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Cobalt Phosphates and Applications

Riadh Marzouki, Mahmoud A. Sayed, Mohsen Graia and Mohamed Faouzi Zid

Abstract

Cobalt phosphates with open framework present various physical performances in relation to their structures. In fact, the development of new materials that could potentially be ionic conductors or ion exchangers led us to examine the Co-P-O and A-Co-P-O crystallographic systems (A: monovalent cation) and their different methods of synthesis. This work consists first of all in highlighting the crystalline phases of cobalt phosphates. Indeed, many works related to the discovery of some of these materials with interesting properties, in particular ionic conductivity, motivated our research and encouraged us to collect several cobalt phosphates and to correlate structure-physical properties in particular electrical properties.

Keywords: cobalt phosphate, structure, open framework, physical property, battery

1. Introduction

The search for new inorganic materials with open frameworks formed by tetrahedra and octahedra sharing corners or edges; delimiting cages (1D), interlayer spaces (2D), or tunnels (3D); or communicating by the intermediate of windows where cations are located is an interesting field with intense activity including several disciplines: solid-state chemistry, physics, mechanics, etc. Synthesis and physicochemical studies of metallophosphate compounds are the driving force behind the recent technological development, and studies are progressing through the exchange of points of view between specialists concerned.

Metallophosphates have a promising field for various applications: electrical, electrochemical, magnetic, and catalytic processes [1–7]. Nevertheless, the introduction of monovalent ions into metallophosphates can lead to materials with interesting properties. This orientation was initiated from the discovery of the ionic conduction properties of NASICON $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ ($\sigma_{300^\circ\text{C}} = 0.2 \text{ S cm}^{-1}$ and $E_a = 0.29 \text{ eV}$) in 1976 [5] followed by olivine series studies of general formula LiMPO_4 ($M = \text{Co}^{2+}, \text{Fe}^{2+}, \text{Mn}^{2+}$) usable in the manufacture of cathodes of rechargeable lithium-ion batteries [7]. These materials have a remarkable structural richness: olivine structure [7], zeolitic structure [8], alluaudite structure [9], melilite structure [10], etc. In relation to their structures, these materials have many physicochemical properties: ionic conduction [10], ion exchange [6, 7], etc. In this context, several researcher groups have tried to explore $\text{CoO-P}_2\text{O}_5$ and $\text{A}_2\text{O-CoO-P}_2\text{O}_5$ systems (A: monovalent metals). This chapter is dedicated to treated physicochemical and structural studies of monovalent cation cobalt phosphates (Li, Na, K, and Ag).

2. Synthesis methods and experimental techniques

The most common synthesis method is the solid-state reaction method. Nevertheless, to minimize the energy consumption and to improve quality of the developed materials (particle size, purity, homogeneity, etc.), other techniques such as hydrothermal method are adopted. In this method, the crystalline products are synthesized at low temperature, generally 150–250°C, and under high pressure.

2.1 Solid-state reaction method

Solid-state reaction route is the most adopted method to prepare single crystals or polycrystalline materials. The essential steps are:

- Mixing and grinding solid reagents and placing the mixture in a container (usually porcelain, alumina, or platinum crucibles).
- Calcination: a first heat treatment at 573–673 K for a few hours to remove the volatile compounds (NH₃, H₂O, CO₂, etc.).
- Grinding another time the remaining mixture to homogenize and reduce the size of the particles which will increase the contact area between the grains.
- Second heat treatment by gradually increasing the temperature to a so-called “pasty” state of the mixture (partially melted mixture). Maintain this temperature for a few days, and then slowly lower it to room temperature.

2.2 Hydrothermal route

The hydrothermal or solvothermal method consists of preparing an aqueous solution containing the reagents dissolved totally or partially. The aqueous solution is transferred either into a Teflon autoclave, both enclosed in metal autoclave.

The preparation in the autoclave is brought to a temperature between 373 and 573 K maintained for a few days in order to obtain single crystals. The maximum temperature is imposed by the resistance of the material constituting the Teflon.

Note: In this chapter, structures have been determined using X-ray diffraction (on single crystal or on powder). Electrical measurements are carried out using often complex impedance spectroscopy.

2.3 Experimental techniques

In this chapter, the structural studies of the studied materials were carried out by X-ray diffraction on single crystals or in some cases X-ray powder diffraction.

Electrical measurements are often performed using the complex impedance spectroscopy technique.

3. Cobalt phosphate

In the literature, there are more than 80 allotropic forms of cobalt phosphates in which cobalt takes different oxidation degrees, sometimes in the same compound. Some cobalt phosphates have distinguishable physical properties in relation to their structures. In this chapter, cobalt monophosphate CoPO₄ will be reported.

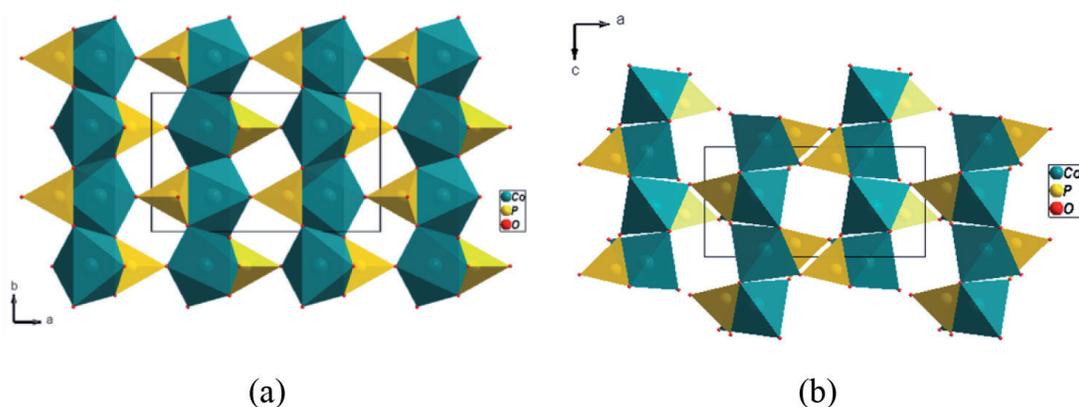


Figure 1.
Projection of CoPO_4 structure along the (a) c axis and (b) b axis.

CoPO_4 [1] material, like FePO_4 structure, is usable in the manufacture of Li-ion batteries. In fact, the lithium extraction from LiCoPO_4 material leads to CoPO_4 compound. The delithiated sample was prepared by electrochemical Li extraction in galvanostatic mode at a C/5-rate from LiCoPO_4 . The latter shows considerable stability during several cycles of charge-discharge of the battery. In fact, CoPO_4 crystallized in the orthorhombic with $Pnma$ space group. The structure is formed by $(\text{CoO}_6)_n$ chains connected with PO_4 tetrahedra to form layers in the ab plane. The connection between layers formed a 3D framework showing several types of tunnels according to $[001]$ and $[010]$ directions (**Figure 1**). In this structure type, the cobalt ion has an oxidation degree of +III.

4. Monovalent metal cobalt phosphate

There are more than 40 monovalent cation cobalt phosphates. The monovalent metal cobalt phosphates will be classified according to the oxygen/phosphorus molar ratio.

4.1 Monophosphates

This family is known as orthophosphate or also monophosphate; it is characterized by its high stability compared to other phosphates. In the structure, $(\text{PO}_4)^{3-}$ tetrahedra are isolated from each other.

The most famous material is lithium cobalt monophosphate LiCoPO_4 (**Figure 2**) [1]. It crystallizes in the orthorhombic system, $Pnma$ space group. It belongs to the olivine family of general formula LiMPO_4 ($M = \text{Fe, Ni, Co, and Mn}$). Xiang Huang et al. [11] have proposed hydrothermal synthesis method of this monophosphate which shows performance in terms of reaction yield and product homogeneity versus dry route. The phospho-olivine series is used in the manufacture of cathodes in Li-ion batteries [12]. LiCoPO_4 - CoPO_4 system shows high stability during several charge-discharge cycles of the battery at room temperature (**Figure 3**). The olivine structure can be described as a compact hexagonal stack of A - B - A - B - A -type oxygen layers. The $A = \text{Na or Co}$ cations occupy half of the octahedral sites AO_6 and the $B = \text{P}$ cations 1/8 of the available tetrahedral P sites of PO_4 tetrahedra.

On the other hand, when lithium is substituted by sodium in different synthesis conditions, the monophosphate NaCoPO_4 may present in four allotropic forms [13, 14]. **Figure 4** groups the polymorphisms in sodium cobalt monophosphate. All sodium materials show open anionic frameworks containing tunnels which contain sodium cations. On the other hand, the structure of the $P2_1/n$ form where

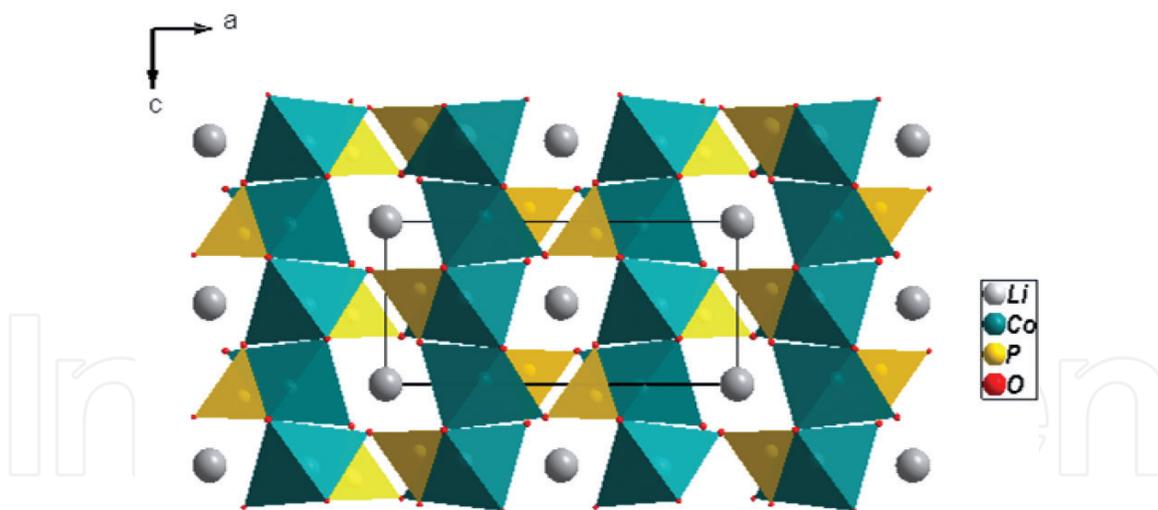


Figure 2.
Projection of LiCoPO_4 structure along $[010]$ direction.

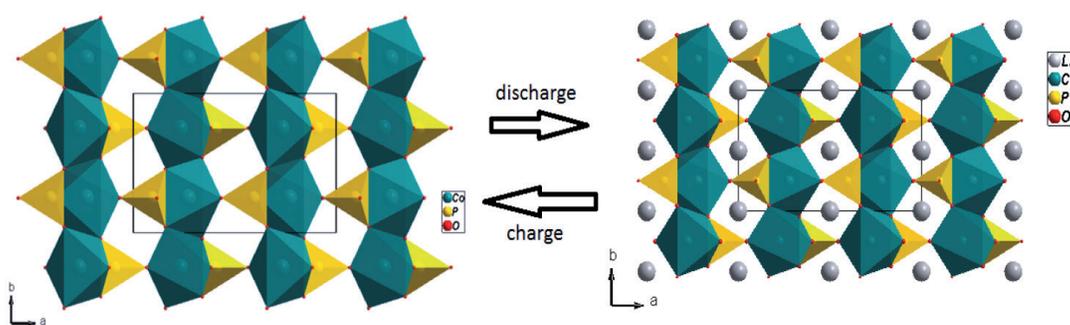


Figure 3.
Lithium insertion/extraction in the olivine structure $\text{CoPO}_4/\text{LiCoPO}_4$.

cobalt is only tetraordinated is related to zeolite ABW ($\text{LiAlSiO}_4 \cdot \text{H}_2\text{O}$) [14]. In NaCoPO_4 ($P2_1/c$ space group subgroup of $Pnma$), Stucky et al. [13] report that the structure is also a distortion of the ABW zeolite structure but that it is a little more complex since the cobalt environment is trigonal bipyramidal. Indeed, the main characteristic of ABW zeolites is their spatial structures which contain pores and channels that can absorb or reject various solids, liquids, or gases. The applications of zeolites are numerous: food supplement for animals, additives for detergents, molecular filters, water treatment, catalysis, etc.

The α - NaCoPO_4 ($P2_1/n$ space group) with maricite type is formed by octahedral chains CoO_6 sharing edge and parallel to the a axis. They are interconnected via the PO_4 tetrahedra, which creates large cavities where Na^+ cations are located [13].

While the phase of the hexagonal system β - NaCoPO_4 is stuffed tridymite type which is a high temperature variety of quartz SiO_2 . These compounds have a lower symmetry than tridymite due to the order of cations within the channels.

The silver cobalt monophosphate AgCoPO_4 [15] has another structure type with a twofold oxygen coordination for silver atoms and a fivefold coordination for cobalt atoms. Indeed, the silver compound crystallizes in the triclinic system, space group $P-1$. A projection of the structure of this phase is shown in **Figure 5**.

Another monophosphate is classified as Na-ionic conductor: $\text{NaCo}_4(\text{PO}_4)_3$ [16] with activation energy $E_a = 0.89$ eV and $\sigma = 10^{-6}$ S cm^{-1} . Indeed, cationic sites, located in wide-sectioned channels (**Figure 7a**), are partially occupied by Na^+ ions and relatively agitated which may explain the sodium mobility in the anionic framework. This compound crystallizes in the monoclinic system, space group $P2_1/n$. The

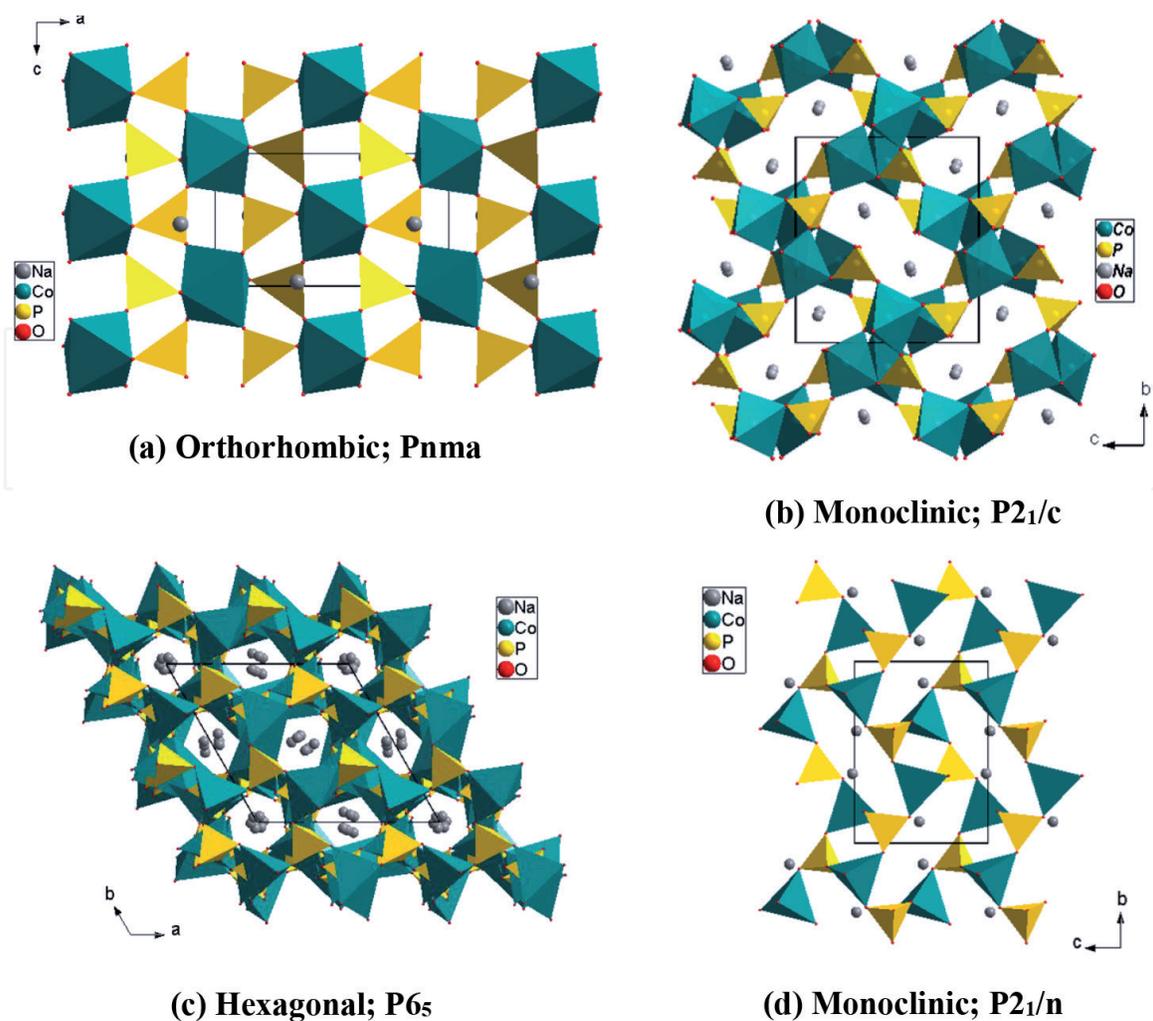


Figure 4.
 Allotropic forms of $NaCoPO_4$: (a) $Pnma$, (b) $P2_1/c$, (c) $P6_5$, and (d) $P2_1/n$ space groups.

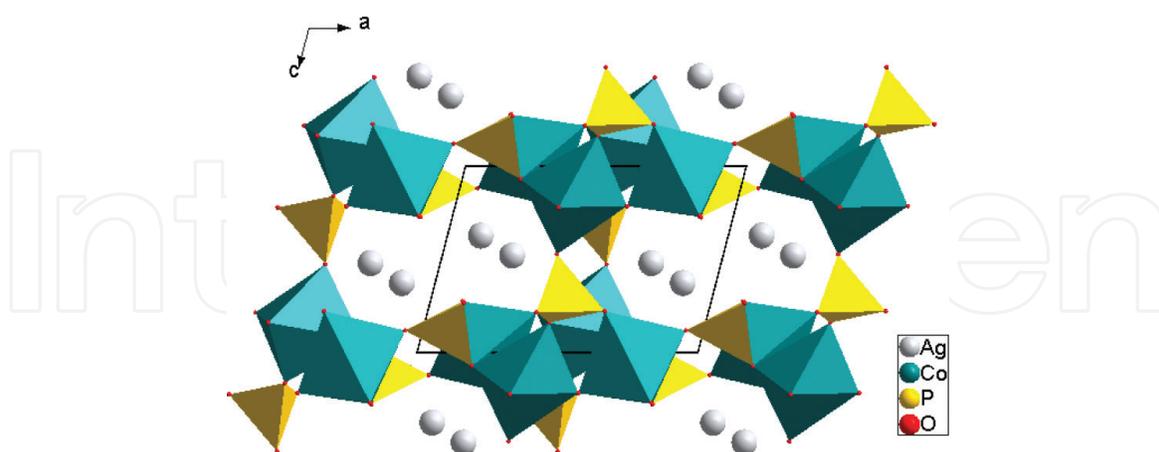


Figure 5.
 Projection of $AgCoPO_4$ structure along $[010]$ direction.

isoformula potassium material $KCo_4(PO_4)_3$ [17] crystallizes, in a different structure, the orthorhombic system, space group $Pnmm$. The structure projection along the $[001]$ direction is shown in **Figure 6(b)**.

The sodium cobalt monophosphate $Na_4Co_7(PO_4)_6$ [18] is synthesized by the dry route. This compound is a member of a family of phases including $Na_4Ni_7(PO_4)_6$ [19] and $K_4Ni_7(PO_4)_6$ [20]. Previous studies have shown that the material $Na_4Ni_7(PO_4)_6$ is classified as fast ionic conductor. Several studies relating to the

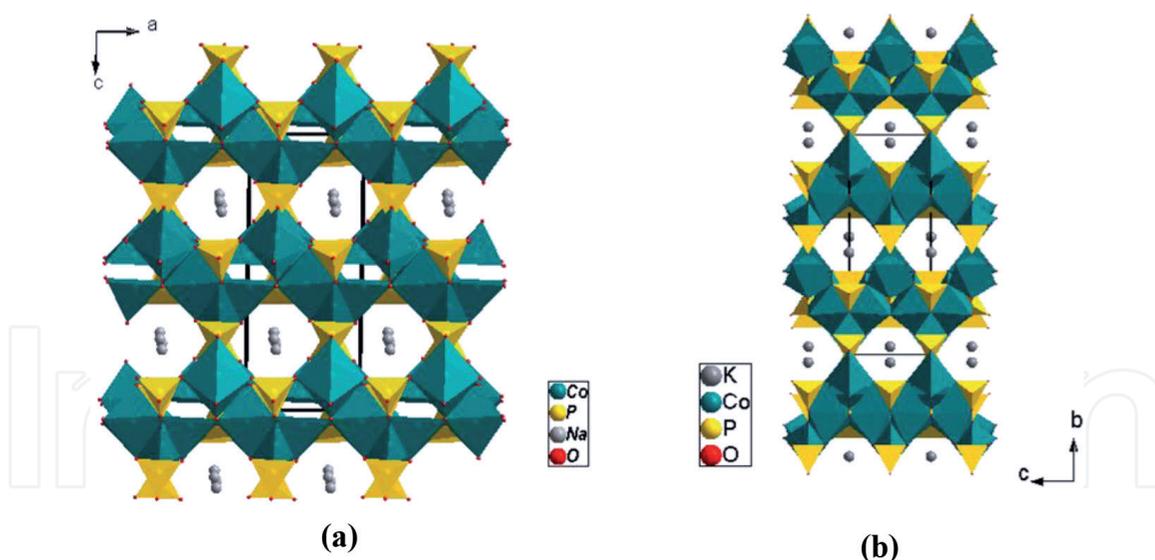


Figure 6.
Projections of (a) $\text{NaCo}_4(\text{PO}_4)_3$ and (b) $\text{KCo}_4(\text{PO}_4)_3$ structures.

substitution of phosphate by arsenate have led to $\text{Na}_4\text{Co}_7(\text{AsO}_4)_6$ ($E_a = 1.00$ eV) [21], $\text{Na}_4\text{Co}_{5.63}\text{Al}_{0.96}(\text{AsO}_4)_6$ ($E_a = 0.53$ eV) [22–24], $\text{Na}_4\text{Li}_{0.62}\text{Co}_{5.67}\text{Al}_{0.71}(\text{AsO}_4)_6$ [25], and $\text{Ag}_4\text{Co}_7(\text{AsO}_4)_6$ ($E_a = 0.61$ eV) [26].

A projection of the structure of $\text{Na}_4\text{Co}_7(\text{PO}_4)_6$ according to [100] is given in **Figure 7**. The anionic framework has both a tetrahedral (CoO_4 and PO_4) and octahedral (CoO_6) environment as well as hexagonal tunnels where the sodium ions lodge.

4.2 Polyphosphates

Short-chain polyphosphates also named n-polyphosphates are characterized by short chains of PO_4^{3-} tetrahedra sharing corners. The general formulas of the phosphate anion are given by $[\text{P}_n\text{O}_{3n+1}]^{(n+2)-}$ with $n > 1$. Oligophosphates for which $n = 2, 3, 4,$ and 5 are known until now. These compounds are infrequent for $n \geq 4$.

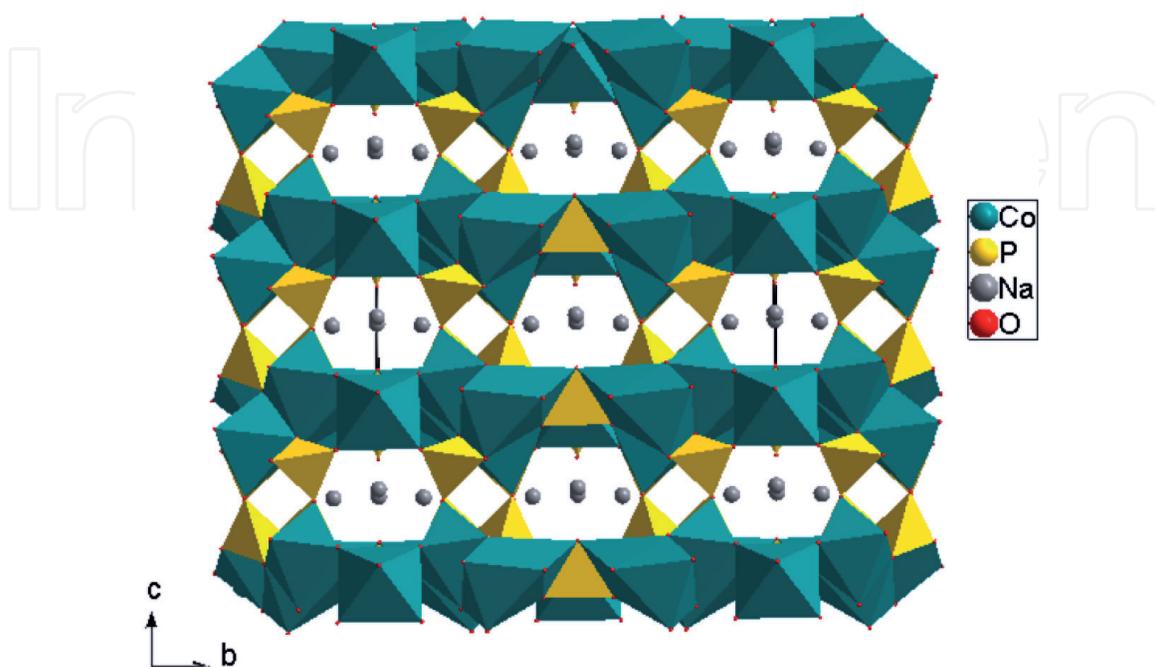


Figure 7.
Projection of $\text{Na}_4\text{Co}_7(\text{PO}_4)_6$ structure along the a axis.

The other type corresponds to polyphosphates with long chains. When n tends to infinity, their phosphate anions take the formula $[\text{PO}_3]_n^{n-}$, thus forming infinite chains of PO_4 tetrahedra. If the tetrahedron chain closes on itself to form rings, the corresponding phosphates are called cyclophosphates. The general formula of the cyclic anion is $[\text{P}_n\text{O}_{3n}]^{n-}$ with $n = 3, 4, 5, 6, 8, 10,$ and 12 .

In this part, a variety of monovalent ion cobalt polyphosphates found in the literature will be mentioned.

4.2.1 Short-chain polyphosphates $[\text{P}_n\text{O}_{3n+1}]^{(n+2)-}$ with $n > 1$

4.2.1.1 Diphosphates ($n = 2$)

The formula of the phosphate anion is $\text{P}_2\text{O}_7^{4-}$, known as diphosphate (or pyrophosphate). The group P_2O_7 consists of two PO_4 tetrahedra sharing a single corner.

Concerning diphosphates of formulation $\text{A}_2\text{CoP}_2\text{O}_7$ (A: Na or K), the sodium compound is presented in three allotropic forms: triclinic (**Figure 8a**), monoclinic (**Figure 8b**), and quadratic (**Figure 8c**) [8, 10].

In the last form, cobalt atoms have purely tetrahedral environment, and the anionic framework is formed by layers formed by $[\text{CoP}_2\text{O}_7]^{2-}$ groups. The Na^+ and/or K^+ cations are located in the interlayer space. Sanz et al. [10] postponed the study of the ionic conductivity of the quadratic form to sodium; their study reveals that it is a fast ionic conductor. Marzouki et al. [27] proposed a modeling of

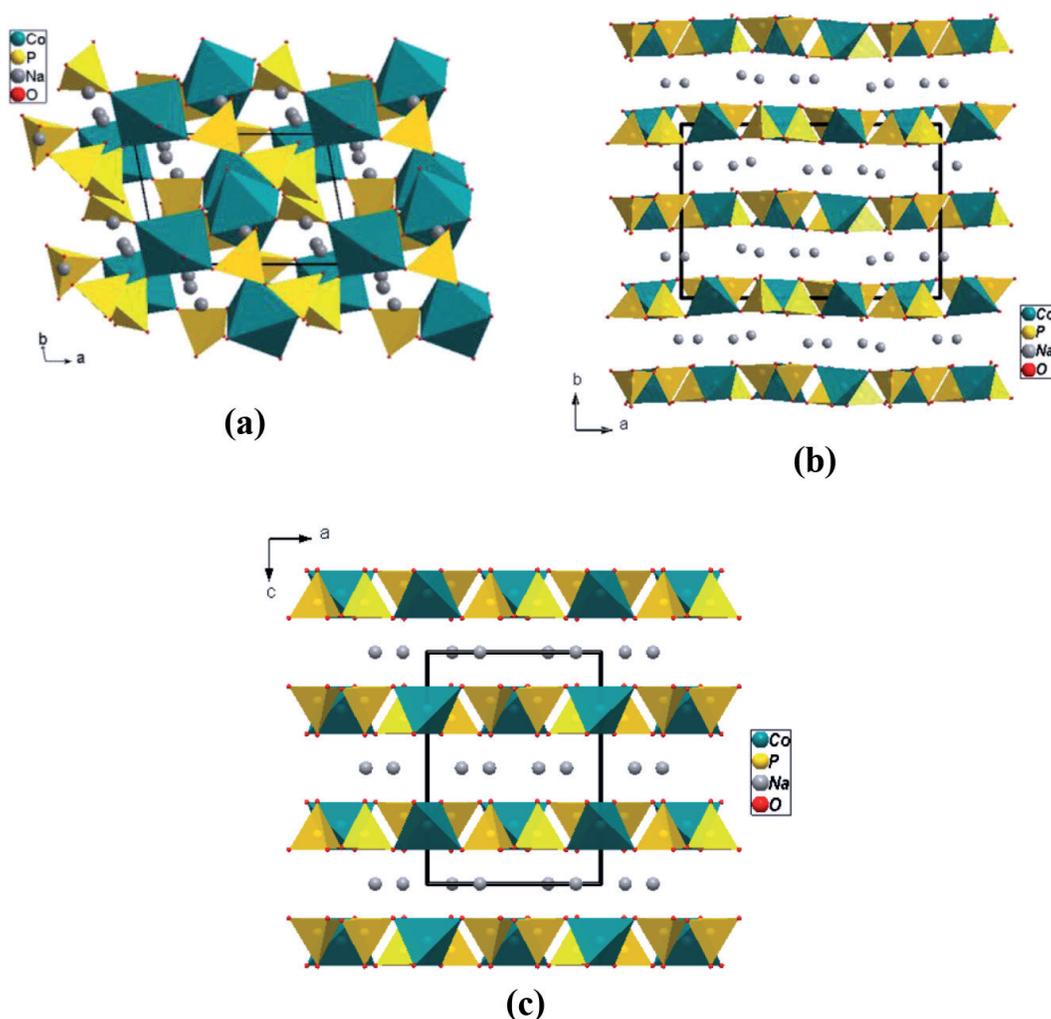


Figure 8.
Projections of polymorphs of $\text{Na}_2\text{CoP}_2\text{O}_7$: (a) triclinic, (b) monoclinic, and (c) tetragonal.

alkaline cation conduction paths in these structures (**Figure 9**). The conductivity in this type of material is bi-dimensional.

The silver cobalt diphosphates include $\text{Ag}_{3.68}\text{Co}_2(\text{P}_2\text{O}_7)_2$ [28] and $(\text{Ag}_{0.58}\text{Na}_{1.42})_2\text{Co}_2(\text{P}_2\text{O}_7)_2$ [29]. They crystallize in the triclinic system, space group P-1. Projection of the mixed Na/Ag metals is presented in **Figure 10**. The cobalt, in this case, is purely octahedral. In the anionic framework, the cohesion between two symmetrical units $\text{Co}(2)\text{P}_2\text{O}_{11}$ is provided by $\text{Co}(1)\text{O}_6$ octahedra to form the $\text{Co}_4\text{P}_4\text{O}_{28}$ unit. According to the three spatial directions, the junction between two $\text{Co}_4\text{P}_4\text{O}_{28}$ units is provided by two P_2O_7 diphosphates forming 3D anionic framework.

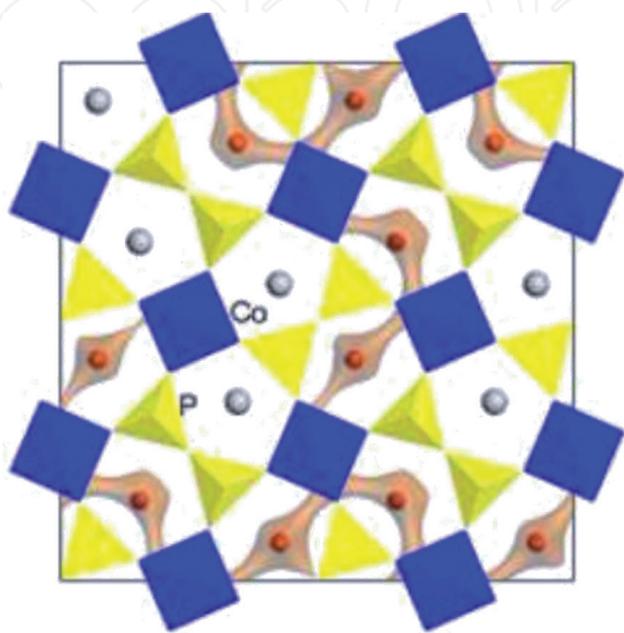


Figure 9.

Bond valence site energy-simulated pathways of Na^+ ions within the $\text{K}_{0.86}\text{Na}_{1.14}\text{CoP}_2\text{O}_7$ structure (Na brown and K gray and the layer at $z = 0$).

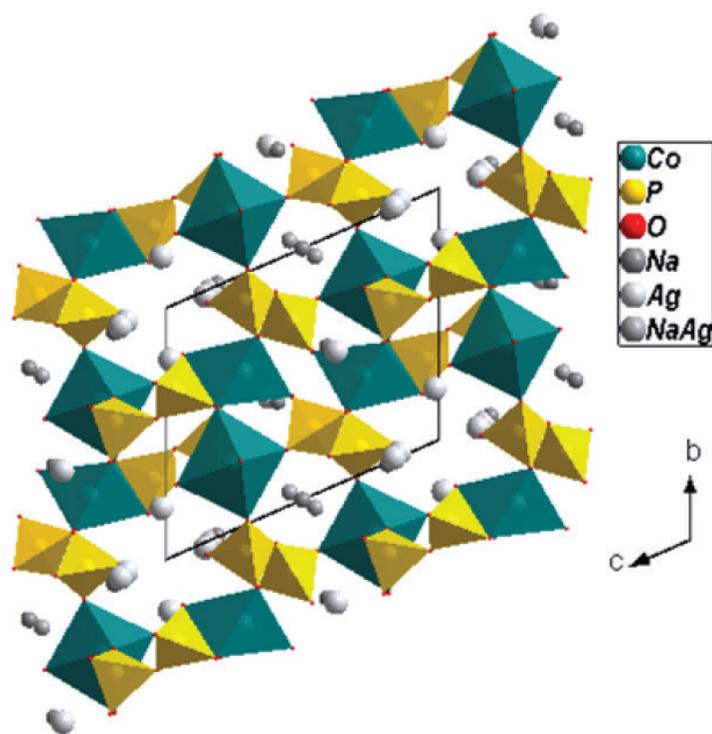


Figure 10.

Projection of $(\text{Ag}_{0.58}\text{Na}_{1.42})_2\text{Co}_2(\text{P}_2\text{O}_7)_2$ structure along the a axis.

Silver transport pathways in $\text{Ag}_{3.68}\text{Co}_2(\text{P}_2\text{O}_7)_2$ are simulated using BVSE calculations. The BVSE simulation shows that the material should be moderate 3D ionic conductor with activation energy value of 1.7 eV. The result is described in **Figure 11**.

The particularity of lithium cobalt diphosphates is the non-stoichiometry in composition. The formulas found in the bibliography are $\text{Li}_{5.88}\text{Co}_{0.06}(\text{P}_2\text{O}_7)_4$ [30] where cobalt and lithium share the same crystallographic sites and $\text{Li}_{4.03}\text{Co}_{1.97}(\text{P}_2\text{O}_7)_2$ [31] where a fraction of cobalt oxidation degree is +III. The projections of their structures are shown in **Figures 12** and **13**.

4.2.1.2 Triphosphates ($n = 3$)

Single monovalent cation cobalt triphosphate is found in the literature. Its formula is $\text{LiCo}_2\text{P}_3\text{O}_{10}$ [32]. This material crystallizes in the monoclinic system, space group $\text{P}2_1/\text{m}$. In the anionic framework, the P_3O_{10} groups ensure cohesion between the infinite chains formed by Co_2O_{10} dimers which are linked

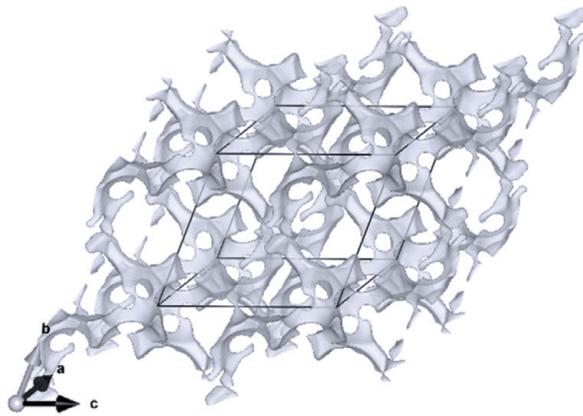


Figure 11.
3D silver transport pathways in $\text{Ag}_{3.68}\text{Co}_2(\text{P}_2\text{O}_7)_2$ with bond valence mismatch of $|\Delta V(\text{Ag})| = 1.3 \text{ u.v}$ (i.e., $\sim 1.7 \text{ eV}$).

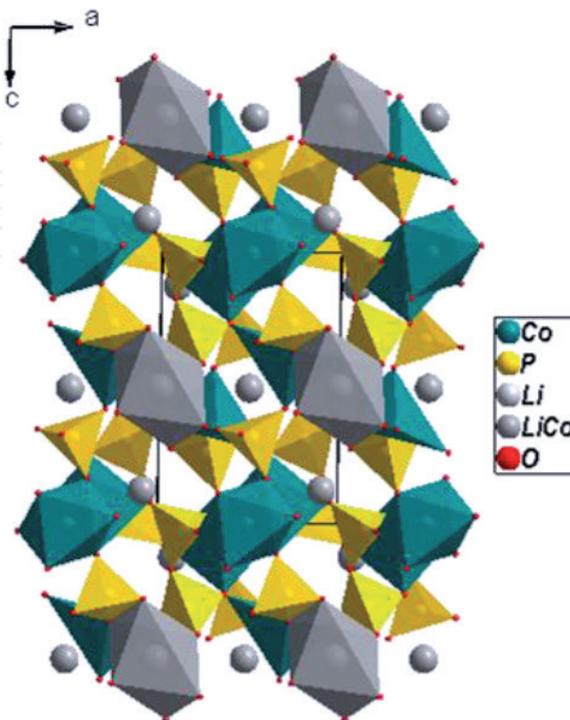


Figure 12.
Projection of $\text{Li}_{5.88}\text{Co}_{0.06}(\text{P}_2\text{O}_7)_4$ structure along b direction.

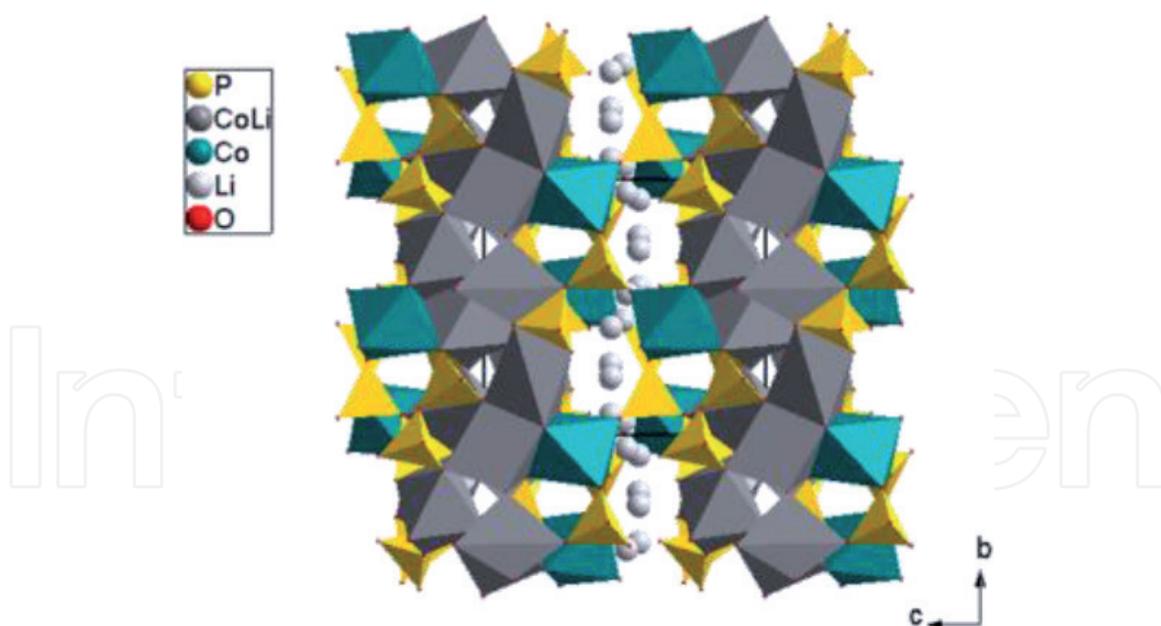


Figure 13.
Projection of $\text{Li}_{4.03}\text{Co}_{1.97}(\text{P}_2\text{O}_7)_2$ structure along a direction.

together by edge sharing. **Figure 14** shows a projection of the structure in the direction $[100]$. The $\text{NaCo}_2\text{As}_3\text{O}_{10}$ triarsenate [33], isostructural with $\text{LiCo}_2\text{P}_3\text{O}_{10}$ triphosphate, shows interesting electrical properties ($E_a = 0.48$ eV; $\sigma_{300^\circ\text{C}} = 1.2 \times 10^{-5} \text{ S cm}^{-1}$).

4.2.1.3 Polyphosphates with long chains $[\text{PO}_3]_n^{n-}$

The first phase seen in the bibliography is tetraphosphate $\text{K}_2\text{Co}(\text{PO}_3)_4$ [34]. This material is synthesized by the dry route; it crystallizes in the monoclinic system, with non-centrosymmetric space group “Cc.” Cobalt has the oxidation state (+II) and is octacoordinated. Phosphate anions of formulation $[\text{PO}_3]_n^{n-}$ (n tends to

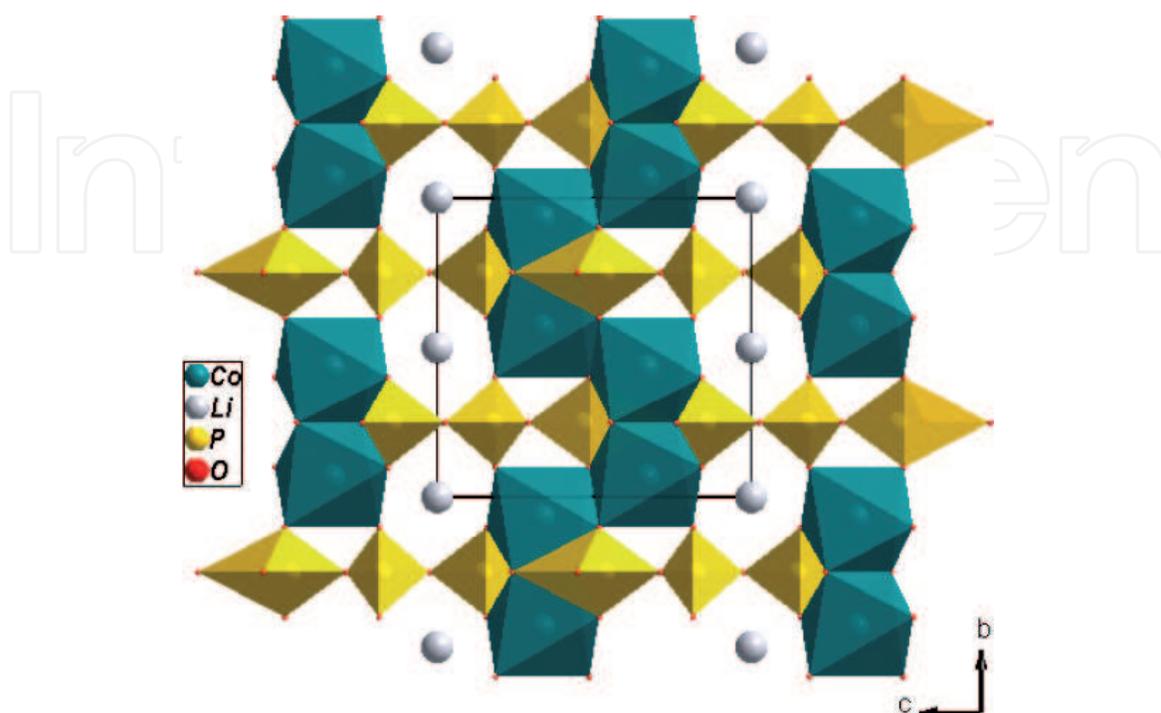


Figure 14.
Projection of $\text{LiCo}_2\text{P}_3\text{O}_{10}$ structure along a direction.

infinity) thus develop into long chains of PO_4 tetrahedra linked together by CoO_6 octahedra to form a 3D framework (**Figure 15**).

As for the lithium compound [35] with $\text{LiCo}_2\text{P}_3\text{O}_9$ formula (**Figure 16**), this material is at a higher symmetry: orthorhombic system, space group P212121 . The Co_2O_{11} dimers, in this case, are formed by two vertex-linked CoO_6 octahedra. They ensure the cohesion between the nn-infinite tetrahedral (PO_3) chains to lead to a three-dimensional framework.

4.2.1.4 Mixed mono-diphosphate $\text{Na}_4\text{Co}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$

Some materials may have more than one type of phosphate group. The material $\text{Na}_4\text{Co}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ [36] has both PO_4 isolated tetrahedra and P_2O_7 diphosphate groups. This mono-diphosphate crystallizes in the orthorhombic system, space

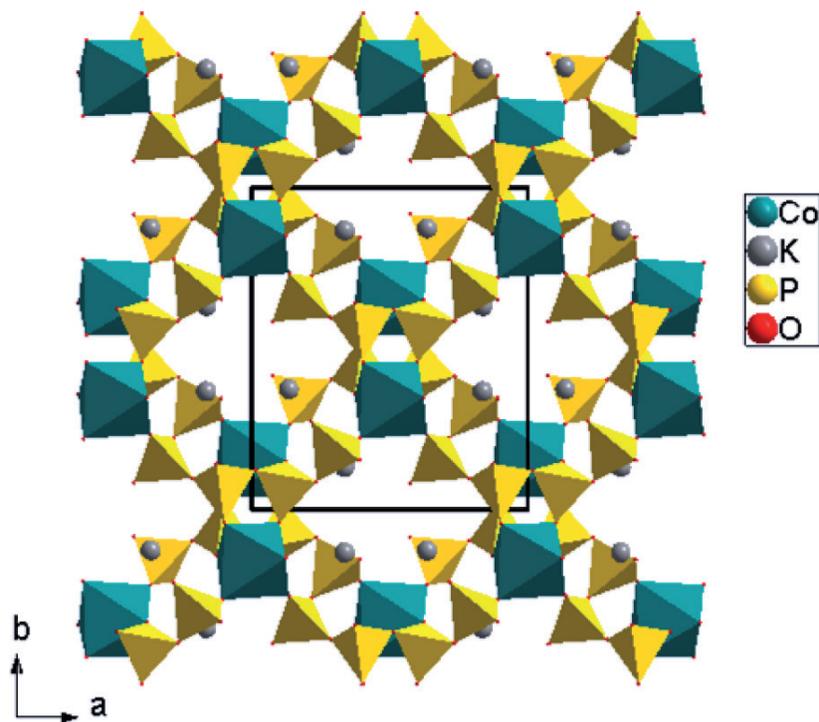


Figure 15.
Projection of $\text{K}_2\text{Co}(\text{PO}_3)_4$ structure along the c axis.

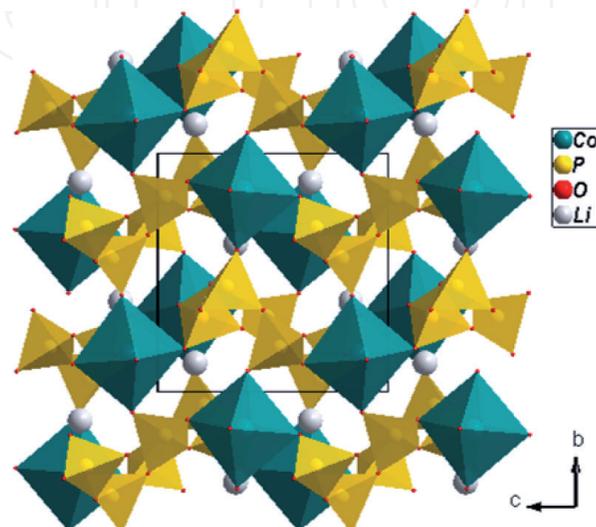


Figure 16.
Projection of $\text{LiCo}_2\text{P}_3\text{O}_9$ structure along the a axis.

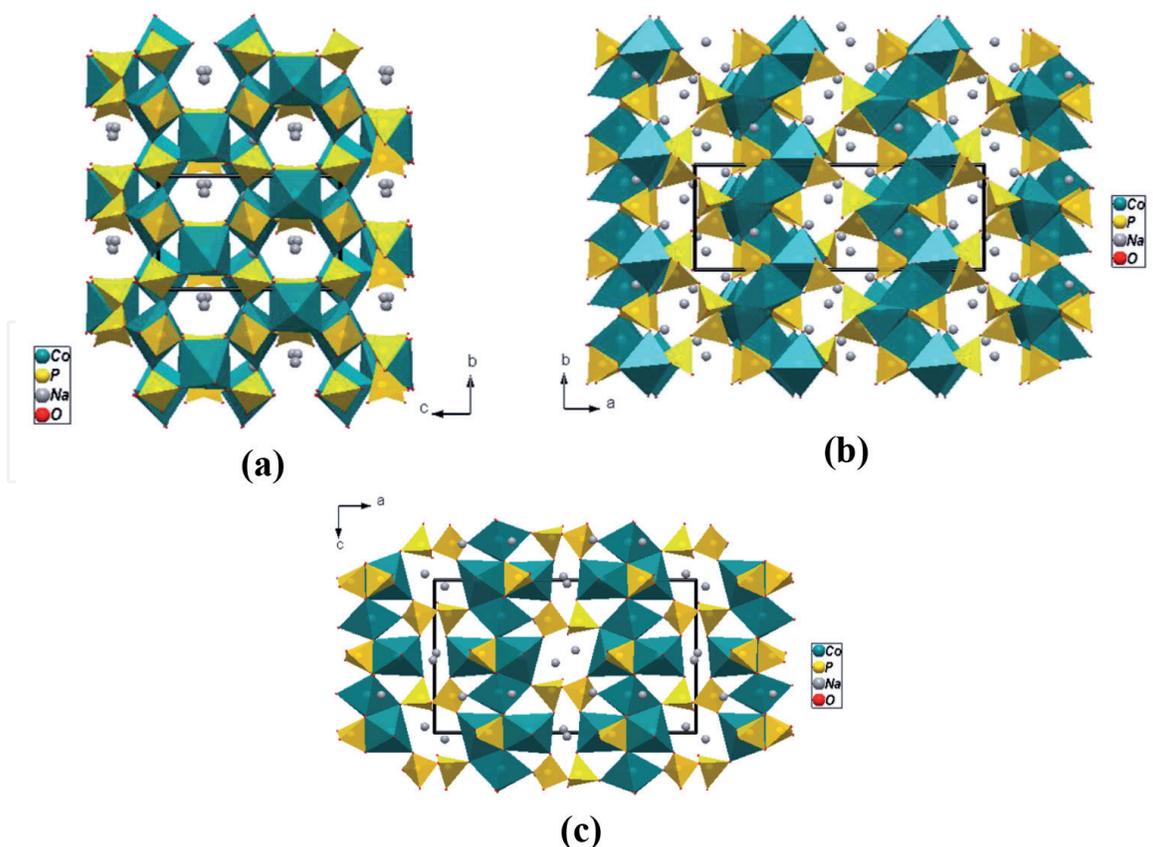


Figure 17.
Projections of $\text{Na}_4\text{Co}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ structure in (a) *a*, (b) *b*, and (c) *c* directions.

group $\text{Pn}2_1\text{a}$. Projections of the three-dimensional framework of this material (**Figure 17**) show that PO_4 monophosphates are bound to CoO_6 octahedra, on the one hand by edge sharing and on the other hand by sharing vertices, while diphosphates join four CoO_{10} units by pooling vertices.

5. Structural factors involved in ionic conductivity: Correlation of structure-electrical properties

Ionic conductors have been intensively researched since the discovery of properties of ionic superconductors [37] whose conductivity is sufficiently high to consider applications as solid electrolytes in batteries [38, 39] in storage devices of energy and sensors [40]. On the other hand, materials with low ionic conductivity remain interesting to elucidate certain mechanisms of cation transport. In these materials, the charge carriers are cations.

The open framework is an essential factor that governs the mobility of cations within a crystal lattice [6, 41, 42]. Among these structures, there are:

- Three-dimensional frameworks with windows or channels: this type of material has an ionic conduction influenced by the size of the bottlenecks separating two adjacent available sites. The existence of wide-sectioned channels between the cationic sites promotes the passage of cations. According to Hong, for fast ionic conduction, the minimum sections of the windows must be greater than or equal to twice the sum of the radii of the cation and the nearest anion [40].
- Layered structures: in this case, mobile ions move in parallel planes, located in the interlayer space. The conduction in this case is probably two-dimensional [27].

- Structures with isolated tetrahedral groups: these structures consist of tetrahedral groups (SiO_4^{3-} , PO_4^{3-} , etc.) connected to each other solely by alkaline ions. These independent tetrahedra facilitate the movement of cations [43–45].

Other factors than the open framework can also promote ionic mobility [40]:

- Site occupation: the partial occupations of the ionic sites (occupancy rate lower than 1) favor the displacement of the mobile ion from one site to another energetically equivalent.
- Coordination polyhedra: the cation environment can play an important role in its mobility. Indeed, mobile ions can cross rectangular faces more easily than triangular faces.
- Ion size: to promote conduction, congestion must be minimized, so the use of small cations is recommended, to facilitate their movement.
- Structural defects: substitution or doping of one or more elements with other(s) having different degrees of oxidation is responsible for the creation of cationic vacancies at the origin of conduction properties in certain materials.

Taking into account the structural factors influencing the conductivity mentioned above, several studies have been devoted to improving the electrical properties of such materials by acting on other factors. This is the case of the total or partial substitution of the mobile species such as in NASICON $\text{Na}_{1+x}\text{Zr}_{2-x}\text{Mg}_{x/2}(\text{PO}_4)_3$ ($0 < x \leq 2$) [46] and in SKELETON phosphates (3D) $\text{A}_3\text{M}_2(\text{PO}_4)_3$: $\text{A} = \text{Li}, \text{Na}, \text{Ag}, \text{K}$, and $\text{M} = \text{Cr}, \text{Fe}$ [47]. The doping of materials by one or more chemical elements can also promote the mobility of cations like the oxides $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_{2-x}\text{T}_x\text{O}_7$ with $\text{T} = \text{Fe}, \text{Co}, \text{Cr}$ [48].

On the other hand, work on a series of materials is being processed in order to show the effect of microstructure optimization (grain size) on conductivity [49]. Moreover, it has been demonstrated in previous studies, such as for LAMOX ceramics ($\text{La}_{2-x}\text{R}_x\text{Mo}_{2-y}\text{W}_y\text{O}_9$ with $\text{R} = \text{Nd}, \text{Gd}, \text{Y}$) [50, 51] and for β -Xenophyllite-type $\text{Na}_4\text{Co}_7(\text{AsO}_4)_6$ [21] and $\text{Ag}_4\text{Co}_7(\text{AsO}_4)_6$ [26], that the electrical properties are related to the relative density of sample (100 porosity), which requires a rigorous control of the microstructure.

6. Conclusion

In this chapter, synthesis methods of cobalt phosphates and metallo-cobalt phosphates in the crystalline form have been described: single crystals and/or polycrystalline powders. The structural studies of the studied compounds show structural diversity with open anionic frameworks showing tunnels (3D) and inter-sheet space (2D). However, it shows that the electrical property is related to the structural characteristics of the material. In order to correlate structure and physical properties especially electrical properties of metallo-cobalt phosphates, structural factors influencing the ionic conductivity have been treated. Based on the structural characteristics, the electrical properties of the crystalline materials can be modeled theoretically, especially in the case of purely ionic conductors. In fact, it is possible to determine the value of the activation energy which corresponds to the minimum energy that must be supplied to an ion to move from one site to another site in the

crystal lattice. In addition, these modelizations are based on the structural data of the crystal. Since the measurements are often performed on ceramics, it is also necessary to take into account the effect of the relative density of the ceramic: effect of the microstructure.

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Riadh Marzouki^{1,2,3*}, Mahmoud A. Sayed^{4,5}, Mohsen Graia²
and Mohamed Faouzi Zid³

1 Chemistry Department, College of Science, King Khalid University, KSA

2 Chemistry Department, Faculty of Sciences, University of Sfax, Tunisia

3 Chemistry Department, Faculty of Sciences, University of Tunis El Manar, Tunisia

4 Physics Department, Faculty of Science, King Khalid University, KSA

5 Physics Department, Faculty of Science, Al-Azher University, Assiut, Egypt

*Address all correspondence to: riadh.marzouki@hotmail.fr

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