_2P_2O_7 \cdot 6H_2O$ (Table 1) precipitates to form raspberry pink crystals. The compound crystallizes in the monoclinic crystal system (space group $P2_1/c$) [7]. The calculated unit cell parameters for $Co_2P_2O_7 \cdot 6H_2O$ (*a* = 0.7202 nm, *b* = 1.8348 nm, and *c* = 0.7677 nm; β = 92.29; *V* = 1.0137 nm^3) are similar to those reported in [7].

The IR spectrum of crystalline $Co_2P_2O_7 \cdot 6H_2O$ contains absorption bands associated with the hydrated diphosphates (Fig. 2). Bands in the regions (cm^{-1}) 3600–3200 ν(OH) and 1650–1580 δ(H_2O) correspond to the stretching and deformation vibrations of water molecules in crystal hydrate; bands in the region 1170–980 cm^{-1} are due to the ν_s, ν_{as} stretching vibrations of PO_3 groups and those in the region 930–720 cm^{-1}, due to the ν_s, ν_{as} stretching vibrations of P–O–P bridge; bands in the region 630–550 cm^{-1} are associated with δ(PO) deformation vibrations of diphosphate anion. The IR spectrum in general run, number of absorption maxima,

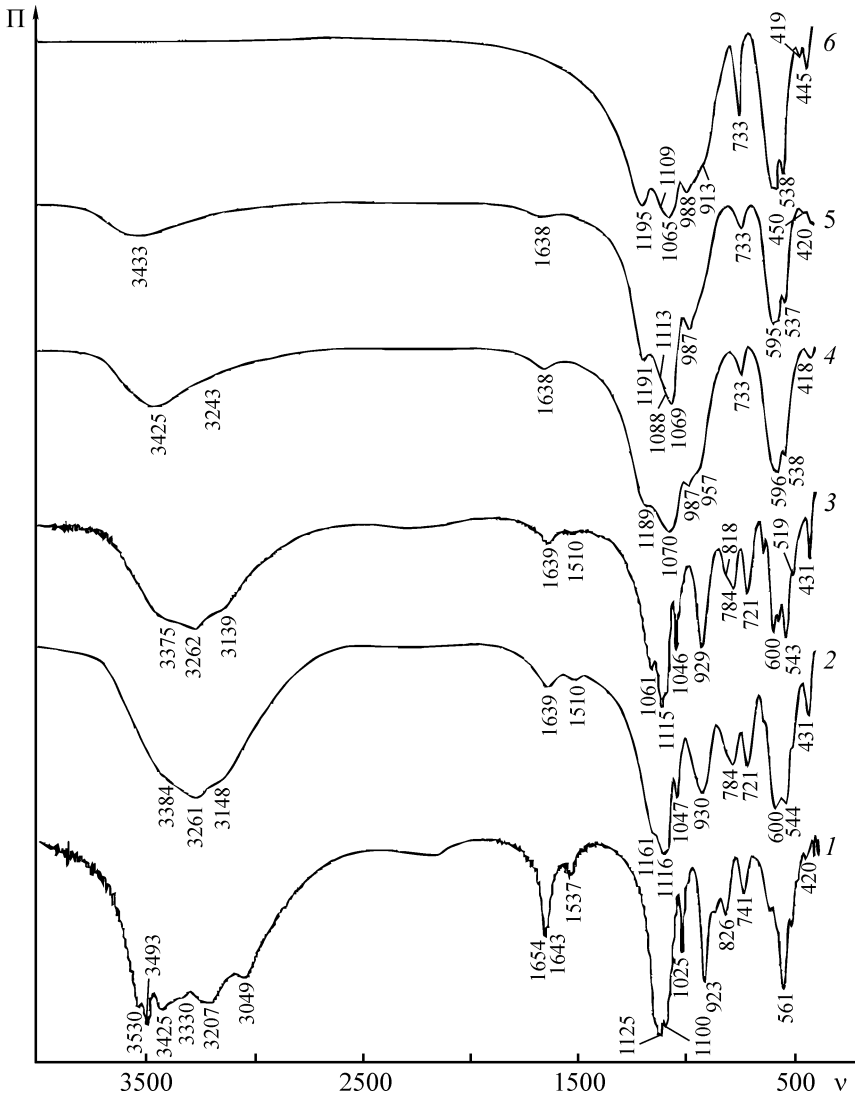


Fig. 2. IR spectra of (*1*) $Co_2P_2O_7 \cdot 6H_2O$ and (*2–6*) products of its heat treatment at different temperatures (A) Absorption (%), (ν) wave number (cm^{-1}). *T* (K): (*2*) 482, (*3*) 583, (*4*) 641, (*5*) 672, and (*6*) 825.

their intensities, and wave numbers resembles spectra known for $Co_2P_2O_7 \cdot 6H_2O$ [14].

According to the DTA data, $Co_2P_2O_7 \cdot 6H_2O$ is stable to 378 K in air (Fig. 3a). The dehydration includes two main stages and is complete at 825 K. The TG curve has two pronounced steps, within 378–482 K and 583–672 K, showing a mass loss owing to removal of 3.98 and 1.69 moles of H_2O, respectively. Heating of starting crystal hydrate within 672–825 K yields completely dehydrated product.

In the products obtained by heating $Co_2P_2O_7 \cdot 6H_2O$ to 482 K (first stage of water removal), a solid phase mainly consisting of two diphosphates is formed (Table 1). According to the X-ray analysis, one is dihydrate of the composition $Co_2P_2O_7 \cdot 2H_2O$ [15] and another, present in minor amount, starting crystal hydrate.

In the IR spectra of the hexahydrate of the rearranged structure the number of ν(OH) bands decreases from 6 to 3 (Fig. 2). In the $\delta(H_2O)$ region, a shoulder at 1643 cm^{-1} disappears and bands at 1654 and 1537 cm^{-1} shift toward low frequency region, which shows that the strength of water binding in crystal hydrate decreases. In the vibration region of diphosphate anions, two intense ν_s(POP) bands are present at 784 and 721 cm^{-1}, indicative of the presence of nonequivalent $P_2O_7^{4-}$ anions of noncentrosymmetrical configuration (POP angle less than 180°). The three bands in the 1000–1200 cm^{-1} region, that are due to the $\nu_s(PO_3)$ stretching vibrations, are also in favor of this

Table 2. Anionic composition of products obtained by heat treatment of $Co_2P_2O_7 \cdot 6H_2O$ in the dynamic mode at a rate of 5 deg min^{-1}

T, K	Mass loss, moles of H_2O	P_{tot}, wt %	Phosphorus content, wt %, in terms of phosphates						
			mono	di	tri	quaternary	penta	hexa	hepta
378	–	15.49	0.7[a]	14.8	–	–	–	–	–
482	3.98	18.85	1.8	17.1	–	–	–	–	–
583	4.13	19.02	5.2	13.0	0.5	0.2	0.1	–	–
641	5.50	20.59	4.6	13.5	1.4	0.4	0.3	0.3	<0.1
672	5.82	20.96	2.3	17.6	1.0	–	–	–	–
825	6.00	21.21	1.2[a]	20.0	–	–	–	–	–

[a] Result obtained in a hydrolysis during preparation of sample to analysis.

configuration, because for unbend $P_2O_7^{4-}$ configuration, two bands are predicted [14, 16].

Such transformations show that diphosphate hexahydrate losses 3.98 moles of H_2O in the form of a molecular unit, with the main structural motive retained:

$$Co_2P_2O_7 \cdot 6H_2O \xrightarrow[-3.98 \text{ moles of } H_2O]{378–482 \text{ K}} Co_2P_2O_7 \cdot 2H_2O.$$

Further heating of the products of partial dehydration of $Co_2P_2O_7 \cdot 6H_2O$ within 482–583 K is accompanied by small mass loss (0.15 moles of H_2O), which leads to complex structural rearrangements. The X–ray analysis of a partially amorphous solid phase revealed only one crystalline diphosphate, $Co_2P_2O_7 \cdot 2H_2O$ (Table 1). This compound was found, as the only intermediate product, in [8]. At the same time, the quantitative chromatography (Table 2) supports the anionic condensation processes and the formation of X–ray amorphous highly condensed phosphates of high polycondensation degree (n = 3–5). The most complex composition have products obtained on heat treatment of $Co_2P_2O_7 \cdot 6H_2O$ at 641 K. They, contrary to the data of [8], are a heterophase mixture of amorphous condensed phosphates (including heptaphosphate) with a linear structure of the anion. The content of diphosphate in the above mixture is no more than 65.5 wt %. Increasing the temperature to 672 K leads to the formation of the intermediate polyphosphates of simpler composition and causes final heat treatment product, anhydrous diphosphate, to crystallize (Tables 1, 2). The formation of its crystalline structure, as a whole, at 825 K is complete. The increase in the reflections' intensities on the diffraction pattern of the diphosphate obtained within 825–1268 K confirms thermal stability and perfect crystalline structure of this compound.

The X–ray and IR spectroscopic analyses of anhydrous diphosphate and the known data for α-$Co_2P_2O_7$ [8, 14, 17] showed that, as in [8], α-$Co_2P_2O_7$ is the final product of $Co_2P_2O_7 \cdot 6H_2O$ heat treatment (Table 1, Fig. 2). The synthesized α -$Co_2P_2O_7$ crystallizes in the monoclinic

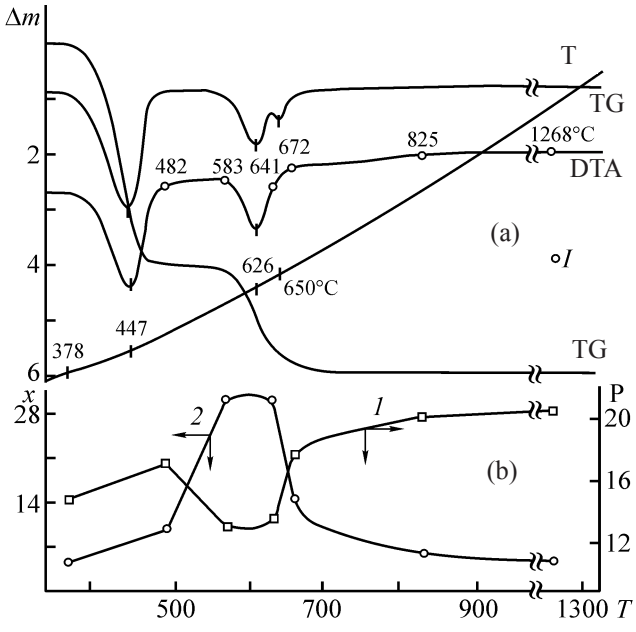
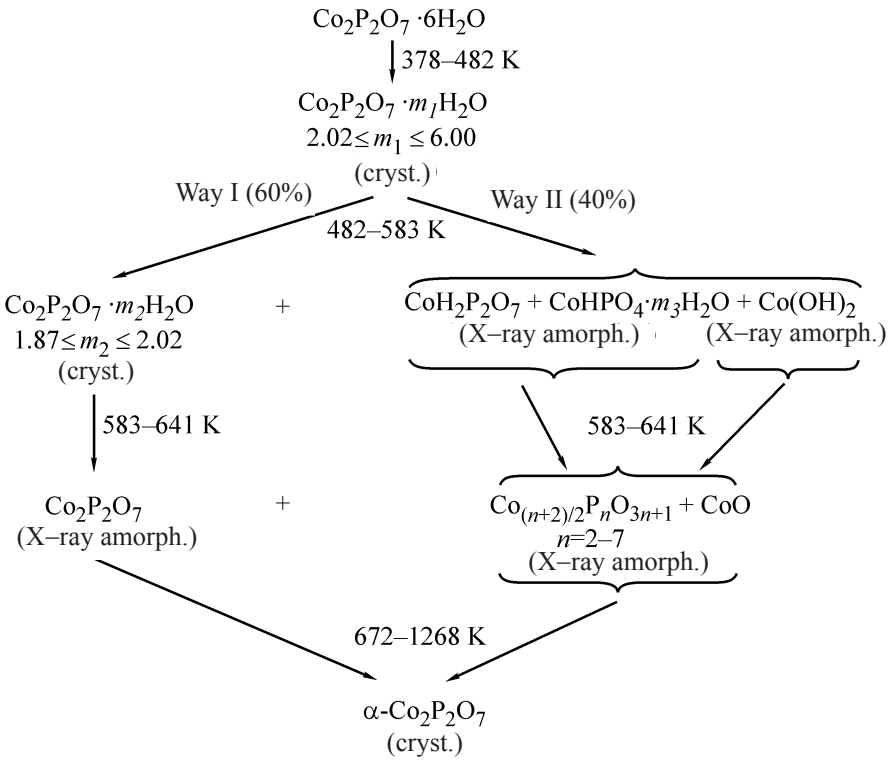


Fig. 3. (a) Thermogravigrams taken during dynamic heating of $Co_2P_2O_7 \cdot 6H_2O$ at a rate of 5 deg min^{-1} and (b) temperature dependences for (*1*) diphosphate content in thermolysis products and (*2*) decomposition degree of diphosphate anion (*I*) Sampling coordinates. (Δm) Mass loss (moles of H_2O), (x) degree of $P_2O_7^{4-}$ decomposition (%), (P) phosphorus content in terms of $P_2O_7^{4-}$ (wt %), and (T) temperature (K).

crystal system (sp.g. $P2_1/c$, $Z = 8$) with the unit cell parameters: $a = 0.6875$ nm, $b = 0.8579$ nm, $c = 0.8894$ nm, and $V = 0.483$ nm^3. The high intensity of the ν_s(POP) band in its IR spectrum, along with two bands and a shoulder in the ν (PO_3) region, show that the symmetry of the diphosphate anion in α-$Co_2P_2O_7$ is low (no higher than C_{2v}). The results obtained agree with a value of 142.6° for a POP angle in α-$Co_2P_2O_7$ [18].

The results of the performed study suggest that the composition of the intermediate and final products of $Co_2P_2O_7 \cdot 6H_2O$ heat treatment, temperature intervals, wherein they are formed and exhibit thermal stability, and the sequence of the thermal and structural transformations accompanying the α-$Co_2P_2O_7$ formation, may be presented by the general scheme, which, as we expected, is more complex than that reported in [8]:



CONCLUSIONS

(1) The dependence of solid–phase composition on the main interaction parameters in the $CoSO_4$–$K_4P_2O_7$–H_2O system was found. The synthesis conditions were determined [reagent ratio $0.1 \le n$ ($P_2O_7^{4-}/Co^{2+}$) ≤ 0.30, solutions' concentration 0.1 M; time of contact of the solid phase with a mother solution 10 days, temperature range 293–298 K, recrystallization]. The crystalline $Co_2P_2O_7 \cdot 6H_2O$ was synthesized and its crystallographic and spectroscopic parameters in the IR region were determined.

(2) It was shown that $Co_2P_2O_7 \cdot 6H_2O$ is stable to 378 K. A further increase in the temperature causes a two step mass loss. The composition and region, wherein the thermally stable intermediate products of $Co_2P_2O_7 \cdot 6H_2O$ heat treatment were formed, were determined. It was established that the crystallization of the final product, anhydrous α-$Co_2P_2O_7$, at 825 K is complete. Increasing the temperature to 1268 K does not affect its structure and chemical composition.

(3) The α-$Co_2P_2O_7$ is formed by two parallel ways. Up to 60% of α-$Co_2P_2O_7$ is formed as a result of the $Co_2P_2O_7 \cdot 6H_2O$ dehydration with the participation of structural water units (first way) and the remaining 40% are formed by the solid state interaction of intermediate products, condensed phosphates and oxides (second way).

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