

**THE SOLUBILITY OF COBALT OXIDE IN THE MELTS OF SYSTEM  
Na<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub>-CoO-NaF**

**Lavryk R.V.**

PhD in Chemistry

National University of Life and Environmental Sciences of Ukraine

**Galimova V.M.**

PhD in Chemistry

National University of Life and Environmental Sciences of Ukraine

**Abstract.** *The solubility of cobalt oxide in the melts of system Na<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub>-CoO-NaF in a wide range of molar ratios Na<sub>2</sub>O:P<sub>2</sub>O<sub>5</sub> (0,5-2,0) and temperatures 800-900 °C at a content of sodium fluoride in 10 and 20 (wt. %). The region of existence and optimal conditions for growing monocrystals of complex phosphate Na<sub>4</sub>Co<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> in melts of system Na<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub>-CoO-NaF are found out. Na<sub>4</sub>Co<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> complex double phosphate was synthesized from the fluxes of Na<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub>-CoO system at slow cooling (with the speed 10 °C per hour) at the range of temperatures 1000-650 °C. Homogeneous fluxes (at 950 °C) with output molar ratio Na<sub>2</sub>O:P<sub>2</sub>O<sub>5</sub> equal 1,1 were saturated with CoO (25 wt. %), using intimate, intermittent mixing during 3-4 hours, raised temperature and crystallized crystals in the abovementioned temperature range. The obtained monocrystals were washed out from the flux residue using the solution of light-salted acid, washed in flowing water and dried at ambient temperature. The outcome of monocrystals was 40-45% by mass, the sizes ranged form 0,1 to 3,5 mm. The*

*synthesized compound is investigated using a series of physical and chemical methods, namely, IR spectroscopy, ESDR, XRD/RSA, XRF, DTA, the temperature of the melting and the complete chemical analysis is realized. The X-ray diffraction analysis of  $\text{Na}_4\text{Co}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  single crystals was carried out and the unit lattice parameters were determined. Phosphate crystals belong to the rhombic crystal system, sp. gr.  $\text{Pna}2_1$ ; crystal lattice parameters are equal to:  $a=18,021(1) \text{ \AA}$ ,  $b=10,389(2) \text{ \AA}$ ,  $c=6,532(2) \text{ \AA}$ ,  $V=1222,47(1) \text{ \AA}^3$ ,  $Z=4$ ,  $c_{\text{calc.}}= 3,47 \text{ gm/cm}^3$ . The specific features of the structure of complex phosphate  $\text{Na}_4\text{Co}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  have been established: the presence of conduction channels for the sodium ion along the  $oy$  axis, the presence of differently coordinated Na and Co polyhedra with an uncharacteristic coordination number. The optimal conditions for the growth of complex phosphate single crystals with a high mass yield are selected. The use of the synthesized compound  $\text{Na}_4\text{Co}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  as a functional material with ion conductivity is suggested.*

**Keywords:** *double phosphates, IR-spectroscopy, XRD/RSA, XRF, growing of single crystals, parameters of crystal lattice.*

**Introduction.** The attention of many researchers is focused on the synthesis, search and creation of functional materials on the basis of phosphate compounds in mono- and polycrystal condition. Their applications include piezoelectric, ferroelectric and pyroelectric materials, they are used as accelerants, laser and optic materials, luminophores and ionic conductors etc. [1, 2]. Phosphate compounds can demonstrate valuable electrophysical properties and being a „cost-effective material” they are successfully used in different areas of electrical engineering [3 - 5]. Solid-state synthesis [6], synthesis of polyphosphoric acids [7, 8], water and thermal syntheses are the most famous among the most widespread methods of

producing double phosphates [9 - 11]. But the best results from the point of view of clarity, sizes, quality and characteristics of substances belong to the method of growing double phosphates monocrystals from solutions-fluxes of alkali metals phosphate systems. Using this method the whole series of phosphates  $M^I M^{II} (PO_3)_3$ ,  $M^I M^{II} PO_4$ ,  $M^I_2 M^{II} P_2 O_7$ ,  $M^I_2 M^{II} (PO_3)_4$ ,  $M^I_2 M^{II} (PO_3)_4$ ,  $M^I M^{II}_4 (PO_4)_3$ ,  $M^I_3 M^{III} (PO_4)_2$ ,  $M^I_3 M^{III}_2 (PO_4)_3$ ,  $M^I M^{III} P_2 O_7$  and  $M^I M^{III} (PO_3)_4$  [3 – 7, 12] which became the basis for developing functional materials for multifaceted purposes were obtained. Doping and metal substitution in phosphate matrices and backbones became a convenient „tool“ for getting various compound properties [13].

The investigation of such substances as  $Na_4 M_3 (PO_4)_2 P_2 O_7$  (where M - Mn, Fe, Co, Ni) [14] which demonstrate the characteristics of high-voltage ion batteries has gained a great popularity in the past couple of years. At this, the materials of abovementioned type have a large cyclicity and duration of operations, the search for methods of substituting Fe and Ni in the structure is in progress. In our opinion, substitution of sodium atoms by lithium could greatly improve the chances of producing materials on the basis of phosphate compounds of such a type.

The aim of research is to find a convenient, express and cheap way of getting monocrystals of a new  $Na_4 Co_3 (PO_4)_2 P_2 O_7$  complex phosphate and investigate its chemical properties.

**Experimental.** *Reagents, Synthesis and Methods.*  $Na_4 Co_3 (PO_4)_2 P_2 O_7$  complex double phosphate was synthesized from the fluxes of  $Na_2 O$ - $P_2 O_5$ - $CoO$  system at slow cooling (with the speed  $10^\circ C$  per hour) at the range of temperatures  $1000$ - $650^\circ C$ . Homogeneous fluxes (at  $950^\circ C$ ) with output molar ratio  $Na_2 O:P_2 O_5$  equal  $1,1$  were saturated with  $CoO$  (25 wt. %), using intimate, intermittent mixing during 3-4 hours, raised temperature and crystallized crystals in the abovementioned temperature range. The obtained monocrystals were washed out

from the flux residue using the solution of light-salted acid, washed in flowing water and dried at ambient temperature. The outcome of monocrystals was 40-45% by mass, the sizes ranged from 0,1 to 3,5 mm.

The investigation of crystal structure of  $\text{Na}_4\text{Co}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  is conducted on diffractometer "Siemens P3/PC" (Mo,  $K_\alpha$ -radiation, graphite monochromator). The reduced structure is solved by direct method, unit cell parameters are refined using the full-matrix least squares on 16 reflexes at  $28^\circ \leq \theta \leq 42^\circ$ . Phosphate crystals belong to the rhombic crystal system, sp. gr.  $\text{Pna}2_1$ ; crystal lattice parameters are equal to:  $a=18,021(1) \text{ \AA}$ ,  $b=10,389(2) \text{ \AA}$ ,  $c=6,532(2) \text{ \AA}$ ,  $V=1222,47(1) \text{ \AA}^3$ ,  $Z=4$ ,  $\rho_{\text{calc}}= 3,47 \text{ gm/cm}^3$ . Integrated intensities are measured using the  $2\theta:\theta$  method  $6^\circ \leq 2\theta \leq 62^\circ$  at scanning rate 2-18 degrees per minute. As a result of experiment a total of 1122 reflections were obtained, 1078 independent reflections with  $I > 6\sigma(I)$  were used for calculations and specifying the  $\text{Na}_4\text{Co}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  structure. In the data file the correction for Lorentz factor and polarization was introduced, the experimental correction for absorption was conducted. The structure calculation was conducted using a complex of programmes "SHELX-97" [15]. End value of divergence factor was  $R_w=0,024$ .

**Results and Discussion.** Positional parameters of atoms with standard deviations in the structure under study are presented in Table 1. The structure comprises three structurally independent nickel atoms that have different coordinating oxygen atoms. Co(1) and Co(2) polyhedra have a form of a broken octahedron with coord. num. of cobalt 6. Co(3) atom creates tetragonal pyramid and has coord. num. 5 (Table 2).

**Table 1. Coordinates of atoms ( $\times 10^4$ ) and equivalent thermal corrections ( $\text{\AA}^2 \times 10^3$ ) for the  $\text{Na}_4\text{Co}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  structure**

<i>Atom</i>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U<sub>eq</sub></i>
Co(1)	3614(5)	47(1)	0	4(1)
Co(2)	1693(6)	- 47(1)	5113(1)	4(1)
Co(3)	2406(6)	2560(1)	2345(31)	4(1)
Na(1)	2968(2)	2514(3)	-2416(7)	14(1)
Na(2)	4609(2)	-5400(4)	5657(7)	14(1)
Na(3)	3899(2)	-2624(4)	3242(7)	12(1)
Na(4)	4934(2)	264(3)	-2765(8)	10(2)
P(1)	3208(1)	120(2)	4929(5)	4(1)
P(2)	2301(1)	-24(2)	43(5)	4(1)
P(3)	9316(2)	7500(1)	4209(1)	4(1)
P(4)	6848(2)	10925(1)	2858(1)	3(1)
O(1)	13194(5)	3462(4)	1592(2)	10(1)
O(2)	12864(5)	7016(4)	2043(2)	12(1)
O(3)	9070(5)	5410(4)	2383(2)	17(1)
O(4)	10375(5)	6813(4)	907(2)	16(1)
O(5)	6411(5)	6178(4)	375(2)	14(1)
O(6)	9180(5)	8428(4)	457(2)	11(1)
O(7)	6146(5)	9772(4)	803(2)	10(1)
O(8)	8240(5)	8583(4)	4987(2)	18(1)
O(9)	12243(5)	6408(4)	4145(2)	15(1)
O(10)	7725(5)	6053(4)	4063(2)	15(1)
O(11)	9061(5)	9403(4)	3432(2)	14(1)
O(12)	5623(5)	12879(4)	3322(2)	14(1)
O(13)	8401(5)	11358(4)	2041(2)	10(1)
O(14)	4809(5)	9760(4)	2796(2)	12(1)
O(15)	4145(3)	-3741(6)	10068(9)	8(2)

**Table 2. Lengths of bonds (Å) in Na<sub>4</sub>Co<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> structure**

Distance	Å	Distance	Å
Co(1)-O(1)	2,068(8)	Na(3)-O(1)	2,316(6)
Co(1)-O(6)	2,110(7)	Na(3)-O(1)	2,407(9)
Co(1)-O(7)	2,120(8)	Na(4)-O(1)	2,479(6)
Co(1)-O(2)	2,070(9)	Na(4)-O(2)	2,334(8)
Co(1)-O(14)	2,072(6)	Na(4)-O(9)	2,311(6)
Co(1)-O(9)	2,111(8)	Na(4)-O(14)	2,332(9)
Co(2)-O(3)	2,062(8)	Na(4)-O(9)	2,238(6)
Co(2)-O(4)	2,224(7)	Na(4)-O(14)	2,559(6)
Co(2)-O(5)	2,089(8)	P(1)-O(1)	1,520(3)
Co(2)-O(8)	2,054(9)	P(1)-O(2)	1,536(3)
Co(2)-O(11)	2,039(6)	P(1)-O(3)	1,557(3)
Co(2)-O(15)	2,032(8)	P(1)-O(4)	1,560(2)
Co(3)-O(4)	2,052(8)	P(2)-O(5)	1,536(3)
Co(3)-O(7)	2,004(7)	P(2)-O(6)	1,557(1)
Co(3)-O(3)	2,039(8)	P(2)-O(7)	1,521(3)
Co(3)-O(13)	2,084(9)	P(2)-O(8)	1,533(3)
Co(3)-O(6)	2,039(6)	P(3)-O(9)	1,528(1)
Na(1)-O(7)	2,379(6)	P(1)-O(3)	1,557(3)
Na(1)-O(2)	2,534(6)	P(1)-O(4)	1,560(2)
Na(1)-O(4)	2,411(6)	P(2)-O(5)	1,536(3)
Na(1)-O(6)	2,632(6)	P(2)-O(6)	1,557(1)
Na(1)-O(5)	2,538(6)	P(2)-O(7)	1,521(3)
Na(1)-O(5)	2,359(6)	P(2)-O(8)	1,533(3)
Na(1)-O(11)	2,547(8)	P(3)-O(9)	1,528(1)
Na(2)-O(5)	2,377(8)	P(3)-O(10)	1,498(2)
Na(2)-O(12)	2,616(6)	P(3)-O(11)	1,503(3)
Na(2)-O(10)	2,478(6)	P(3)-O(12)	1,650(3)
Na(2)-O(10)	2,435(6)	P(4)-O(12)	1,630(2)
Na(2)-O(15)	2,457(6)	P(4)-O(13)	1,512(3)
Na(3)-O(1)	2,597(6)	P(4)-O(14)	1,513(3)
Na(3)-O(1)	2,352(6)	P(4)-O(15)	1,503(3)
Na(3)-O(1)	2,404(8)		

Tetrahedra [PO<sub>4</sub>] that create two orthophosphate groups and nickel polyhedra are merged through co-vertices and co-edges in imperfect spheres, perpendicular to direction [100]. Chains from Co(2)O<sub>6</sub>-Co(3)O<sub>5</sub> polyhedra which are merged at vertices by O(3) and O(4) atoms and parallel the direction can be

distinguished [010]. They are intersected by the chains of  $\text{Co(1)O}_6$ -  $\text{Co(3)O}_5$  polyhedra that have the common vertices of O(6) and O(7) atoms and oriented alongside [011]. Diphosphate groups  $[\text{P}_2\text{O}_7]$  merge abovementioned spheres in a backbone whose voids contain sodium atoms. We have to admit that Co-O bonding distances in octahedra (mean  $\sim 2,085 \text{ \AA}$ ) are fully coordinated to nickel (II) coord. num. 6. In  $\text{Co(3)O}_5$  polyhedra Co-O average bonding distance is  $2,040 \text{ \AA}$ , with that the length of Co-O at the bottom of pyramid  $0,04$ - $0,09 \text{ \AA}$  is shorter than Co(3)-O(13) compound which takes axial vertex.  $[\text{PO}_4]$  and  $[\text{P}_2\text{O}_7]$  groups (Table 3) are isolated and have a common structure. The angle  $\angle \text{P(3)-O(12)-P(4)}$  in the nonlinear group is  $130,6(4)^\circ$ , mean ranges P-O equal to  $1,544(2) \text{ \AA}$ ,  $\angle \text{O-P-O}$  mean angle is  $109,5(1)^\circ$ . All these values correspond to almost ideal tetrahedron.

The presence of three different sodium polyhedra with different coordination numbers:  $[\text{Na(1)O}_7]$ ,  $[\text{Na(2)O}_5]$ ,  $[\text{Na(3)O}_5]$  and  $[\text{Na(4)O}_6]$  can be regarded as a structure peculiarity. Sodium polyhedra are assembled by common vertices and edges in endless chains that go along the directions [100] and [011] in the structure. In doing so, the direction of sodium polyhedra chains coincides with orientation of the channels in the backbone Co-P. It enables to expect the presence of valuable characteristics of  $\text{Na}_4\text{Co}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  compound, namely, ionic conductivity.

The chemical composition of the synthesized compound  $\text{Na}_4\text{Co}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  is proved by the full chemical analysis (Table 3).

**Table 3. Results of chemical analysis of synthesized compound (wt. %)**

Formula of compound	$\text{Na}_2\text{O}$		$\text{CoO}$		$\text{P}_2\text{O}_5$	
	calc.	obtained	calc.	obtained	calc.	obtained
$\text{Na}_4\text{Co}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$	19,65	20,95	44,85	43,90	35,50	36,00

IR - spectroscopy of  $\text{Na}_4\text{Co}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  double phosphate which is investigated using UR-20 and UR-10 equipment (Carl Zeiss) by KBr pressed disc method is presented. It is found out that infra-red spectrum of absorption corresponds to  $\text{Na}_4\text{Ni}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  [15], which proves the isostructirality of substances. Significant waves of fluctuation which are  $\tau(\text{PO}_3)$ ;  $\delta_s$ ,  $\delta_{as}(\text{P-O}) + \nu(\text{MO}) - 500\text{-}600\text{ cm}^{-1}$ ;  $\nu_s(\text{P-O-P})$  and  $\nu_{as}(\text{P-O-P}) - 700\text{-}1000\text{ cm}^{-1}$  are typical for phosphates which contain  $[\text{P}_2\text{O}_7]$  - group.

Thermal investigations of  $\text{Na}_4\text{Co}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  synthesized phosphate were conducted using the derivatograph Q-1500 „Paulik” (Hungary). The sample was heated at  $20\text{-}1000^\circ\text{C}$  in dynamic regime of heating the temperature in platinous cylidrical crucibles (the heaviest compound was 0,293 gm, heating rate – 5 degrees per minute<sup>-1</sup>). Having conducted derivatographic research we have found out that double phosphate has a phase transition at  $755^\circ\text{C}$  fluxed without decomposition at  $765^\circ\text{C}$ .

Sodium atoms in the volumetric backbone of  $\text{Na}_4\text{Co}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  phosphate compound play a very important role – they are directly involved in the construction of phosphatic-nickel backbone. It is unambiguously traced in the projected structure on the square [001] (Fig. 2).  $\text{Na}(2)\text{O}_5$  and  $\text{Na}(3)\text{O}_5$  sodium polyhedra have uncharacteristic coordination number and that is why taking into consideration that oxygen atoms are located at a longer distance, we can conditionally believe that Na(2) and Na(3) atoms have oxygen surrounding from 6 atoms. Na(1) atom creates imperfect  $\text{Na}(1)\text{O}_7$  polyhedra through contacting with two isolated groups  $[\text{PO}_4](\text{P}(1)\text{O}_4$  and  $\text{P}(2)\text{O}_4)$ . Na(1) and Na(2) atoms contacting through O(5) merged by O(10)-O(15) edge and through O(1) atom from  $\text{Na}(4)\text{O}_6$  polyhedra into the endless chain along the oy axis. At this conductivity „channel” for sodium ion (similar channels also exist along direction [011]) is created).



Sodium atoms do not have any contacts along the *oz* axis. These “branched” bonds of alkali metal atoms influence greatly the formation of  $\text{Na}_4\text{Co}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  backbone structure.

The spectra of diffuse reflection of polycrystal samples were collected using spectrophotometer “Specord 40” within the range of wave numbers 50000-12000  $\text{cm}^{-1}$ .  $\text{Na}_4\text{Co}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  spectrum which has a characteristic shape typical for Co (II) high-spin compounds of octahedroid-type. In accordance with the energetic scheme of  $\text{Co}^{2+}$  levels of polyoctahedroid symmetry the following band ratio can be foreseen. The more intensive absorption band ( $\sim 20000 \text{ cm}^{-1}$ ) is determined by  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  pass, and the shoulder on the high-energetic band side is determined by forbidden spin-passes or spin-orbital interaction. Within the range of ( $\sim 14000 \text{ cm}^{-1}$ ) a weak low-intense shoulder which is substantiated by  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$  pass is observed. But this pass is very weak in intensity, that is why it is seldom observed in Co (II) electronic spectra.

**Conclusion.** In the fluxes of  $\text{Na}_2\text{O}$ - $\text{P}_2\text{O}_5$ - $\text{CoO}$  system in the range of temperatures 1000-650° C a region of crystallization of  $\text{Na}_4\text{Co}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  complex double phosphate is isolated. Optimal conditions for growing compound monocrystals with high outcome are found out (more that 40-45 wt. %), their physical and chemical characteristics were investigated and compound’s melting point was specified - 765°C. The complex phosphate was investigated by spectroscopic methods and complete differential thermal and chemical analyses were conducted. Crystal structure of  $\text{Na}_4\text{Co}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  synthesized compound using RSA method was investigated and the peculiarities of its structure were specified: the presence of conductivity “channels” for sodium ion along the *oy* axis, orthophosphate groups and nickel polyhedral are merged through common vertices and edges in imperfect spheres, perpendicular to direction [100]; in the

structure there are sodium polyhedral with different coordination number 7, 6 and 5. Obtained findings can provide and assist in creating materials on the basis of  $\text{Na}_4\text{Co}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$  compound.

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