

A Novel Non-stoichiometric Phosphate $\text{Ba}_{0.94}\text{Co}_{0.81}\text{Cr}_{1.84}(\text{PO}_4)_3$ with the $\alpha\text{-CrPO}_4$ Structure: Synthesis and Crystal Structure

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Abstract

Due to their interesting structural flexibility, affordable synthesis, and various properties, scientists have recently focused on developing novel phosphates containing transition metals with numerous promising structures. Using a typical solid-state reaction, a new phosphate $\text{Ba}_{0.94}\text{Co}_{0.81}\text{Cr}_{1.84}(\text{PO}_4)_3$ is elaborated as a single crystal, and its structure is determined by X-ray diffraction technique. It crystallizes in the orthorhombic system with the *Imma* space group and the unit cell parameters $a = 10.4773$ (4) Å, $b = 13.1814$ (5) Å, and $c = 6.6117$ (2) Å. The structure of this novel compound is characterized by partially occupied sites situated on the special positions *4e*, *4a*, and *8g*. The crystal framework is constructed from isolated polyhedra CoO_6 , PO_4 , and Cr_2O_{10} dimers resulting from edge-sharing CrO_6 octahedra. The linkage between Cr_2O_{10} units and PO_4 tetrahedra via common corners and edges results in a sheet parallel to the (b,c) plane. Alternating PO_4 tetrahedra and CoO_6 octahedra form linear chains running along the *b*-axis. The interconnection of the sheets and chains forms the crystal framework, exhibiting two types of intersecting tunnels containing Ba^{2+} ions.

Keywords

Phosphate, Single crystal X-ray diffraction, Crystal structure

Introduction

Today, there are a number of research works on the synthesis and study of transition-metal based phosphates with different structures [1-4], which present interesting properties such as electrode material for rechargeable batteries [5], magnetic [6-9], luminescence [10], and catalysis [11]. The physical properties of phosphates are related to their crystal structure and to the nature of transition metals. For instance, transition-based phosphates with Li^+ and Na^+ in the tunnels or cavities would provide Na^+ and Li^+ mobility in the structure. Olivine, NASICON, and Alluaudite are widely investigated phosphates for their promising properties such as electrode materials for batteries [5, 12-14]. Furthermore, the $\alpha\text{-CrPO}_4$ family of phosphates showed a growing interest due to their promising structural features such as large tunnels which could house a wide selection of metals.

The CrPO_4 compound [15] exhibits two phases with different structures. The low-temperature $\beta\text{-CrPO}_4$ [16] phase crystallizes in the *Cmcm* space group of the orthorhombic system, whose structure consists of infinite chains formed by sharing the trans-edges of CrO_6 octahedra parallel to the *c* axis. These chains are linked together by the vertices of PO_4 tetrahedra to form the crystal framework. This type of structure can be adopted for arsenates, and vanadates as well [17-19]. Above 1175 °C, the light green beta form transforms into a dark blue alpha form.

The high-temperature phase α - $CrPO_4$ [15] crystallizes in the orthorhombic system with the *Imma* space group. Its structure is constructed from an ordered skeleton of bonded CrO_6 octahedra and PO_4 tetrahedra producing two types of large tunnels running along [010] and [100] directions.

Recently, α - $CrPO_4$ type phosphate α - $Na_2Ni_2Fe(PO_4)_3$ has been used as an anode for sodium-ion battery, when cycled at a voltage range of 0.03 - 3.0 V, displaying a high capacity of 370 mAh.g⁻¹ [20]. In addition, vanadium-based phosphate $NaV_3(PO_4)_3$ has been synthesized via a facile sol-gel method and produced a high reversible capacity of 140 mAh.g⁻¹ with good cycling stability in the voltage range of 0.0 - 3.0 V versus Na⁺/Na.

In the context of new phosphates elaboration and characterization, we report in this work, the crystal growth, and the structural study of a new non-stoichiometric phosphate with α - $CrPO_4$ structure containing cobalt and chromium metals.

Materials and Methods

Crystal synthesis

Crystals of $Ba_{0.94}Co_{0.81}Cr_{1.84}(PO_4)_3$ were synthesized by a conventional solid-state reaction in air from the precursors $BaCO_3$, $CoCO_3$, Cr_2O_3 , and $NH_4H_2PO_4$, which were weighted in stoichiometric proportions corresponding to the molar ratio Ba:Co:Cr:P = 1:1:2:3. The precursors were mixed by grinding with an agate mortar. The mixture was heated successively at 400, 600, 750, 900, and 940 °C, with intermittent grinding, in order to homogenize the product and also to increase the contact surface between the grains to promote the diffusion reaction. The obtained solid is melted at 1200 °C and kept at this temperature for 30 min followed by slow cooling at a rate of about 5 °C/h. The final product contained green crystals of appropriate size for X-ray diffraction study.

Structure determination

X-ray diffraction data of the single crystal $Ba_{0.94}Co_{0.81}Cr_{1.84}(PO_4)_3$ were collected at 296 K, using Bruker X8 APEX diffractometer with monochromatic MoK α radiation using an incident wavelength $\lambda = 0.71073$ (Å). APEX2 [21] software was used for data collection and SADABS [22] was used for the absorption correction by a multi-scan semi-empirical method. The structure of title crystal was solved via the direct method and refined by using SHELXT 2014 [23] and SHELXL 2014 [24] programs incorporated in the WinGX

program [25]. For structural drawing, DIAMOND was used [26]. The structure is determined at nanometric scale.

Results and Discussion

The structural determination from single X-ray diffraction data shows that it crystallizes with the α - $CrPO_4$ structure-type. Nine atomic positions compose the asymmetric unit, including 1 Ba, 1 Co, 1 Cr, 2 P, and 4 O atoms. These atoms are all in special positions, except the oxygen atoms (O1, O2) that are in general positions. The two phosphorus atoms are located at Wyckoff positions *8g* and *4e* of the *Imma* space group. In addition, Cr and Co are located at *8g* and *4a* special positions with partial occupancies of 92% and 80% respectively, Ba atom occupy 93% of the special position *4e*. The oxygens are located at Wyckoff positions *16j*, *8b*, and *8i*, which yields to the final chemical formula $Ba_{0.94}Co_{0.81}Cr_{1.84}(PO_4)_3$. Crystal data, data collection, and structure refinement parameters are listed in table 1. Atomic positions, atomic displacement, and geometric parameters are given in table 2, table 3, and table 4, respectively.

The structure of this phosphate is constructed from two

Table 1: Crystal data and structure refinement details of $Ba_{0.94}Co_{0.81}Cr_{1.84}(PO_4)_3$.

Crystal data	
Chemical formula	$Ba_{0.94}Co_{0.81}Cr_{1.84}(PO_4)_3$
M_r (g/mol)	1113.18
Crystal system, space group	Orthorhombic, <i>Imma</i>
Temperature (K)	296
a, b, c (Å)	10.4773 (4), 13.1814 (5), 6.6117 (2)
V (Å ³)	913.11 (6)
Z	2
Radiation type	Mo K α
μ (mm ⁻¹)	8.16
Data collection	
Diffractometer	Bruker X8
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8356, 1211, 1196
R_{int}	0.027
$(\sin\theta/\lambda)_{max}$ (Å ⁻¹)	0.839
Refinement	
$R[F^2 > 2s(F^2)], wR(F^2), S$	0.020, 0.050, 1.25
No. of reflections	1211
No. of parameters	56
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	2.38, -1.32

Table 2: Atomic positions, equivalent displacement parameters, and occupancies rates.

Atom	Wyckoff site	x	y	z	U_{eq}	Occ. (<1)
Ba	<i>4e</i>	0.500000	0.750000	0.89616 (2)	0.00831 (7)	0.9342 (17)
Co	<i>4a</i>	0.500000	0.500000	0.500000	0.00298 (11)	0.808 (3)
Cr	<i>8g</i>	0.250000	0.63251 (3)	0.250000	0.00780 (9)	0.921
P1	<i>8g</i>	0.250000	0.42937 (3)	0.250000	0.00433 (9)	
P2	<i>4e</i>	0.500000	0.750000	0.40313 (10)	0.00430 (12)	
O1	<i>16j</i>	0.36222 (8)	0.50536 (7)	0.29346 (15)	0.00664 (15)	
O2	<i>16j</i>	0.28288 (10)	0.36556 (8)	0.06588 (17)	0.00977 (17)	
O3	<i>8b</i>	0.500000	0.65452 (10)	0.5335 (2)	0.0077 (2)	
O4	<i>8i</i>	0.38118 (13)	0.750000	0.2638 (2)	0.0071 (2)	

Table 3: Anisotropic displacement parameters.

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ba	0.00766 (9)	0.01222 (9)	0.00504 (9)	0.000	0.000	0.000
Co	0.00312 (17)	0.00244 (17)	0.00339 (18)	0.000	0.000	0.00034 (11)
Cr	0.00779 (14)	0.00576 (14)	0.00984 (15)	0.000	-0.00076 (10)	0.000
P1	0.00464 (17)	0.00342 (18)	0.00493 (18)	0.000	-0.00057 (12)	0.000
P2	0.0041 (2)	0.0032 (2)	0.0057 (3)	0.000	0.000	0.000
O1	0.0058 (3)	0.0060 (3)	0.0081 (3)	-0.0013 (3)	-0.0015 (3)	0.0008 (3)
O2	0.0108 (4)	0.0084 (4)	0.0101 (4)	0.0028 (3)	-0.0009 (3)	-0.0041 (3)
O3	0.0083 (5)	0.0051 (5)	0.0095 (6)	0.000	0.000	0.0022 (4)
O4	0.0055 (5)	0.0084 (5)	0.0074 (5)	0.000	-0.0020 (4)	0.000

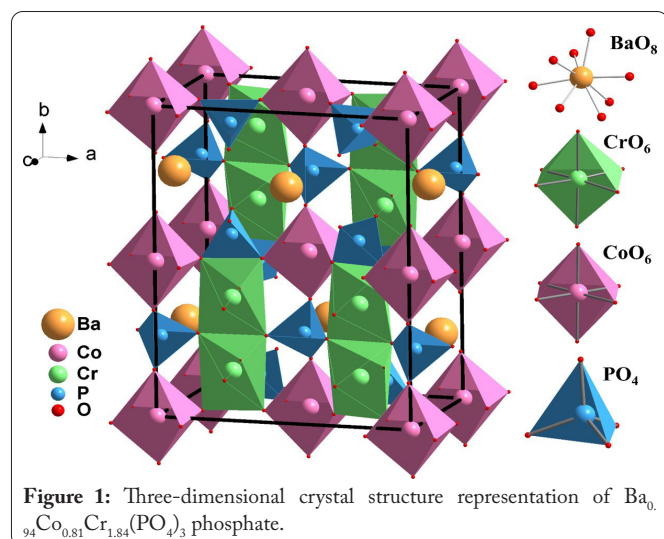
Table 4: Selected interatomic distances (Å) and angles (°).

Distances (Å)			
Ba—O3 ⁱ	2.7081 (15) × 2	P1—O2 ^{ix}	1.5192 (11) × 2
Ba—O4 ^{ii,iii}	2.7312 (14) × 2	P1—O1 ^{ix}	1.5711 (10) × 2
Ba—O2 ^{iv,v,vi,vii}	2.7493 (11) × 4	P2—O3	1.5254 (14)
Co—O1 ^{vi,viii,vi}	1.9884 (9) × 4	P2—O3 ⁱ	1.5255 (14)
Co—O3 ^{vi}	2.0488 (14) × 2	P2—O4 ⁱ	1.5485 (14) × 2
Cr—O1 ^{ix}	2.0674 (10) × 2		
Cr—O4 ^x	2.0726 (9) × 2		
Cr—O2 ^{xi,xii}	2.1169 (11) × 2		
Angles (°)			
O3—Ba—O3 ⁱ	55.39 (6)	O1 ^{vi} —Co—O3 ^{vi}	92.23 (4)
O3—Ba—O4 ⁱⁱ	142.01 (3)	O1 ^{viii} —Co—O3 ^{vi}	87.77 (4)
O3 ⁱ —Ba—O4 ⁱⁱ	142.01 (3)	O1 ^v —Co—O3 ^{vi}	92.23 (4)
O3—Ba—O4 ⁱⁱⁱ	142.01 (3)	O1—Co—O3	92.23 (4)
O3 ⁱ —Ba—O4 ⁱⁱⁱ	142.01 (3)	O1 ^{vi} —Co—O3	87.77 (4)
O4 ⁱⁱ —Ba—O4 ⁱⁱⁱ	54.23 (6)	O1 ^{viii} —Co—O3	92.23 (4)
O3—Ba—O2 ^{iv}	109.77 (3)	O1 ^v —Co—O3	87.77 (4)
O3 ⁱ —Ba—O2 ^{iv}	79.82 (3)	O3 ^{vi} —Co—O3	180.0
O4 ⁱⁱ —Ba—O2 ^{iv}	62.72 (3)	O1 ^{ix} —Cr—O1	71.67 (5)
O4 ⁱⁱⁱ —Ba—O2 ^{iv}	107.21 (3)	O1 ^{ix} —Cr—O4	171.51 (4)
O3—Ba—O2 ^v	79.82 (3)	O1—Cr—O4	102.85 (4)
O3 ⁱ —Ba—O2 ^v	109.77 (3)	O1 ^{ix} —Cr—O4 ^x	102.85 (4)
O4 ⁱⁱ —Ba—O2 ^v	107.21 (3)	O1—Cr—O4 ^x	171.51 (4)
O4 ⁱⁱⁱ —Ba—O2 ^v	62.72 (3)	O4—Cr—O4 ^x	83.30 (6)
O2 ^{iv} —Ba—O2 ^v	169.53 (5)	O1 ^{ix} —Cr—O2 ^{xi}	88.00 (4)
O3—Ba—O2 ^{vi}	79.82 (3)	O1—Cr—O2 ^{xi}	93.11 (4)
O3 ⁱ —Ba—O2 ^{vi}	109.77 (3)	O4—Cr—O2 ^{xi}	85.80 (5)
O4 ⁱⁱ —Ba—O2 ^{vi}	62.72 (3)	O4 ^x —Cr—O2 ^{xi}	93.17 (5)
O4 ⁱⁱⁱ —Ba—O2 ^{vi}	107.21 (3)	O1 ^{ix} —Cr—O2 ^{xii}	93.11 (4)
O2 ^{iv} —Ba—O2 ^{vi}	67.29 (5)	O1—Cr—O2 ^{xii}	88.00 (4)
O2 ^v —Ba—O2 ^{vi}	111.68 (5)	O4—Cr—O2 ^{xii}	93.17 (5)
O3—Ba—O2 ^{vii}	109.77 (3)	O4 ^x —Cr—O2 ^{xii}	85.80 (5)
O3 ⁱ —Ba—O2 ^{vii}	79.82 (3)	O2 ^{ix} —Cr—O2 ^{xii}	178.63 (6)
O4 ⁱⁱ —Ba—O2 ^{vii}	107.21 (3)	O2 ^{ix} —P1—O2	112.76 (9)
O4 ⁱⁱⁱ —Ba—O2 ^{vii}	62.72 (3)	O2 ^{ix} —P1—O1 ^{ix}	109.26 (6)
O2 ^{iv} —Ba—O2 ^{vii}	111.68 (5)	O2—P1—O1 ^{ix}	112.09 (6)
O2 ^v —Ba—O2 ^{vii}	67.29 (5)	O2 ^{ix} —P1—O1	112.09 (6)
O2 ^{vi} —Ba—O2 ^{vii}	169.53 (5)	O2—P1—O1	109.26 (6)
O1—Co—O1 ^{vi}	180.0	O1 ^{ix} —P1—O1	100.78 (7)
O1—Co—O1 ^{viii}	93.10 (6)	O3—P2—O3 ⁱ	111.19 (12)
O1 ^{vi} —Co—O1 ^{viii}	86.90 (6)	O3—P2—O4 ⁱ	109.64 (4)
O1—Co—O1 ^v	86.90 (6)	O3 ⁱ —P2—O4 ⁱ	109.64 (4)
O1 ^{vi} —Co—O1 ^v	93.10 (6)	O3—P2—O4	109.64 (4)
O1 ^{viii} —Co—O1 ^v	180.0	O3 ⁱ —P2—O4	109.64 (4)
O1—Co—O3 ^{vi}	87.77 (4)	O4 ⁱ —P2—O4	107.02 (11)

Note: Symmetry codes : (i) -x+1, -y+3/2, z; (ii) -x+1, -y+3/2, z+1; (iii) x, y, z+1; (iv) -x+1, y+1/2, -z+1; (v) x, -y+1, -z+1; (vi) -x+1, -y+1, -z+1; (vii) x, y+1/2, -z+1; (viii) -x+1, y, z; (ix) -x+1/2, y, -z+1/2; (x) -x+1/2, -y+3/2, -z+1/2; (xi) x, -y+1, -z; (xii) -x+1/2, -y+1, z+1/2.

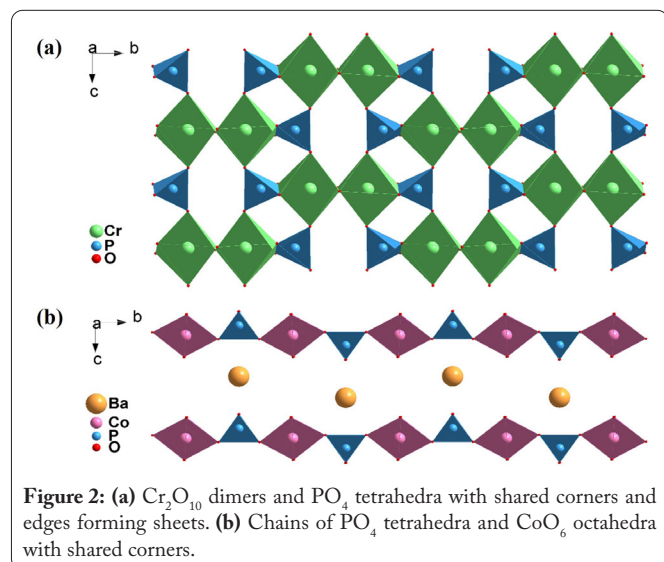
independent PO_4 tetrahedra, CoO_6 octahedra and Cr_2O_{10} dimers (Figure 1). The crystal framework can be easily described by considering the combination of two main blocks:

Initially the sheet parallel to the (b,c) plane is built from the interconnection between Cr_2O_{10} units and PO_4 tetrahedra via common oxygen corners and edges (Figure 2a). Secondly the



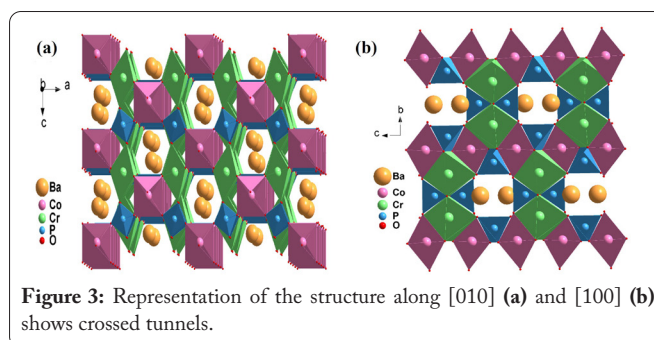
chain parallel to the b-axis is formed by alternating CoO_6 octahedra and PO_4 tetrahedra (Figure 2b). Neighboring sheets are connected through chains of alternating PO_4 and CoO_6 polyhedra, parallel to the b-axis, inducing two types of tunnels running along [010] and [100] directions, where Ba^{2+} ions are located as illustrated in figure 3a and figure 3b, respectively.

The CoO_6 octahedron is slightly distorted with $Co-O$ distances ranging from 1.9884 (9) Å to 2.0488 (2) Å, while the CrO_6 octahedron is distorted with $Cr-O$ distances varying between 2.0674 (2) Å to 2.1169 (2) Å. The average distance value of 2.0085 Å for Co^{2+} is lower than that of 1.968(2) Å observed in $NaCoPO_4$ [27]. On the other hand, the average $\langle Cr-O \rangle$ distance of 2.0856 Å is slightly higher than 1.972 Å reported in α - $CrPO_4$ [28].



Conclusion

In summary, a new phosphate $Ba_{0.94}Co_{0.81}Cr_{1.84}(PO_4)_3$ belonging to the structure α - $CrPO_4$ type was synthesized by solid-state reaction. It crystallizes in the orthorhombic system with the $Imma$ space group. The structural refinement indicates different partial cationic distributions. The three-



dimensional framework is constructed from CoO_6 and CrO_6 and PO_4 polyhedra that share edges and/or corners, inducing two types of tunnels along the [010] and [100] directions in which barium cations are situated.

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Conflict of Interest

None.

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