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High-temperature reactions in the $Co_3Cr_4(PO_4)_6$–$Cr(PO_3)_3$ system

New compound $CoCr_2(P_2O_7)_2$ and its properties

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Abstract A new dichromium(III) cobalt(II) diphosphate(V) of the formula $CoCr_2(P_2O_7)_2$ was detected in the $Co_3Cr_4(PO_4)_6$–$Cr(PO_3)_3$ system. The new compound was obtained as a result of high-temperature solid-state reactions between $CoCO_3$, Cr_2O_3 and $(NH_4)_2HPO_4$ as well as between $Cr(PO_3)_3$ and $Co_3Cr_4(PO_4)_6$. $CoCr_2(P_2O_7)_2$ was characterized using XRD, DTA and IR methods. Results demonstrated that $CoCr_2(P_2O_7)_2$ crystallizes in the triclinic system and its unit cell parameters were calculated. Its infrared spectrum was presented. $CoCr_2(P_2O_7)_2$ melts incongruently at 1270±10 °C with a formation of solid α-$CrPO_4$. The compound $Co_3Cr_4(PO_4)_6$, component of the system under study, was obtained for the first time as a pure phase. Its thermal stability was also investigated. $Co_3Cr_4(PO_4)_6$ is stable in air up to 1410 ± 20 °C.

Keywords Chromium cobalt phosphate · System CoO–P_2O_5–Cr_2O_3 · $CoCr_2(P_2O_7)_2$ · XRD · DTA · IR

Introduction

The phosphates(V) of di- and trivalent metals are the objects of extensive studies as they have many possibilities of application. Some of such phosphates exhibit anticorrosion properties [1], and the other can be used as ceramic pigments [2, 3], as an anode material for lithium-ion batteries [4] or as efficient catalysts [5, 6]. Research work aimed at synthesis and characterization of new phosphates(V) is very important for designing of new materials which can be applied in different areas of contemporary technology. Such new phosphates can be formed *inter alia* in the ternary oxide system CoO–P_2O_5–Cr_2O_3. Cobalt(II) phosphates(V) and chromium(III) phosphates(V), forming in the lateral systems of the mentioned ternary oxide system, are known and widely investigated [1, 2, 4–9], but only one article [10] was found referring to a phase, which is formed with an involvement of all three oxides, i.e. $Co_3Cr_4(PO_4)_6$. The compound was synthesized by heating the mixture of Co_3O_4, Cr_2O_3 and $NH_4H_2PO_4$ at a molar ratio 1:2:6 up to 1000 °C for 300 h [10]. The authors [10], however, could not obtain $Co_3Cr_4(PO_4)_6$ as a pure phase. However, they assumed that this compound is isostructural with the compounds from the family $M_3^{2+}M_4^{3+}(PO_4)_6$, and on this basis, the structure of $Co_3Cr_4(PO_4)_6$ was solved [10]. The compound crystallizes in the triclinic system, and its unit cell parameters are the following: $a = 7.8561$ Å, $b = 9.2350$ Å, $c = 6.2785$ Å, $\alpha = 108.173°$, $\beta = 101.808°$, $\gamma = 105.329°$ [10]. To the best of our knowledge, there is no literature information on thermal stability of $Co_3Cr_4(PO_4)_6$.

Therefore, it follows from literature survey that, till now, there were no systematic investigations on phase formation in the CoO–P_2O_5–Cr_2O_3 system. The main aim of the presented work was to check whether in one of the cross sections of the CoO–P_2O_5–Cr_2O_3 system, i.e. in the system $Co_3Cr_4(PO_4)_6$–$Cr(PO_3)_3$, any new phosphate(V) is formed and if so—the second point of the study was to determine some of its physicochemical properties. Additionally, necessary investigations, verifying and supplementing literature data relating to $Co_3Cr_4(PO_4)_6$, were conducted.

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Experimental

As the initial reagents were used: Cr_2O_3 (p.a., Aldrich, Germany), $CoCO_3$ (p.a., Fluka, Switzerland), $(NH_4)_2HPO_4$ (p.a., POCh, Poland).

Reactions were conducted by the conventional method of calcining samples [9–14]. Appropriate portions of reacting substances were homogenized by grinding, pressed into pellets and heated in air atmosphere in several stages, until an equilibrium state was attained. The first heating stage (at 350 °C) of samples containing in initial mixtures precursors of CoO and P_2O_5 was applied mainly to remove NH_3, H_2O and CO_2, so they were pressed into pellets only from the second heating stage. Next, the heating temperature was gradually increased, because it follows from our earlier studies that heating immediately at higher temperatures leads to obtaining the samples in glass form. After each heating stage, samples were gradually cooled down in the furnace to room temperature and next the pellets were ground and examined by XRD method or by DTA, too. Generally, to avoid the melting of the samples the maximum temperature of their heating was several dozen of °C lower than their melting temperatures, which were read from their DTA curves.

The XRD method was used to determine the type of the phases occurring in particular samples [13, 14]. The powder diffraction patterns of samples were recorded with the aid of the Empyrean II diffractometer (PANalytical, Netherlands) using CuK_α radiation with graphite monochromator. The identification of phases, present in the samples, was conducted based on their XRD characteristics contained in the PDF cards. The powder diffraction pattern of the new compound was indexed by means of the POWDER programme [15]. The internal standard was α-Al_2O_3. The parameters of the unit cell were refined by the refinement programme of DHN/PDS package.

Thermal stability of some obtained samples was investigated using the F.Paulik–J.Paulik–L.Erdey-type derivatograph Q – 1500 D (MOM, Hungary), in the temperature range 20–1400 °C, at a heating rate of 7.5 °C min^{-1} and sample mass 500 mg. The investigations were conducted also in temperature range 20–1500 °C using an optical pyrometer (Raytek, model RAYMM1MHSF2V, Germany).

The density of the new compound was determined with the help of an Ultrapyc 1200e ultrapycnometer (Quantachrome Instruments, USA) using argon (5 N purity) as a pycnometric gas. The measurements were taken in five repetitions using $\sim$2 g of each sample for the test.

The IR spectroscopic measurement (the Specord M 80 spectrometer, Carl Zeiss, Germany) was conducted applying the technique of pressing pastilles of the sample with KBr [13, 16, 17] at the ratio 1:300 by weight.

Results and discussion

Synthesis and thermal stability of $Co_3Cr_4(PO_4)_6$

Preliminary stage of the study was devoted to verification and supplementation of the information needed for realization of the main aim of the work and concerning one of the components of $Co_3Cr_4(PO_4)_6$–$Cr(PO_3)_3$ system, i.e. $Co_3Cr_4(PO_4)_6$.

The authors [10] have synthesized a compound of the composition corresponding to the formula $Co_3Cr_4(PO_4)_6$. Despite the prolonged heating time of the reactants mixture (300 h) in the temperature range of 800–1000 °C, they have not obtained a monophase sample. Therefore, the aim of the first stage of the study was to obtain pure $Co_3Cr_4(PO_4)_6$ compound and to determine its thermal stability in air atmosphere. The stoichiometric mixture of $CoCO_3$, Cr_2O_3 and $(NH_4)_2HPO_4$ was heated in the following stages: 350 °C(12 h) + 500 °C(12 h) + 650 °C(12 h) + 700 °C (12 h) + 950 °C(12 h) + 1050 °C(12 h) × 2 + 1100 °C (12 h) × 2 + 1200 °C(12 h). XRD phase analysis of the sample obtained after its last heating stage has proved that it is monophase, because its diffractogram contains only a set of lines characteristic for $Co_3Cr_4(PO_4)_6$ (PDF 49-0499). These results testify that shorter heating stages, but at higher temperatures (in comparison with those given in the literature [10]) allowed to obtain pure $Co_3Cr_4(PO_4)_6$ compound, according to the complete stoichiometric reaction:

$$3\ CoCO_{3(s)} + 2\ Cr_2O_{3(s)} + 6\ (NH_4)_2HPO_{4(s)} = Co_3Cr_4(PO_4)_{6(s)} + 3\ CO_{2(g)} + 12\ NH_{3(g)} + 9\ H_2O_{(g)}. \quad (1)$$

As thermal stability of $Co_3Cr_4(PO_4)_6$ has not been known, it was subjected to DTA measurements in air in the temperature range 20–1400 °C. In this range on DTA curve, no thermal effects were recorded. This result means that $Co_3Cr_4(PO_4)_6$ undergoes decomposition or melting at temperature higher than 1400 °C. In order to assess its thermal stability, the sample containing $Co_3Cr_4(PO_4)_6$ was heated in air in a horizontal tube furnace equipped with an optical pyrometer. Based on the result of the study, it was found that the resulting compound is stable in air up to 1410 ± 20 °C.

It is known from the literature that the second compound, constituting the system under study, i.e. $Cr(PO_3)_3$, decomposes to $Cr_2P_4O_{13}$ and P_2O_5 at 1325 °C [9].

Reactions in the $Co_3Cr_4(PO_4)_6$–$Cr(PO_3)_3$ system

In order to determine the kind of phases forming in the system $Co_3Cr_4(PO_4)_6$–$Cr(PO_3)_3$ 11 mixtures of $CoCO_3$,

Cr_2O_3 and $(NH_4)_2HPO_4$ were prepared. The composition of initial mixtures, in terms of the components of the system $Co_3Cr_4(PO_4)_6$–$Cr(PO_3)_3$ as well as of the system CoO–P_2O_5–Cr_2O_3, is given in Table 1. All the samples were heated in the following stages: 350 °C(12 h) + 500 °C(12 h) + 650 °C(12 h) + 700 °C(12 h) + 950 °C(12 h) + 1050 °C (12 h) × 2, while samples 5–11 were additionally heated at 1100 °C (12 h) twice. Table 1 presents XRD analysis results for the samples after their last heating stage. In the diffractograms of all the investigated samples, a set of unidentified lines denoted by X was detected. However, only as a result of heating a mixture initially containing 33.33 mol% $Co_3Cr_4(PO_4)_6$ and 66.67 mol% $Cr(PO_3)_3$ [in terms of the components of the system $Co_3Cr_4(PO_4)_6$ –$Cr(PO_3)_3$] a monophase sample was obtained whose diffractogram consisted only of a set of unidentified lines X. These lines were not assigned to any initial reactants as well as to any previously known phases that belong to the lateral binary systems constituting the ternary oxide system CoO–P_2O_5–Cr_2O_3. It has been concluded that the recorded set of lines X is an XRD characteristic of a new compound of the formula $CoCr_2(P_2O_7)_2$ that is formed according to the complete stoichiometric reaction:

$$CoCO_{3(s)} + Cr_2O_{3(s)} + 4\,(NH_4)_2HPO_{4(s)} = CoCr_2(P_2O_7)_{2(s)} + CO_{2(g)} + 8\,NH_{3(g)} + 6\,H_2O_{(g)}. \quad (2)$$

In the component concentration range up to 33.33 mol% of $Co_3Cr_4(PO_4)_6$ (in terms of the components of the $Co_3Cr_4(PO_4)_6$–$Cr(PO_3)_3$ system), in the cross section under study, $Cr(PO_3)_3$ also occurs. In the remaining component concentration range, i.e. above 33.33 mol% of $Co_3Cr_4(PO_4)_6$, apart from $CoCr_2(P_2O_7)_2$, $Co_3Cr_4(PO_4)_6$ is formed.

The new compound has been also obtained by reaction occurring by heating the stoichiometric mixture of $Cr(PO_3)_3$ and $Co_3Cr_4(PO_4)_6$ in the following stages: 700 °C(12 h) + 950 °C(12 h) + 1050 °C(12 h) ×2 + 1100 °C(12 h) ×2:

$$2Cr(PO_3)_{3(s)} + Co_3Cr_4(PO_4)_{6(s)} = 3\ CoCr_2(P_2O_7)_{2(s)}. \quad (3)$$

In the next stage of the study, two mixtures (Table 1, samples 12 and 13) were prepared with their compositions being very close to that which corresponds to the formula $CoCr_2(P_2O_7)_2$ but not representing the system under study (Fig. 1). Heating conditions for sample 13 were the same as for samples 1–4, while sample 12 was additionally heated at 1100 °C (12 h) twice (as samples 5–11). After the last heating stage, besides of $CoCr_2(P_2O_7)_2$, the other compounds were also identified in sample 12 and 13 (Table 1). The obtained results additionally prove that the composition of the new phase corresponds to the formula $CoCr_2(P_2O_7)_2$.

Figure 1 shows the positions of: the $Co_3Cr_4(PO_4)_6$–$Cr(PO_3)_3$ cross section studied, samples 12 and 13 as well as the new obtained compound in the component concentration triangle of the ternary oxide system.

Some properties of the new compound $CoCr_2(P_2O_7)_2$

In a further part of the work, some physicochemical properties of the new compound were investigated. $CoCr_2(P_2O_7)_2$ has a patina colour; its density amounts to

Table 1 Composition of initial mixtures and their composition after the last heating stage

No.	Composition of initial mixtures in terms of the components of the system $Co_3Cr_4(PO_4)_6$–$Cr(PO_3)_3$/mol%		Composition of initial mixtures in terms of oxides percentage/mol%			Phase composition of samples after their last heating stage
	$Co_3Cr_4(PO_4)_6$	$Cr(PO_3)_3$	CoO	P_2O_5	Cr_2O_3	
1	5.00	95.00	6.52	68.48	25.00	X, $Cr(PO_3)_3$
2	11.11	88.89	12.50	62.50	25.00	
3	20.00	80.00	18.75	56.25	25.00	
4	30.00	70.00	23.68	51.32	25.00	
5	33.33	66.67	25.00	50.00	25.00	X
6	36.00	64.00	25.96	49.04	25.00	X, $Co_3Cr_4(PO_4)_6$
7	50.00	50.00	30.00	45.00	25.00	
8	57.14	42.86	28.12	46.88	25.00	
9	66.67	33.33	33.33	41.67	25.00	
10	80.00	20.00	35.29	39.71	25.00	
11	95.00	5.00	37.01	37.99	25.00	
12	–	–	24.32	48.65	27.03	X, α-$CrPO_4$
13	–	–	24.00	52.00	24.00	X, $Cr(PO_3)_3$

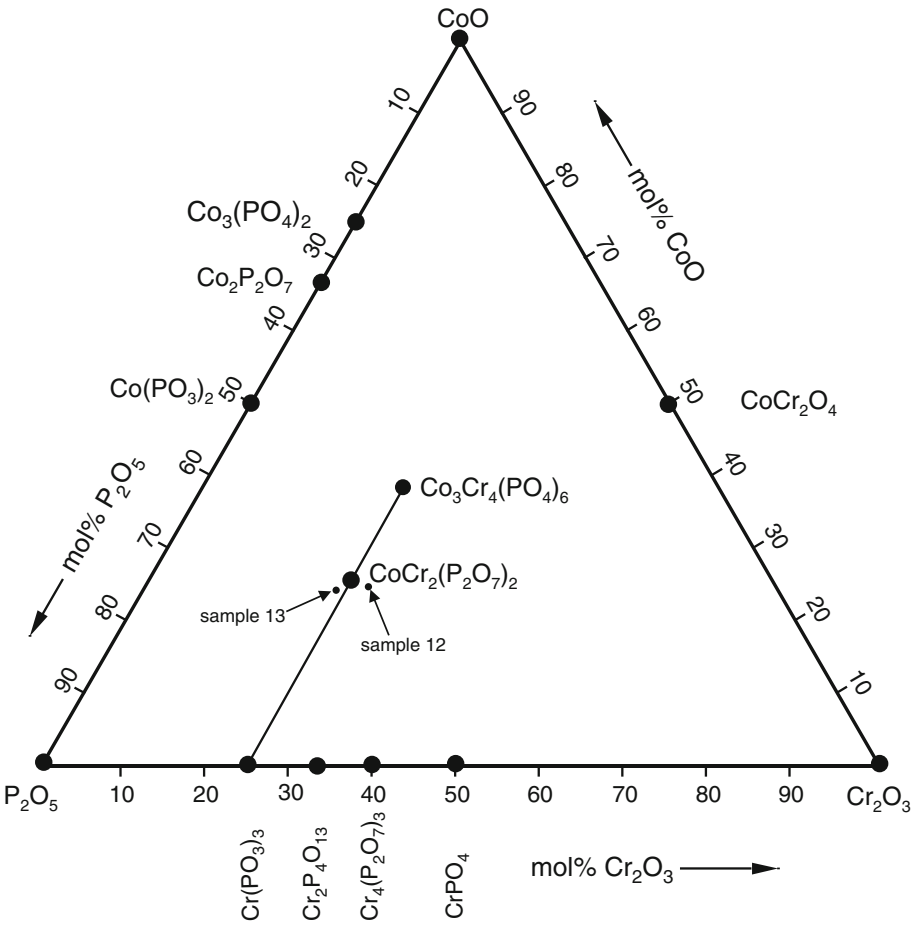

Fig. 1 Positions of the $Co_3Cr_4(PO_4)_6$–$Cr(PO_3)_3$ cross section studied, samples 12 and 13 as well as the new obtained compound in the component concentration triangle of the CoO–P_2O_5–Cr_2O_3 system

$d_{obs} = 3.63(5)$ g cm^{-3}. Figure 2 shows a powder diffraction pattern of the new compound, whereas Table 2 presents the results of its indexing. $CoCr_2(P_2O_7)_2$ crystallizes in the triclinic system. The parameters of its primitive unit cell are as follows: $a = 6.684(3)$ Å, $b = 10.295(5)$ Å, $c = 20.136(9)$ Å, $\alpha = 121.41(8)°$, $\beta = 94.25(4)°$, $\gamma = 86.04(4)°$. The unit cell volume $V = 1178.5$ Å^3; the number of stoichiometric formula units in the unit cell $Z = 5$; the XRD calculated density $d_{calc} = 3.60$ g cm^{-3}.

It is known from the literature that there exist compounds of the formulae $CuFe_2(P_2O_7)_2$ [18] and $CuIn_2(P_2O_7)_2$ [19], i.e. with a composition analogous to the composition of the obtained new compound. However, some considerable differences between the powder diffraction patterns of $CoCr_2(P_2O_7)_2$ and $CuM_2(P_2O_7)_2$ (M = Fe, In) indicate that these compounds are not isostructural.

In the DTA curve of $CoCr_2(P_2O_7)_2$, two endothermic effects were recorded (Fig. 3), with onset temperatures 1270 and 1350 °C, respectively. In order to determine the type of the transformation that the first effect is due to, a sample of $CoCr_2(P_2O_7)_2$ was heated for 2 h at 1285 °C, i.e. at the temperature of the maximum of this effect, and next it was rapidly cooled to room temperature and subjected to XRD analysis. The obtained results indicate that the first endothermic effect is due to incongruent melting of $CoCr_2(P_2O_7)_2$ with a formation of solid α-$CrPO_4$.

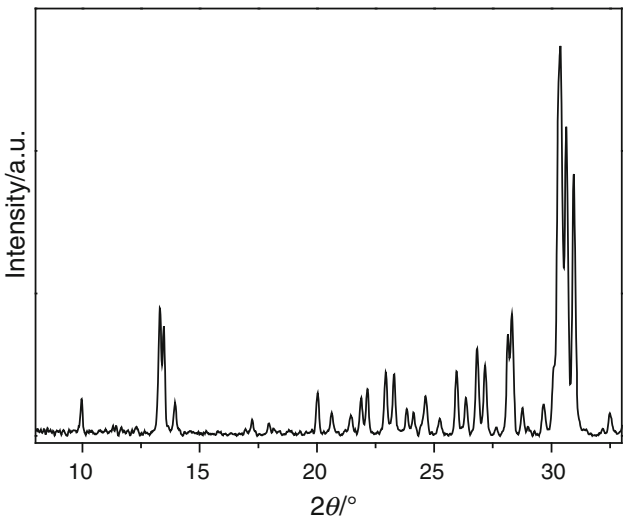

Fig. 2 Powder diffraction pattern of $CoCr_2(P_2O_7)_2$

Table 2 Indexing results for the $CoCr_2(P_2O_7)_2$ powder diffraction pattern

No	d_{exp}/Å	d_{calc} /Å	*h k l*	I/I_0/%
1	8.8363	8.8462	0 −1 2	9
2	6.6321	6.6137	0 −1 3	28
3	6.5491	6.5593	0 1 1	22
4	6.3256	6.3064	−1 0 1	6
5	5.1287	5.1230	1 −1 2	5
6	4.9279	4.9310	0 −2 3	4
7	4.4219	4.4231	0 −2 4	12
8	4.2970	4.2921	0 0 4	5
9	4.1311	4.1217	−1 −2 3	6
10	4.0547	4.0551	−1 −2 1	11
11	4.0042	4.0002	−1 1 2	13
12	3.8684	3.8744	1 −1 4	16
13	3.8112	3.8061	0 2 1	16
14	3.7246	3.7277	1 2 0	6
15	3.6806	3.6839	−1 0 4	7
16	3.6057	3.6071	1 −2 0	11
17	3.5202	3.5184	−1 −1 5	5
18	3.4270	3.4233	0 −3 −3	17
19	3.3759	3.3747	1 1 3	10
20	3.3155	3.3139	1 −1 5	21
21	3.2761	3.2751	−1 2 1	17
22	3.1655	3.1706	0 −3 1	22
23	3.1469	3.1519	2 1 0	35
24	3.0988	3.0984	−1 −3 4	7
25	3.0059	3.0092	−1 −1 6	9
26	2.9844	2.9814	2 1 1	10
27	2.9374	2.9364	−2 0 3	100
28	2.9140	2.9139	1 −3 4	92
29	2.8847	2.8850	2 −1 3	72
30	2.7508	2.7504	0 1 5	6

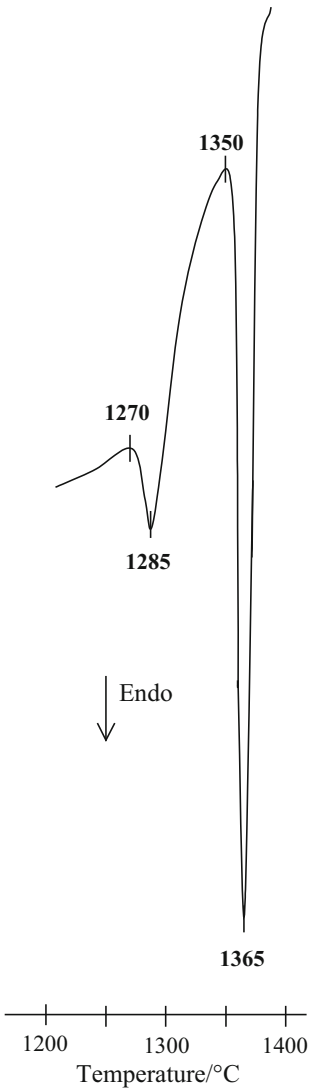

Fig. 3 Fragment of DTA curve of $CoCr_2(P_2O_7)_2$

The IR spectrum of $CoCr_2(P_2O_7)_2$ is shown in Fig. 4. Univocal attribution of the recorded absorption bands to the specific vibrations is not possible, because the full structure of the new compound is unknown. However, probable attribution can be made in the light of literature data [20–25]. IR spectrum of $CoCr_2(P_2O_7)_2$ is complex, but in general, four characteristic groups of bands are observed in the range 1500–300 cm^{-1}. The broadening character observed in the region 1270–1190 cm^{-1} corresponds to asymmetric stretching vibration of O–P–O groups, while the next broad band in the region 1120–1000 cm^{-1} is related to the symmetric stretching vibration of those linkages, e.g. O–P–O [20–22]. The absorption bands at 970, 945, 925 are assigned to the asymmetric stretching vibration of P–O–P linkages, while

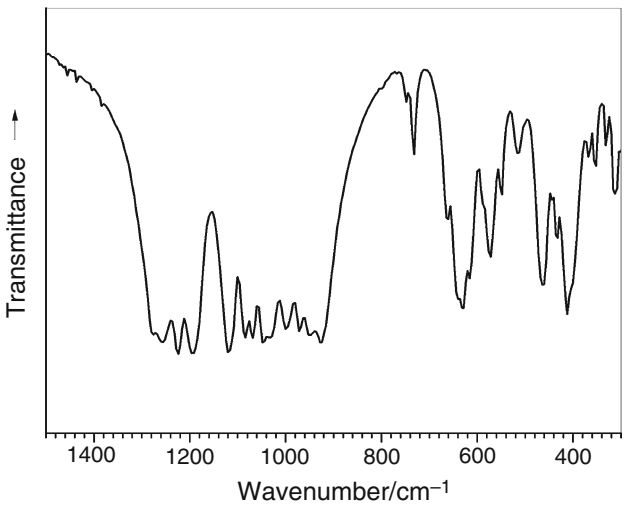

Fig. 4 IR spectrum of $CoCr_2(P_2O_7)_2$

the relatively weak band around 725 cm^{-1} is due to the symmetric stretching vibration of those linkages: P–O–P [20–23]. A weak band registered at 745 cm^{-1} occurring in the IR spectrum of $CoCr_2(P_2O_7)_2$ is probably due to symmetric stretching vibration of the P–O bonds with an internal oxygen atom [23, 24]. The shoulder at about 625 cm^{-1} can be assigned to asymmetric bending vibrations of the O–P–O groups [20, 21] and to stretching vibrations of the Cr–O bonds [20, 23, 25]. The absorption bands at 570, 540, 510 and 460 cm^{-1} may be assigned either to the harmonics of P–O–P bending vibration or to the characteristic frequency of the $P_2O_7^{2-}$ group [21, 22, 25]. Stretching vibration of Co–O bonds appears in the spectra below 400 cm^{-1} [22, 25].

Studies on the other properties of the new obtained compound $CoCr_2(P_2O_7)_2$, especially from the point of view of its application as ceramic pigment, are in progress.

Conclusions

The results obtained in this study showed that in the ternary oxide system $CoO–P_2O_5–Cr_2O_3$, besides $Co_3Cr_4(PO_4)_6$, a new compound of the stoichiometric formula $CoCr_2(P_2O_7)_2$ is also formed in air atmosphere. The new compound, forming in the cross section $Co_3Cr_4(PO_4)_6–Cr(PO_3)_3$, was obtained as a result of reaction between $CoCO_3$, Cr_2O_3 and $(NH_4)_2HPO_4$, mixed at a molar ratio 1:1:4 as well as in the reaction of mixture of $Cr(PO_3)_3$ and $Co_3Cr_4(PO_4)_6$ (2:1). $CoCr_2(P_2O_7)_2$ has a patina colour and crystallizes in the triclinic system with the primitive unit cell parameters: $a = 6.684(3)$ Å, $b = 10.295(5)$ Å, $c = 20.136(9)$ Å, $\alpha = 121.41(8)°$, $\beta = 94.25(4)°$, $\gamma = 86.04(4)°$. The volume of such selected unit cell is $V = 1178.5$ $Å^3$, and the number of stoichiometric formula units in the unit cell $Z = 5$ and the density, calculated from the unit cell parameters, is 3.60 g cm^{-3}. $CoCr_2(P_2O_7)_2$ melts incongruently at 1270±10 °C with a formation of solid α-$CrPO_4$. $Co_3Cr_4(PO_4)_6$ compound, one of the components of the system studied, was obtained for the first time as a pure phase. It is stable in air up to 1410 ± 20 °C.

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References

1. Jašková V, Kalendová A. Anticorrosive coatings containing modified phosphates. Prog Org Coat. 2012;75:328–34.
2. Meseguer S, Tena MA, Gargori C, Badenes JA, Llusar M, Monrós G. Structure and colour of cobalt ceramic pigments from phosphates. Ceram Int. 2007;33:843–9.
3. Llusar M, García A, Gargori C, Galindo R, Badenes JA, Monrós G. Synthesis of dophosphate $Mn_{2-x}Mg_xP_2O_7$ solid solutions woth thortveitite structure: new pink ceramic dyes for the colouration of ceramic glazes. J Eur Ceram Soc. 2012;32:765–76.
4. Choi C, Seo S-D, Shim H-W, Dar MA, Cho IS, Kim D-W. Facile synthesis and electroactivity of 3-D hierarchically superstructured cobalt orthophosphate for lithium-ion batteries. J Alloy Compd. 2015;652:100–5.
5. Xu S, Yan X, Bu Q, Xia H. Highly efficient conversion of carbohydrates into 5-hydroxymethylfurfural using the bi-functional $CrPO_4$ catalyst. RSC Adv. 2016;6:8048–52.
6. Di T, Zhu B, Zhang J, Cheng B, Yu J. Enhanced photocatalytic H_2 production on CdS nanorod using cobalt-phosphate as oxidation cocatalyst. Appl Surf Sci. 2016;389:775–82.
7. Sarver JF. Compound formation and phase-equilibrium relationships in the systems $CoO–P_2O_5$ and $NiO–P_2O_5$. Trans Br Ceram Soc. 1966;65:191–8.
8. De Guire MR, Prasanna TRS, Kalonji G, O'Handley RC. Phase equilibria in the iron oxide–cobalt oxide–phosphorus oxide system. J Am Ceram Soc. 1987;70:831–7.
9. Bosacka M, Jakubus P, Rychłowska-Himmel I. Obtaining of chromium(III) phosphates(V) in the solid-state and their thermal stability. J Therm Anal Calorim. 2007;88:133–7.
10. Belik AA, Pokholok KV, Malakho AP, Khasanov SS, Lazoryak BI. Synthesis and structure of phosphates $M_3R_4(PO_4)_6$ (M = Cu, Co; R = Fe, Cr, Ga, In) and their interaction with hydrogen. Zh Neorg Khim. 2000;45:1633–48.
11. Blonska-Tabero A, Bosacka M, Dabrowska G, Filipek E, Piz M, Rychlowska-Himmel I, Tabero P, Tomaszewicz E. The synthesis and properties of the phases obtained by solid-solid reactions. J Min Metall. 2008;44B:19–26.
12. Těšitelová K, Šulcová P. Synthesis and study of $Bi_2Ce_2O_7$ as inorganic pigment. J Therm Anal Calorim. 2016;125:1047–52.
13. Bosacka M, Filipek E, Paczesna A. Unknown phase equilibria in the ternary oxide $V_2O_5–CuO–In_2O_3$ system in subsolidus area. J Therm Anal Calorim. 2016;125:1161–70.
14. Souza MT, Cesconeto FR, Arcaro S, Teixeira AHB, Raupp-Pereira F, Montedo ORK, Novaes de Oliveira AP. Synthesis and characterization of Li_2TiSiO_5 obtained by melting and solid-state reaction. J Therm Anal Calorim. 2017;127:463–7.
15. Taupin D. A powder-diagram automatic-indexing routine. J Appl Crystallogr. 1973;6:380–5.
16. Świderski G, Kalinowska M, Rusinek I, Samsonowicz M, Rzączyńska Z, Lewandowski W. Spectroscopic (IR, Raman) and thermogravimetric studies of 3d-metal cinchomeronates and dinicotinates. J Therm Anal Calorim. 2016;126:1521–32.
17. Tabero P, Frackowiak A. Synthesis of $Fe_8V_{10}W_{16}O_{85}$ by a solution method. J Therm Anal Calorim. 2016;125:1445–51.
18. Weimann I, Jahn T, Feller J, Zak Z. Synthesis, crystal structure and characterization of the copper iron phosphate $Cu_8Fe_2O_5(PO_4)_4$. Z Anorg Allg Chem. 2014;640:219–23.
19. Hanzelmann C, Weimann I, Feller J, Žak Z. Synthesis and characterization of the new copper indium phosphate $Cu_8In_8P_4O_{30}$. Z Anorg Allg Chem. 2014;640:213–8.
20. Abo-Naf SM, El-Amiry MS, Abdel-Khalek AA. FT-IR and UV-Vis optical absorption spectra of γ-irradiated calcium phosphate glasses doped with Cr2O3, V2O5 and Fe2O3. Opt Mater. 2008;30:900–9.

21. Lezama L, Rojo JM, Mesa JL, Rojo T. Synthesis and magnetic and electrical properties of the molybdenum and tungsten pyrophosphates MP_2O_7 (M = Mo, W). J Solid State Chem. 1995;115:146–51.
22. Etcheverry SB, Baran EJ. Diphosphate as a bidentate ligand. Spectroscopic study of the bis(ethylenediamine)diphosphatocobaltate(III) anion. Z Anorg Allg Chem. 1979;457:197–202.
23. Fuks H, Kaczmarek SM, Bosacka M. EPR and IR investigations of some chromium(III) phosphate(V) compounds. Rev Adv Mater Sci. 2010;23:14–34.
24. Tarte P, Rulmont A, Sbai K, Simonot-Grange MH. Vibrational spectrum of $KM^{II}P_3O_9$ tricyclophosphates with the benitoite structure. Spectrochim Acta. 1987;43A:337–43.
25. Voitenko LV, Zhilyak ID, Kopilevich VA. Double hydrated cobalt(II) copper(II) and nikel(II) copper(II) ammine diphosphates. Zh Prikl Khim. 2005;78:369–72.