

# Crystal Structure of Baryum Dicobalt Iron (III) Three (Orthophosphate) Belonging to $\alpha$ -CrPO<sub>4</sub> Family

Adam Bouraima<sup>1,2</sup>, Jean Jacques Anguile<sup>2</sup>, Abderrazzak Assani<sup>1</sup>, Mohamed Saadi<sup>1</sup>, Thomas Makani<sup>2</sup>, Lahcen El Ammari<sup>1</sup>

<sup>1</sup>Laboratoire de Chimie du Solide Appliqué, Faculté des Sciences, Mohammed V University in Rabat, BP 1014, Rabat, Morocco

<sup>2</sup>Laboratoire de Chimie des Matériaux Inorganiques, Faculté des Sciences, Université des Sciences et Techniques de Masuku,

BP 943, Franceville, Gabon

Email: [abourae@gmail.com](mailto:abourae@gmail.com)

**How to cite this paper:** Bouraima, A., Anguile, J.J., Assani, A., Saadi, M., Makani, T. and El Ammari, L. (2020) Crystal Structure of Baryum Dicobalt Iron (III) Three (Orthophosphate) Belonging to  $\alpha$ -CrPO<sub>4</sub> Family. *Open Journal of Inorganic Chemistry*, 10, 1-5.

<https://doi.org/10.4236/ojic.2020.101001>

**Received:** July 30, 2019

**Accepted:** December 4, 2019

**Published:** December 4, 2019

Copyright © 2020 by author(s) and Scientific Research Publishing Inc.

This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

## Abstract

The new compound, BaCo<sub>2</sub>Fe(PO<sub>4</sub>)<sub>3</sub>, has been synthesized by solid state reaction. The analysis by X-ray diffraction technique showed that it crystallizes in the orthorhombic system with the space group Imma. The structure is closely linked to that of  $\alpha$ -CrPO<sub>4</sub> type structure. In this structure, two oxygen atoms (O<sub>1</sub>, O<sub>2</sub>) are in general position and the others in special positions. The three-dimensional network of the crystal structure is made up of two types of chains running to [001] direction. The first chain is originated from two edge-sharing CoO<sub>6</sub> octahedra leading to the formation of Co<sub>2</sub>O<sub>10</sub> dimers that are connected to two PO<sub>4</sub> tetrahedra by a common edge. The junction of FeO<sub>6</sub> octahedra and PO<sub>4</sub> tetrahedra sharing vertices allowed to built the second chain. These chains are linked together by common vertices of tetrahedra PO<sub>4</sub> to form an open three-dimensional framework that delimits two types of tunnels parallel to [010] and [100] where the Ba<sup>II</sup> cations are located. Indeed, each Barium cation is surrounded by eight oxygen atoms.

## Keywords

$\alpha$ -CrPO<sub>4</sub>, X-Ray Diffraction, Network, Framework, Tunnels

## 1. Chemical Context

The interest shown by researchers in recent years in the structural study of phosphates is of paramount importance in the sense or they are engaged in the development of new materials based on transition metal phosphates. Indeed the

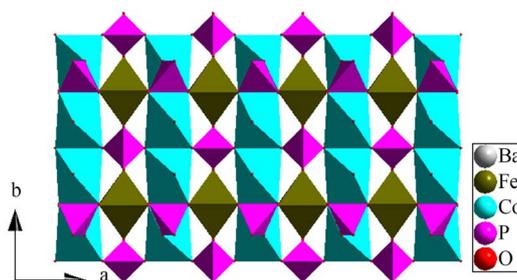
tetrahedral character phosphates related to octahedral transition metals led to open structures having structural characteristics favorable to the mobility of ions. Very often, the presence of transition metal cations in the structure gives rise to remarkable magnetic properties, such as ferro [1], antiferro [2] or ferromagnetic behavior [3]. Moreover, one of the axes developed by our team in our laboratory is the search for new materials based phosphate belonging to the family of alluaudite [4] or  $\alpha$ -CrPO<sub>4</sub> [5] type structure owing to their outstanding potentialities, particularly, as a new promising cathode material for batteries devices [6] [7] [8]. The crystal structures belonging to  $\alpha$ -CrPO<sub>4</sub> family shows a great similarity with of the alluaudite structure, can thus be represented by the general formula A(2)A(1)M(1)M(2)<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>. Hence, the octahedral M(1) and M(2) sites, accommodating di- or trivalent cations, are connected to the PO<sub>4</sub> groups leading to an open framework. The resulting configuration let appear tunnels where the mono- and/or bivalent cations are localized. The cations corresponding positions in tunnels are symbolized by the A(2) and A(1) sites.

In the same concept, our team recently isolated, and then characterize the crystal structures belonging to these different family such as Na<sub>2</sub>Co<sub>2</sub>Fe(PO<sub>4</sub>)<sub>3</sub> [9], Na<sub>1</sub>,<sub>67</sub>Zn<sub>1</sub>,<sub>67</sub>Fe<sub>1</sub>,<sub>33</sub>(PO<sub>4</sub>)<sub>3</sub> [10] and Ag<sub>1.655</sub>Co<sub>1.64</sub>Fe<sub>1.36</sub>(PO<sub>4</sub>)<sub>3</sub> [11] belonging to the alluaudite type structure. Besides, bivalent and trivalent based phosphates, namely SrNi<sub>2</sub>Fe(PO<sub>4</sub>)<sub>3</sub> [12], SrCo<sub>2</sub>Fe(PO<sub>4</sub>)<sub>3</sub> [13] and MMn<sup>II</sup><sub>2</sub>Mn<sup>III</sup>(PO<sub>4</sub>)<sub>3</sub> (M = Pb, Sr, Ba) [14] [15] [16], with rarely observed mixed-valent Mn<sup>II/III</sup> cations, are isolated and their structures are isotype with  $\alpha$ -CrPO<sub>4</sub>. Continuing our investigation of the ternary system MO-M'O-P<sub>2</sub>O<sub>5</sub> (M = bivalent cation and M' = metal of transition), we had success to synthesize a new transition metal phosphate compound named BaCo<sub>2</sub>Fe(PO<sub>4</sub>)<sub>3</sub>. The present work reports synthesis and crystal structure of the new Baryum cobalt iron phosphate, isolated within the BaO-CoO-Fe<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> quaternary, belonging to the  $\alpha$ -CrPO<sub>4</sub> type structure.

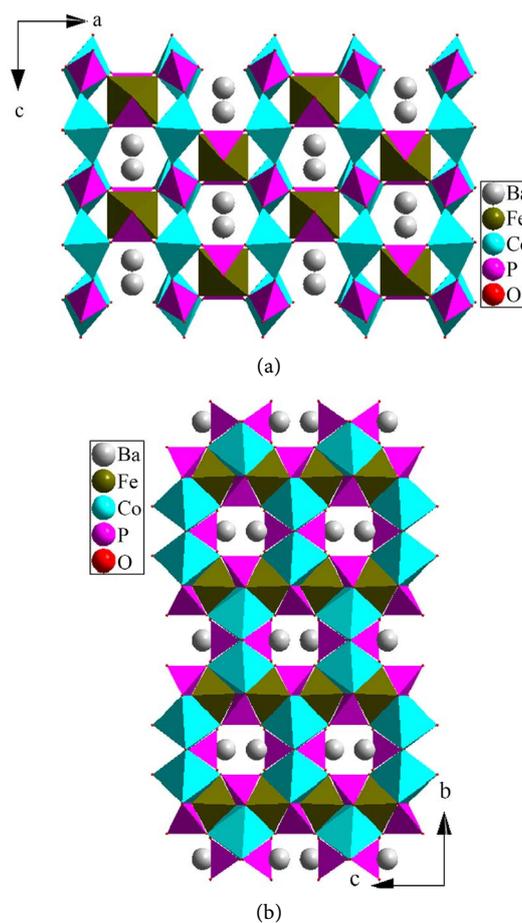
## 2. Structural Commentary

The crystal data for title compound show that they are isostructural, crystallize with the  $\alpha$ -CrPO<sub>4</sub> structure. In this structure, all atoms are in special positions, except two oxygen atoms (O<sub>1</sub>, O<sub>2</sub>) which are in general position of the Imma space group. The asymmetric unit contains six cationic sites including two for Ba, two for P and two M(1) and M(2)<sub>2</sub> containing the cobalt and iron atoms. This asymmetric unit formed by a sequence octahedral and tetrahedral giving a three-dimensional structure constructed on the basis of PO<sub>4</sub> tetrahedra, FeO<sub>6</sub> and CoO<sub>6</sub> octahedra. The connection different between polyhedral produces two chain types running along [001]. The first chain is built up from two edge-sharing CoO<sub>6</sub> octahedra leading to the formation of Co<sub>2</sub>O<sub>10</sub> dimers which are connected to two PO<sub>4</sub> tetrahedra by a common edge. The second one is formed by alternating FeO<sub>6</sub> octahedra and PO<sub>4</sub> tetrahedra sharing vertices (Figure 1). The junction of both chains, by sharing common vertices of tetrahedra PO<sub>4</sub>, gives arise an open three-dimensional framework that delimits two types of tunnels parallel to [010] and [100] where the Ba<sup>II</sup> cations are accommo-

dated as shown in **Figure 2(a)** and **Figure 2(b)**. The new structure namely  $\text{BaCo}_2\text{Fe}(\text{PO}_4)_3$  is characterized by a single type of baryum atom surrounded by eight oxygen atoms with Ba-O bond length varies between 2.7290 Å and 2.7621 Å. Moreover, the bond valence sums for the different crystallographic site calculated using the empirical parameters [17] is 2.28, 2.95, 1.949, 4.847, 4.969 for  $\text{Ba}^{\text{II+}}$ ,  $\text{Fe}^{\text{III+}}$ ,  $\text{Co}^{\text{II+}}$ ,  $\text{P1}^{\text{V+}}$ ,  $\text{P2}^{\text{V+}}$  respectively. The bond valence sum is very close to the ideal value, thus confirming the non-disordered distribution of  $\text{Fe}^{\text{III+}}$  and  $\text{Co}^{\text{II+}}$  on the  $M(1)$  and  $M(2)$  sites.



**Figure 1.** View of two types channels along  $c$  axis [18].



**Figure 2.** (a) View along  $a$  axis polyhedral of  $\text{SrCo}_2\text{Fe}(\text{PO}_4)_3$  of tunnels parallel to the  $(010)$  plane. (b) Polyhedral representation of  $\text{SrCo}_2\text{Fe}(\text{PO}_4)_3$  with channels running parallel to  $[010]$ .

### 3. Synthesis and Crystallization

Commercially available  $\text{Fe}(\text{NO})_3 \cdot 9\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{HPO}_4$ ,  $\text{Ba}(\text{NO}_3)_2$ , and  $(\text{CH}_3\text{COO})_2\text{Co} \cdot 4\text{H}_2\text{O}$  were used as starting for the synthesis of new compound,  $\text{BaCo}_2\text{Fe}(\text{PO}_4)_3$ . This phase has been synthesized by solid-state reaction by mixing a stoichiometric amount of the starting precursors. The mixture is finely ground in an agate mortar for a sufficient time then heat treatments, realized in platinum crucible, up to 873 K, the reaction mixture is heated in a crystallization furnace to the melting point, situated at 1246.150 K. The molten product was then cooled to room temperature at  $5^\circ\text{K/h}$  rate. The final product contains brown crystals with a suitable size for the X-ray diffraction corresponding to the title compound.

### 4. Conclusion

We have been able to synthesize, by diffusion in the solid state, the new phosphate of formula. Its crystalline structure was determined from the X-ray diffraction data. It crystallizes in orthorhombic mesh with the Imma space group,  $a = 10,5067(2)\text{\AA}$ ,  $b = 13,3155(3)\text{\AA}$  and  $c = 6,6471(2)\text{\AA}$  as the mesh parameters. The particularity of this new phosphate is that it is similar to  $\alpha\text{-CrPO}_4$ , its structure is formed to tetrahedrons and octahedra  $\text{CoO}_6$  and  $\text{FeO}_6$ . The combination of these different coordination polyhedra leads to the formation of a sheet, the latter are linked together by chains to build a three-dimensional network releasing tunnels in which are housed the  $\text{Ba}^{2+}$  cations.

### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

### References

- [1] Wright, A.J., Ruiz-Valero, C. and Attfield, J.P. (1999) Weak Ferromagnetism and Framework Switching in  $\text{KMnHP}_3\text{O}_{10}$ . *Journal of Solid State Chemistry*, **145**, 479-483. <https://doi.org/10.1006/jssc.1999.8167>
- [2] Mesa, J.L., Pizarro, J.L., Lizama, L., Escobal, J., Arriortua, M.I. and Rojo, T. (1998) Spectroscopic and Magnetic Properties of the  $\text{MNi}(\text{AsO}_4)$  ( $\text{M}=\text{Li}, \text{Na}$ ) Arsenates and Crystal Structure Refinement of  $\text{LiNi}(\text{AsO}_4)$ . *Journal of Solid State Chemistry*, **141**, 508-513. <https://doi.org/10.1006/jssc.1998.8006>
- [3] Attfield, J.P., Cheetman, A.K., Johnson, D.C. and Torardi, C.C. (1987) Preparation, Structure, and Magnetic Properties of a New Form of Chromium Orthoarsenate:  $\beta\text{-CrAsO}_4$ . *Inorganic Chemistry*, **26**, 3379-3383. <https://doi.org/10.1021/ic00267a033>
- [4] Moore, P.B. (1971) Crystal Chemistry of the Alluaudite Type Structure: Contribution to the Paragenesis of Pegmatite Phosphate Giant Crystals. *American Mineralogist*, **56**, 1955-1975.
- [5] Attfield, J.P. and Cheetham, A.K. (1988) Synchrotron X-Ray and Neutron Powder Diffraction Studies of the Structure of  $[\text{Alpha}]\text{-CrPO}_4$ . *Journal of Applied Crystallography*, **21**, 452-457. <https://doi.org/10.1107/S0021889888004625>
- [6] Trad, K., Carlier, D., Croguennec, L., Wattiaux, A., Ben Amara, M. and Delmas, C.

- (2010)  $\text{NaMnFe}_2(\text{PO}_4)_3$  Alluaudite Phase: Synthesis, Structure, and Electrochemical Properties as Positive Electrode in Lithium and Sodium Batteries. *Chemistry of Materials*, **22**, 5554-5562. <https://doi.org/10.1021/cm1015614>
- [7] Kim, J., Kim, H., Park, K.-Y., Park, Y.-U., Lee, S., Kwon, H.-S., Yoo, H.-I. and Kang, K. (2014) Alluaudite  $\text{LiMnPO}_4$ : A New Mn-Based Positive Electrode for Li Rechargeable Batteries. *Journal of Materials Chemistry A*, **2**, 8632-8636. <https://doi.org/10.1039/C4TA00955J>
- [8] Huang, W.F., Li, B., Saleem, M.F., Wu, X., Li, J.J., Lin, J., Xia, D., Chu, W.S. and Wu Z.Y. (2015) Self-Assembled Alluaudite  $\text{Na}_2\text{Fe}_{3-x}\text{Mn}_x(\text{PO}_4)_3$  Micro/Nanocompounds for Sodium-Ion Battery Electrodes: A New Insight into Their Electronic and Geometric Structure. *Chemistry: A European Journal*, **21**, 851-860. <https://doi.org/10.1002/chem.201403062>
- [9] Bouraima, A., Assani, A., Saadi, M., Makani, T. and El Ammari, L. (2015) Crystal Structure of Disodium Dicotalt(II) Iron(III) Tris-(orthophosphate) with an Alluaudite-Like Structure. *Acta Crystallographica Section E*, **71**, 558-560. <https://doi.org/10.1107/S2056989015007926>
- [10] Khmias, J., Assani, A., Saadi, M. and El Ammari, L. (2015) Crystal Structure of a Sodium, Zinc and Iron (III)-Based Non-Stoichiometric Phosphate with an Alluaudite-Like Structure:  $\text{Na}_{1.67}\text{Zn}_{1.67}\text{Fe}_{1.33}(\text{PO}_4)_3$ . *Acta Crystallographica Section E*, **71**, 690-692. <https://doi.org/10.1107/S2056989014026930>
- [11] Bouraima, A., Makani, T., Assani, A., Saadi, M. and El Ammari, L. (2017) Crystal Structure of a Silver-, Cobalt- and Iron-Based Phosphate with an Alluaudite-Like Structure:  $\text{Ag}_{1.655}\text{Co}_{1.64}\text{Fe}_{1.36}(\text{PO}_4)_3$ . *Acta Crystallographica Section E*, **73**, 890-892. <https://doi.org/10.1107/S205698901700740X>
- [12] Ouatta, S., Assani, A., Saadi, M. and El Ammari, L. (2015) Crystal Structure of Strontium Dinickel Iron Orthophosphate. *Acta Crystallographica Section E*, **71**, 1255-1258. <https://doi.org/10.1107/S205698901501779X>
- [13] Bouraima, A., Makani, T., Assani, A., Saadi, M. and El Ammari, L. (2016) Crystal Structure of STRONTIUM Dicotalt Iron(III) Tris-(orthophosphate):  $\text{SrCo}_2\text{Fe}(\text{PO}_4)_3$ . *Acta Crystallographica Section E*, **72**, 1143-1146. <https://doi.org/10.1107/S2056989016011373>
- [14] Alhakmi, G., Assani, A., Saadi, M. and El Ammari, L. (2013) *Acta Crystallographica Section E*, **69**, i40. <https://doi.org/10.1107/S1600536813016504>
- [15] Alhakmi, G., Assani, A., Saadi, M., Follet, C. and El Ammari, L. (2013b) A New Mixed-Valence Lead (II) Mangan-Ese (II/III) Phosphate (V):  $\text{PbMn}^{\text{II}}_2\text{Mn}^{\text{III}}(\text{PO}_4)_3$ . *Acta Crystallographica Section E*, **69**, i56. <https://doi.org/10.1107/S1600536813020977>
- [16] Assani, A., Saadi, M., Alhakmi, G., Houmadi, E. and El Ammari, L. (2013) A New Mixed-Valence Lead(II) Mangan-Ese(II/III) Phosphate(V):  $\text{PbMn}^{\text{II}}_2\text{Mn}^{\text{III}}(\text{PO}_4)_3$ . *Acta Crystallographica Section E*, **69**, i60. <https://doi.org/10.1107/S1600536813023106>
- [17] Brown, I.D. and Altermatt, D. (1985)  $\text{PbMn}^{\text{II}}_2\text{Mn}^{\text{III}}(\text{PO}_4)_3$ . *Acta Crystallographica Section B*, **41**, 244-247. <https://doi.org/10.1107/S0108768185002063>
- [18] Brandenburg, K. (2006) Diamond. Crystal Impact GbR, Bonn.