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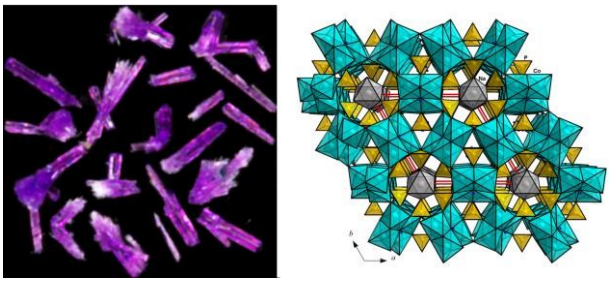
The novel phosphate hydroxide $Na_{2-x}Co_6(OH)_3[HPO_4][H_{x/3}PO_4]_3$ with the mineral ellenbergerite topology and alkaline cations in the framework channels. The compound shows strong antiferromagnetic interaction and magnetic transition at T_N = 44 K.



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ARTICLE TYPE

A novel cobalt sodium phosphate hydroxide with the ellenbergerite topology: crystal structure and physical properties

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The novel phase $Na_{2-x}Co_6(OH)_3[HPO_4][H_{x/3}PO_4]_3$ ($x \approx 1.1$) was prepared by hydrothermal synthesis at 553K. Its crystal structure was determined using single-crystal X-ray diffraction data and refined against F^2 to $R = 0.052$, including positions of all hydrogen atoms. The compound crystallizes in the hexagonal space group $P6_3mc$, with unit-cell parameters $a = 12.630(3)$ Å, $c = 5.017(1)$ Å, $V = 693.1(3)$ Å^3, and $Z = 2$. The crystal structure is based on a 3*D* framework built from CoO_6 octahedra and PO_4 tetrahedra. Channels in the [001] direction accommodate columns of Na-centered octahedra sharing faces. The compound is a new structural representative of the topology shown by aluminosilicate mineral ellenbergerite and its numerous natural and synthetic varieties. Magnetic susceptibility measurements revealed a strong antiferromagnetic interaction and magnetic transition to low temperature spin-canted phase at $T_N = 44$ K. The physical properties of the title compound are found to be very similar to those of the structurally related arsenate $Co_{1-x}Co_6(OH)_3[H_{2x/3}AsO_4]_3[HAsO_4]$ and vanadate $Co_7(OH)_2(H_2O)[VO_4]_4$.

Introduction

The first row transition metal phosphates are of considerable permanent interest due to their promising physical properties. They are used as non-linear optical materials, magnets, ionic conductors, battery materials and molecular sieves, to name it few.[1-3] Particularly, cobalt phosphates with open-framework structures are highly desirable for industrial processes because of their efficacy in catalysis and gas separation.[4,5]

A scarcity of cobalt in the Earth crust results in the rarity of cobalt minerals. Cobalt shows close geochemical relationship with iron, - one of the vastly spread elements. Close sizes of these two divalent Co^{2+} and Fe^{2+} cations allow an isomorphic substitution of iron for cobalt in the structures of minerals and it is this substitution that disperses cobalt in nature. Rare occurrence of cobalt mineralization exhibits mainly sulphurous, arsenics and antimonies compounds, but no cobalt phosphate minerals were discovered up to now.

Several hexagonal Co-phases produced *via* hydrothermal synthesis and exhibiting electronic and magnetic properties, e.g. Co-vanadate $Co_6(OH)_2(H_2O)[VO_4]_4$,[6] Co-tellurite $Co_6(OH)_4[TeO_3]_4$,[7] Co-arsenate $Co_{1-x}Co_6(OH)_3[HAsO_4][H_{2x/3}AsO_4]_3$[8] and Co-phosphite $Co_{5,5}(OH)_3[HPO_3][HPO_3]_3$[9-11] have similar structural topologies to that of aluminosilicate mineral ellenbergerite $(Mg,Ti)Mg_3(Mg,Al)_3(OH)_3[HSiO_4][H_{0.33}SiO_4]_3$.[12] All these compounds with porous 3*D*-frameworks show magnetic interactions between metal centers. In the paper[13] they were called as dumortierite-like materials where mineral dumortierite, $(Al,Mg,Fe^{3+})Al_6(O,OH)_3[BO_3][SiO_4]_3$ has a similar strongly pseudo-hexagonal, but orthorombic structure.

We present here the crystal structure and physical properties of a novel sodium cobalt phosphate with the ellenbergerite topology obtained under hydrothermal conditions, in comparison with its natural and synthetic structural analogues and modifications. The Na-based layered and tunnel-type transition metal oxides are of great potential since their high capacity and safety open way to low cost cathode materials. These oxides stand for the promising alternative to widely used Li-based compounds.[14] For example, the Na_xCoO_2 has been considered as an excellent and stable positive electrode similar to its highly efficient Li counterpart.[15] The necessary preconditions for new cathode materials are high mobility of the alkali ions and the presence of transition metals capable for a reversible change of their oxidation state. These demands are met in the title compound. While the presence of hydroxyl groups hampers its potential for use in Na-based batteries, the investigation of the physical properties can help in a future design of new open-framework sodium cobalt phosphates.

Experimental

Synthesis and chemical composition

The new phase – lilac crystals of needle-prismatic shape with a maximum lengthening of 0.1 mm (Fig.1) – was obtained by hydrothermal synthesis. A mixture of 0.5 g $CoCl_2$, 0.5 g Na_3PO_4 and 0.5 g Na_2CO_3 was placed in a 5ml. stainless steel bomb with

distilled water filling 0.8 of the volume. A small amount of H_3BO_3 (5 wt.%) was added to the starting materials as a mineralizer. The experiment was performed at a temperature of 553 K and a pressure of 70 bars over a period of 18 days. The reaction products were the new phase in an amount estimated of 85 % of the total yield and a white powder. After cooling of the furnace the crystals were washed with water, dried and analyzed on a scanning electron microscope (SEM)[‡] for composition and by single-crystal X-ray diffraction for structure. The JEOL SEM (JSM-6480LV) was equipped with an energy dispersive X-ray detector INCA Energy-350 and an INCA Wave-500 four-crystal wave diffraction spectrometer. The crystals were stable under conditions of measuring, that is 20 kV and 0.7 nA. X-ray spectral analysis revealed the presence of Co, P, Na and O in the samples; an approximate semiquantitatively determined Co:P:Na ratio was found as 6:4:1. The very thin crystals (about 5-10 μm) did not allow getting a good sample surface necessary for a quantitative analysis. However, the found ratio of metal atoms is fully consistent with the results of our X-ray diffraction structural study.

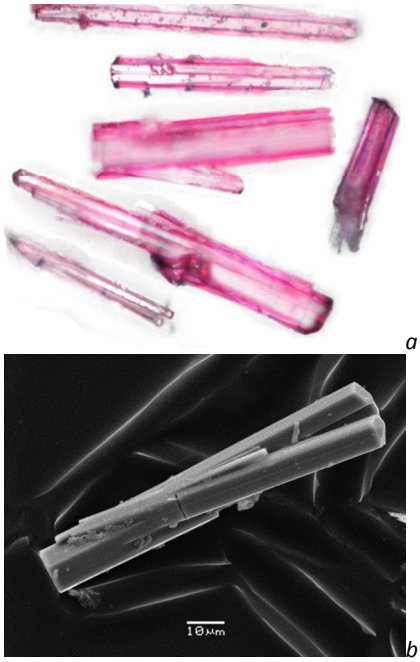

Fig.1 Photo of crystals of the title compound (a) and SEM image, showing the prismatic morphology of the studied crystal (b)

Magnetic and thermodynamics measurements

Physical properties, i.e. specific heat and magnetization, of the $Na_{2-x}Co_6(OH)_3[HPO_4][H_{x/3}PO_4]_3$ were studied on the pressed powder sample with mass of about 4 mg. The specific heat C_p was studied by the relaxation method using the calorimeter option of "Quantum Design" Physical Property Measurement System PPMS-9T. The magnetization M in the temperature range T = 2 ÷ 300 K under magnetic field up to B = 7 T was measured by SQUID magnetometer of "Quantum Design" Magnetic Property Measurement System MPMS-7T.

X-ray analysis

The determination of unit-cell parameters and data collection were performed on an Xcalibur-S area detector diffractometer using Mo*K*α radiation (graphite monochromator). The intensities were corrected for Lorentz and polarization effects, and a numerical absorption correction based on Gaussian integration over a multifaceted crystal model was applied. In Table 1, we report the crystallographic characteristics of the new phase and the experimental conditions of data collection and refinement.

All of the calculations were performed in a framework of the WinGX32 software package.[16] Atomic scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography.[17] The crystal structure was solved *via* direct methods in the space group $P6_3mc$ using the SIR-92 program[18] and refined against the F^2 data with SHELXL[19] to the final R factor of 0.052 (for 661 unique reflections with $I > 2\sigma(I)$), using anisotropic displacement parameters.

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-6666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD429235.

Table 1. Crystal Data and Details of the X-ray Data Collection and Refinement

Crystal data	
Chemical formula, M (g mol^{-1})	$Na_{0.912}Co_6(OH)_3[HPO_4][H_{0.363}PO_4]_3$, 807.51
Crystal. system, Space group	hexagonal, $P6_3mc$ (no. 186)
a, c (Å)	12.630(3), 5.0170(10)
V (Å^3), Z	693.1(3), 2
D_c (g cm^{-3})	3.869
Crystal size (mm)	0.01 × 0.02 × 0.11
Crystal colour	lilac
Absorption coeff. μ(mm^{-1})	7.63
Data collection	
Diffractometer	Xcalibur-S, CCD
Radiation	Mo-K_α (λ = 0.71073 Å)
Temperature (K)	293(2)
Scanning mode	ω
Measuring range	$2\vartheta_{max}$ = 57.88°
Reflections (total)	12169
R_{int}, $R(\sigma)$	0.1186, 0.0402
h, k, l range	$-17 \le h \le 17$, $-17 \le k \le 17$, $-6 \le l \le 6$
Refinement	
Reflections unique/ observed ($I > 2\sigma(I)$)	695, 661
Number of refined parameters	65
Absorption correction, T_{max}, T_{min}	numerical, 0.780, 0.886
Extinction coefficient	0.0011(4)
R (observed reflections)	0.0520
R, w R_2 (all reflections)	0.0554, 0.0747
Goodness of fit S	1.278
δρ (max/min) (e Å^{-3})	0.953, -1.901

Structure refinement

The found structure contains partly populated atomic positions and is thus characterized by presence of vacancy defects and some statistical disorder. So, refinement of the site occupancy factor of Na1 on a 2*a* Wyckoff position resulted in a value of 0.152(4). This parameter was fixed in the final cycles of refinement.

The quality of our X-ray data was sufficient to localize hydrogen atoms. The 3 independent positions of H atoms were obtained by difference-Fourier techniques and refined with common free isotropic displacement parameters. The O–H

distances were fixed by hard restrains to an empirical value of 0.85 Å in order to obtain comparable H-bond geometries, not affected by arbitrary scatter of refined O–H bond lengths. According to these localized hydrogen atoms, O6 forms an OH group bridging four Co atoms. Besides, a terminal hydroxide was found on O4 on a 2*a* Wyckoff position, giving rise to an $[HPO_4]^{2-}$ anion. Note that the occupancy of hydrogen atom H3 near O4 was fixed to the idealized value of 1/6. The position of hydrogen atom H2 near O2 has also to be partly occupied because it correlates with vacancies in the Na1 site. Thus, O2 forms with 18% probability an OH group. In this way, a charge-balanced formula is achieved. Accordingly, we consider the vacancy at Na1 sites and the assignment of OH or O at O2 as statistically distributed in the structure.

Table 2 presents the final results of the atom positions and equivalent isotropic displacement parameters. Characteristic distances are given in Table 3, geometric characteristics of hydrogen bonds in Table 4. A bond-valence calculation (Table 5) has been performed using the algorithm and parameters offered in the work.[20, 21] Valence contributions of the H atoms were estimated from the O–O distances following equations presented in the study.[22] Data from Table 5 clearly confirm the assignment of OH ligands.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2)

Atom	*x/a*	*y/b*	*z/c*	U_{eq}/ U_{iso}
Co1	0.07765(7)	0.65220(8)	0.0896(9)	0.0110(2)
P1	0.15516(12)	0.84484(12)	0.5676(12)	0.0147(6)
P2	0.33333	0.66667	-0.1362(12)	0.0096(9)
Na1*	0.0	0.0	0.7724(19)	0.023(2)
O1	0.0750(4)	0.7284(4)	0.7286(12)	0.0134(11)
O2	0.0855(4)	0.9145(4)	0.5241(16)	0.031(2)
O3	0.1888(4)	0.8112(4)	0.2987(17)	0.0176(17)
O4	0.33333	0.66667	0.551(3)	0.043(5)
O5	0.3992(3)	0.6008(3)	-0.0406(19)	0.0202(18)
O6	0.0497(7)	0.5248(3)	0.4015(9)	0.0135(16)
H1	0.080(13)	0.540(7)	0.558(12)	0.10(6)
H2*	0.058(13)	0.942(13)	0.65(5)	0.10(6)
H3*	0.3956(11)	0.6978(6)	0.45(5)	0.10(6)

*Occupancy factors are: 0.912 for Na1, 0.363 for H2 and 1/3 for H3

Table 3. Interatomic Distances (Å)

Co octahedron		Na octahedron	
Co – O1	2.058(5)	Na – O2	2.247(10)x3
O1	2.059(5)	O2	2.256(9)x3
O3	2.070(4)	<Na–O>	2.252
O5	2.077(5)		
O6	2.143(6)		
O6	2.209(6)		
<Co–O>	2.103		
P1 tetrahedron		**P2 tetrahedron**	
P1 – O1	1.533(5)x2	P2 – O5	1.519(7)x3
O3	1.537(8)	O4	1.568(17)
O2	1.540(8)	<P2–O>	1.531
<P1–O>	1.536		

Table 4. Geometric characteristics of hydrogen bonds

D – H····A	D – H, Å	H····A, Å	D····A, Å	∠ D – H····A,°
O6 – H1····O5	0.85(1)	2.41(6)	3.255(9)	169(6)
O2 – H2····O2	0.85(1)	2.5(2)	3.128(9)	129(9)
O4 – H3····O3	0.85(1)	2.59(1)	3.405(9)	160(1)

Table 5. Bond valence data for $Na_{0.912}Co_6(OH)_3[HPO_4][H_{0.363}PO_4]_3$

Atom	Co	Na	P1	P2	H1	H2	H3	Σ
O1	0.372		$1.248_{\times 2\downarrow}$					1.99
	0.371							
O2		$0.142_{\times 3\downarrow}$	1.225			0.01		1.85
		$0.139_{\times 3\downarrow}$				0.33		
O3	$0.360_{\times 2\rightarrow}$		1.235				0.06	2.02
O4				1.135			0.94	2.08
O5	$0.353_{\times 2\rightarrow}$			$1.296_{\times 3\downarrow}$	0.07			2.07
O6	$0.296_{\times 2\rightarrow}$				0.93			2.02
	$0.247_{\times 2\rightarrow}$							

The symbols ↓ and → show a multiplication of the corresponding contributions in the columns and rows due to symmetry.

Results and Discussions

Description of the crystal structure

The main structural elements of the title compound are shown in Fig. 2. The Co^{2+} and Na^+ ions are surrounded by O atoms, forming octahedral configurations. The CoO_6 polyhedra are significantly distorted with Co–O bond lengths that vary from 2.058(5) Å to 2.208(6) Å. The NaO_6 octahedra "strung" on the six-fold screw axis are characterized by Na–O distances of 2.248(10)x3 Å and 2.255(9)×3 Å. Co-centred octahedra sharing faces form dimers that are extended in double chains along [001]. These chains of faces- and edges sharing octahedra are further arranged in a three-dimensional framework through vertex bridging (Fig. 3, 4). The NaO_6 octahedra share opposite faces to form single columns stretched out the *c*-axis. Phosphorus atoms in two symmetrically independent positions are tetrahedrally coordinated. In regular $P1O_4$ tetrahedra the P1–O bond lengths range from 1.533(5) to 1.540(8) Å. The $P2O_4$ polyhedra on the three-fold axes are strongly distorted with three P2–O distances equal to 1.519(7) Å and one equal to 1.575(17) Å, matching hydroxyl group. Each P1-centered tetrahedron unites the column of NaO_6 octahedra with two CoO_6 octahedral chains, while the P2-centered tetrahedron shares three vertices with CoO_6 polyhedra, thus, strengthening the framework.

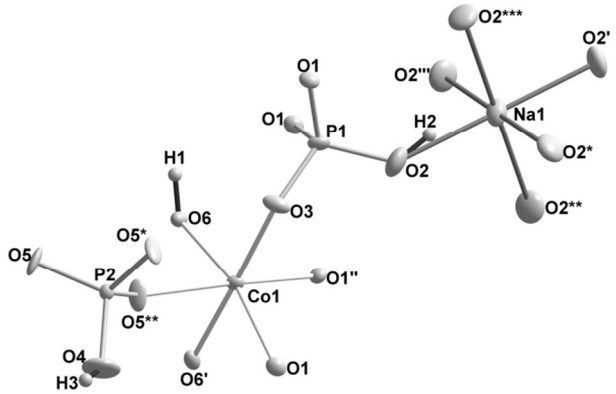

Fig. 2 Basic structural units with atom labeling scheme. Displacement ellipsoids are presented at the 50% probability level. Symmetry codes: (*) 1–*y*, 1+*x*–*y*, *z*; (**)–*x*+*y*, 1–*x*, *z*; (') –*x*, 1–*y*, –½+*z*; ('') –*x*, –*x*+*y*, –½+*z*; (***)1+*x*–y, 1+*x*, ½+*z*; (''') –1+*y*, –*x*+*y*, ½+*z*.

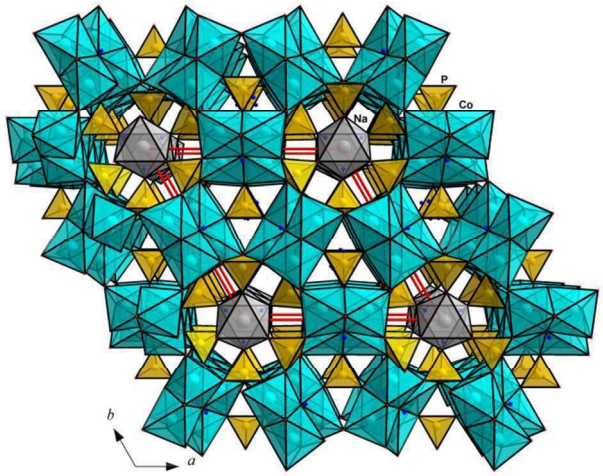

Fig. 3 The title crystal structure in an axonometric projection.

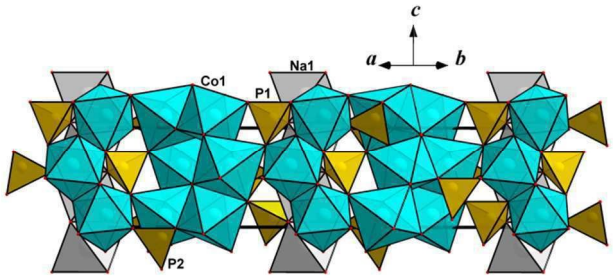

Fig. 4 The title crystal structure shown along the [110] direction.

Therefore, the crystal structure has hexagonal channels extended along the six-fold screw axis. These channels are centred by columns of face-sharing NaO_6 octahedra attached to the framework by rings of phosphate tetrahedra. Smaller triangular channels built by CoO_6 polyhedra enclose HPO_4 tetrahedra by means of vertex bridging. This framework with rod-like components[13] is responsible for the needle-like morphology of synthesized crystals (Fig. 1). The structural formula of the new phase looks like $Na_{0.912}Co_6(OH)_3[HPO_4][H_{0.363}PO_4]_3$ (*Z*=2). It is important to note that the proportion of vacancies at the Na site is correlated with the H amount in the same channels. It means that the capacity of the structure for Na is strongly coupled with the total of OH groups in the vertices of P1-centered tetrahedra. The crystal chemical formula presented in the general form as $Na_{2-x}Co_6(OH)_3[HPO_4][H_{x/3}PO_4]_3$ reflects this model.

Our phosphate crystal structure likewise other structures of the dumortierite family is very flexible; for this reason they are able to accommodate a wide variety of atoms. Minerals of this group contain mostly Al^{3+} or Mg^{2+} and Fe^{3+} cations in the octahedral positions of the framework.[12,23-31] Larger range of cations (different first raw transition metals and magnesium) in this site is known for synthetic phases.[6-11,32-34] Small triangular channels may be chiefly occupied by planar BO_3 groups, sometimes by SiO_4, HPO_4 or HPO_3 tetrahedra, or pyramidal TeO_3 and SeO_3 oxocomplexes.

A main crystal chemical dissimilarity between the title compound and other natural and synthetic phases with the ellenbergerite topology occurs in a composition of octahedra in the hexagonal tunnels. Generally, divalent Mg^{2+}, Co^{2+} and trivalent Al^{3+} cations populate their centres. In some mineral structures these positions may be vacant or occupied by Ti^{4+} or Nb^{5+}.[30,31] Differently, the columns of octahedra centred by alkaline Na atoms are placed in these channels in our structure (Fig. 3). As has been mentioned in the paper[26], no full occupancy seems possible for face sharing octahedra in hexagonal channels because of a very short distance between two adjacent in the [001] direction cations. Our structure refinement in full agreement with the aforesaid observation has shown that NaO_6 octahedra contain vacancies: the distance between the two neighbouring Na atoms of 2.5085(5) Å corresponds to about of 90% occupancy of their sites.

The localization and refinement of the hydrogen atoms have allowed the implementation of a rigorous interpretation of the peculiarities of the hydrogen bonds in the structure (Table 4: note that the H···Acceptor (*A*) distances and O–H···*A* angles refer to unified X-ray positions of H atoms). With O···O distances between 3.128(9) and 3.405(9) Å, they are classed as very weak[35] and are rather rare.[36] The system of O–H···O asymmetric hydrogen bonds between hydroxyl groups and oxygen atoms supplies additional cross-linking in the structure. The hydroxyl group O6–H1 bridging four Co atoms plays the role of a donor providing hydrogen bonding to the oxygen atom O5, and thus strengthening the framework of Co octahedra as shown in Fig. 5a. An oxygen vertex of the Na-centred octahedron O2 forms with 18% probability an OH group (O2–H2); this oxygen atom O2 also acts as an acceptor of the disordered bifurcated O2–H2···O2'(O2'') hydrogen bond (Fig. 5b). As we pointed out, the H2 position is coupled with the vacancies in the NaO_6 polyhedron. Atom O4 at the vertex of the $P2O_4$ tetrahedron is involved as a donor in the hydrogen bonding with a framework atom O3 forming the weakest O4–H3···O3 contact as long as 3.405(9) Å (Fig. 5c).