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Synthesis, Crystal Structure and Electrical Properties of a New Mixed Compound $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$

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ABSTRACT

A new cobalt diphosphate $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$, is synthesized by solid state reaction method and characterized by single-crystal X-ray diffraction. The title material crystallizes in the triclinic space group P-1 with a = 6.4170(3) Å, b = 9.4510(2) Å, c = 10.9350(3) Å, α = 115.240(2)˚, β = 80.190(3)˚ and γ = 106.810(2)˚. The structure presents a centro-symmetrical clusters $Co_4P_4O_{28}$ consists of two Co_2O_{11} units and two P_2O_7 pyrophosphate groups. The junction between clusters is assured by two P_2O_7 groups to form a three-dimensional anionic framework having different interconnecting tunnels running along [100] and [010]. The former contains the Na^+ and Ag^+ cations. The conductivity measurements of $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$ are studied over a temperature interval from 783 to 903 K using the frequency response analyzer with 0.5 V amplitude signal over the range of 13 MHz - 5 Hz.

Keywords: Diphosphate; X-Ray Diffraction; Anionic Framework; Tunnels; Conductivity

1. Introduction

Phosphate materials have vast applications in several domains as electric, pyroelectric, ferroelectric, magnetic, catalytic processes, state laser materials, etc. [1-7]. During the last years, there have been many studies of the compounds with general formula $A_2BP_2O_7$ (A = monovalent cation, B = divalent ion) concerned the structural features and the electrical properties [8-12]. With regard to cobalt phases members, electrical studies were performed only for the tetragonal formula $Na_2CoP_2O_7$ (bidimensional) [8]. It shows that the latter is an ionic conductor material. We have now prepared a new mixed diphosphate of the triclinic form. The synthesis, the structural study and the electrical properties of $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$ (tridimensional) material are discussed here.

2. Experimental

2.1. Synthesis of the Title Compound

A mixture of high-purity reagents ($NaNO_3$/$AgNO_3$, $Co(NO_3)_2{\cdot}6H_2O$ and $NH_4H_2PO_4$) as polycrystalline form, with a Na:Ag:Co:P molar ratio of 1:1:1:2, is dissolved in deionised water to give a pink solution. After evaporation to dryness at 70˚C in the oven, the residue, placed in porcelain crucible, is slowly annealed in air to 400˚C for 24 h, in order to eliminate volatile products. In a second step, it was progressively heated at 620˚C for 5 days. The sample was slowly cooled at 5˚C/24 h to 580˚C and finally quenched to room temperature. Purple single crystals of the title compound are extracted from the flux matrix with boiling water. A qualitative EDX (energy-dispersive X-ray spectroscopy) analysis (model: Philips XL 30) detected the presence of Na, Ag, Co, P and oxygen elements. A polycrystalline powder of $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$ was obtained by treating a stoichiometric mixture of the above reagents. The powder X-ray diffraction pattern was in agreement with single-crystal structure.

2.2. Materials and Physical Measurements

Impedance spectroscopy measurements were carried out in a Hewlet-Packar 4192-A automatic bridge monitored by a HP microcomputer. Impedance spectra were recorded in the 13 MHz - 5 Hz frequency range with 0.5 V alternative signal. Pellet was prepared by uniaxial shaping followed by isostatic pressing at 2.5 kbar and sintering at 540˚C for 2 h in air with 5 $K{\cdot}min^{-1}$ heating and cooling rates. The thickness and surface of pellet were about 0.356 cm and 0.454 cm^2 having a geometric factor of e/S = 0.78 cm^{-1}. Platinum electrodes were painted in the two faces of the pellet with a platinum paste to ensure good electric contacts and then painted pellet was carried out at steady-state temperatures in still air.

*Corresponding author.

2.3. Crystal Structure Determination

A suitable single crystal with dimensions 0.24 × 0.21 × 0.16 mm^3 was chosen for the structure determination. The data were collected on an Enraf-Nonius CAD-4 diffractometer using the MoK_α (λ = 0.71069 Å) radiation at room temperature. The structure was determinate by direct methods using SHELXS-97 program [13]. In the closest solution proposed by program, only some atoms of cobalt and phosphor were located. Using SHELXL-97 program [14], refinements followed by Fourier differences are necessary to find the positions of others atoms remaining in the lattice to an R factor of 2.55% for all reflections. The structure graphics were drawn with diamond 2.1 supplied by Crystal Impact [15]. A summary of crystallographic data, recording conditions and structure refinement results of the title compound is given in **Table 1**.

The atomic coordinates and isotropic thermal factors are presented in **Table 2**. **Table 3** contains the main interatomic distances in coordination polyhedra of the studied structure.

3. Results and Discussion

The title compound is a new member of isostructural phases family including $Na_7Mg_{4,5}$ $(P_2O_7)_4$ 2) [16], $Na_2CoP_2O_7$ 3) [17], $Na_{3.12}$ $Fe_{2.44}$ $(P_2O_7)_2$ 4) [18], $Na_{3.64}$ $Mg_{2.18}(P_2O_7)_2$ 5) and $Na_{3.64}Ni_{2.18}(P_2O_7)$ 6) [19]. This family of phases crystallizes in a centrosymmetric lattice, in

Table 1. Crystal data refinement results of $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$ compound.

Crystal data	
Crystal shape: Prism	Color: Purple
Crystal system: Triclinic	Space group: P-1
Cell parameters: a = 6.417(3) Å α = 115.24(2)° b = 9.451(2) Å β = 80.19(3)° c = 10.935(3) Å γ = 106.81(2)°	V = 573.4(3) $Å^3$ Z = 2 ρ = 3.801 g·cm^{-3} T = 298 K
Data collection	
4980 measured reflections	2166 reflections with I > 2σ(I)
2491 independent reflections	R_{int} = 0.02
H = −8→8	T_{min} = 0.554; T_{max} = 0.402
K = −12→12	θ_{max} = 26.97°; θ_{min} = 2.06°
L = −13→13	Decay = 1%
Refinement	
R [I > 2σ(I)] = 0.0255	wR_2 (F^2) = 0.0618
S = 1.07	Extinction coefficient: 0.0031 (6)
$\Delta\rho_{max}$ = 0.71 e·$Å^{-3}$	$\Delta\rho_{min}$ = −0.56 e·$Å^{-3}$
258 parameters	2491 reflections

Table 2. Atomic coordinates and isotropic thermal factors of $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$.

Atoms	x	y	z	U_{iso}*	Occupancy
Co1	0.3545(7)	0.26562(5)	0.76417(4)	0.00967(2)	1
Co2	0.2783(7)	0.61021(5)	0.71736(4)	0.01031(2)	1
P1	0.4257(3)	0.65654(1)	0.95528(8)	0.00855(8)	1
P2	0.2858(4)	0.27129(1)	0.46202(8)	0.00982(8)	1
P3	0.1219(3)	0.63778(1)	0.18316(9)	0.00952(8)	1
P4	−0.0770(4)	0.10713(1)	0.28674(9)	0.01362(9)	1
O1	0.6880(4)	0.2606(3)	0.7245(2)	0.0182(5)	1
O2	0.2116(5)	0.4255(3)	0.5341(3)	0.0215(6)	1
O3	0.4444(4)	0.5208(3)	0.8156(2)	0.0112(5)	1
O4	0.0304(4)	0.2645(3)	0.8112(3)	0.0206(6)	1
O5	0.2278(4)	0.5753(3)	0.0322(2)	0.0140(5)	1
O6	−0.0161(4)	0.5167(3)	0.7972(3)	0.0195(6)	1
O7	0.9557(5)	−0.0518(4)	0.8485(3)	0.0369(8)	1
O8	0.5668(4)	0.7289(3)	0.6619(3)	0.0221(6)	1
O9	0.2841(4)	0.0145(3)	0.6998(3)	0.0153(5)	1
O10	0.3788(4)	0.2781(3)	0.9609(2)	0.0162(5)	1
O11	0.1141(5)	0.7259(3)	0.6656(4)	0.0310(7)	1
O12	0.9249(4)	0.8744(3)	0.5989(3)	0.0145(5)	1
O13	0.3769(4)	0.2275(3)	0.5562(2)	0.0170(5)	1
O14	0.3543(4)	0.7872(3)	0.9368(3)	0.0164(5)	1
Na1	0.024(2)	0.2050(4)	0.0244(2)	0.019(3)	0.899(2)
Ag1	0.027(4)	0.212(3)	0.016(2)	0.017(3)	0.101(2)
Na2	0.592(3)	0.0065(6)	0.8113(5)	0.0229(7)	0.340(2)
Ag2	0.5754(4)	−0.0075(2)	0.8338(3)	0.0229(7)	0.503(9)
Ag3	0.6006(2)	−0.0203(7)	0.8560(7)	0.0229(7)	0.157(8)
Ag4	0.7170(2)	0.0533(1)	0.54694(9)	0.0492(5)	0.313(2)
Na3	0.7170(2)	0.0533(1)	0.54694(9)	0.0492(5)	0.424(7)
Na4	1/2	0	1/2	0.043(2)	0.526(2)
Na5	0.2060(2)	0.5653(9)	0.4081(7)	0.0278(1)	0.912(2)
Ag5	0.2430(3)	0.5330(2)	0.3776(7)	0.0390(3)	0.088(2)

$^*U_{éq} = (1/3) \sum_i\sum_j U^{ij}a_i^*a_j^*a_i \cdot a_j$.

Table 3. Main interatomic distances (Å) in $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$ compound.

Octahedron Co(1)O6		**Octahedron Co(2)O6**	
Co1—O4	2.053 (3)	Co2—O11	2.006 (3)
Co1—O9	2.096 (2)	Co2—O8	2.012 (3)
Co1—O1	2.120 (3)	Co2—O2	2.031 (3)
Co1—O13	2.132 (3)	Co2—O6	2.060 (3)
Co1—O10	2.134 (3)	Co2—O3	2.165 (2)
Co1—O3	2.149 (2)	Co2—O14	2.302 (3)
Tetrahedron P(1)O4		**Tetrahedron P(2)O4**	
P1—O10i	1.502 (3)	P2—O2	1.505 (3)
P1—O14	1.532 (2)	P2—O13	1.510 (2)
P1—O3	1.532 (2)	P2—O8iii	1.514 (3)
P1—O5ii	1.592 (3)	P2—O12iii	1.617 (3)
Tetrahedron P(3)O4		**Tetrahedron P(4)O4**	
P3—O4iv	1.506 (2)	P4—O7v	1.500 (3)
P3—O6iv	1.511 (3)	P4—O11iv	1.514 (3)
P3—O1iii	1.531 (3)	P4—O9vi	1.517 (3)
P3—O5	1.598 (3)	P4—O12iii	1.637 (3)

Symmetry codes: (i): −x + 1, −y + 1, −z + 2; (ii): x, y, z + 1; (iii): −x + 1, −y + 1, −z + 1; (iv): −x, −y + 1, −z + 1; (v): −x + 1, −y, −z + 1; (vi): −x, −y, −z + 1.

the space group P-1. The 3 structure is to claim to be not centrosymmetric (P1 GE). For $Na_2CoP_2O_7$ material, we note the stoichiometry of the chemical composition. The report of the formula as determined from 3) Na/Co = 2, which agrees with the results found in the structural study of the title compound (Na, Ag)/Co = 2.

The asymmetric unit in $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$ compound is shown in **Figure 1**. The structure is composed of two octahedrons sharing corner and forming Co_2O_{11} group. The latter is linked on one side by edge with P_2O_7 group. On the other side, a second diphosphate is connected sharing corners with $Co1O_6$ and $Co2O_6$. The compensation of charge in the asymmetric unit is ensured by Ag^+ and Na^+ cations.

In the anionic framework, the Co_2O_{11} octahedral groups are arranged in the (1 –1 0) plane (**Figure 2**). The connection between two Co_2O_{11} units and two diphosphate groups is assured by mixed bridges Co1–O–P and sharing edges with $Co1O_6$ octahedra, to form the $Co_4P_4O_{28}$ cluster (**Figure 3**).

Along the three directions of the cell, the junction between these clusters is provided by two diphosphates groups sharing a corner with the CoO_6 octahedra thus forming a three-dimensional framework (**Figure 4**). However, the structure belongs to the dichromate family [20] which the conformation of this group is eclipsed.

The three-dimensional network shows the existence of two types of tunnels along [100] with hexagonal and decagonal sections (**Figure 5(a)**). A projection of the anionic framework in the *b* direction is given in **Figure 5(b)**.

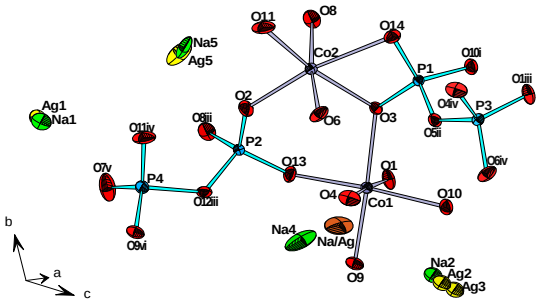


Figure 1. Asymmetric unit of $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$ compound.

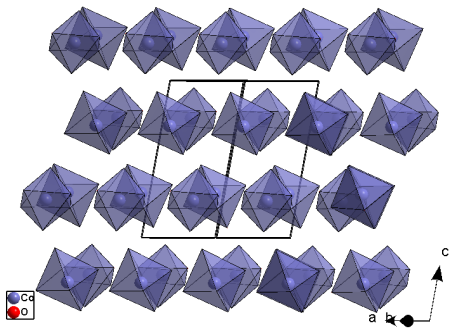


Figure 2. Octahedral representation of the structure showing the arrangement of Co_2O_{11} groups in the (1 –1 0) plane.

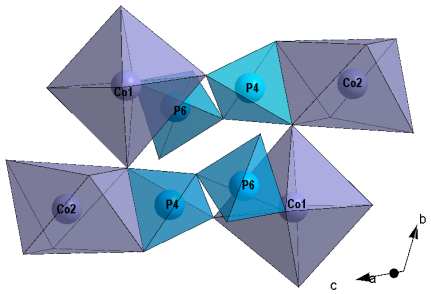


Figure 3. Projection of $Co_4P_4O_{28}$ cluster of $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$ viewed near the [100] direction.

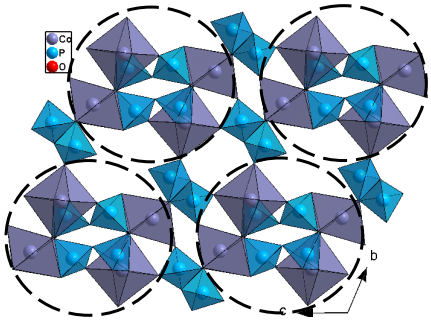
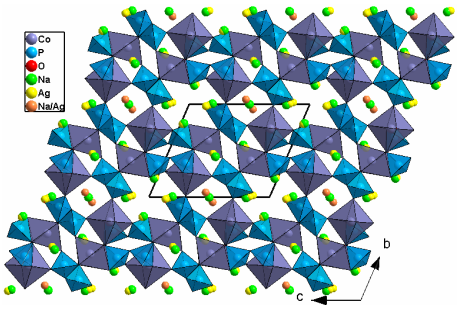
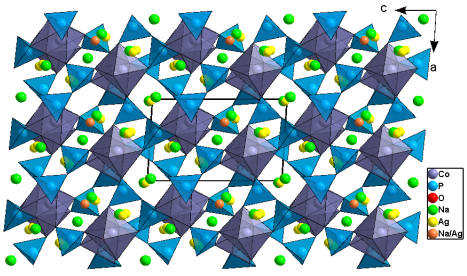


Figure 4. Junction between clusters ensured by the diphosphate groups in *bc* plane of $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$ compound.



(a)



(b)

Figure 5(a). Projection of $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$ structure along [100] direction showing tunnels where monovalent cations are located; (b): Projection of $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$ structure along [010] direction showing the windows and the channels.

It shows the presence of channels and quadrilateral windows along this direction. The monovalent cations are located in these tunnels.

The electrical properties of the title compound are investigated using complex impedance spectroscopy (CIS). The electrical data exploitation was realized in the thermal range 783 - 903 K. The Nyquist plots at different temperature for $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$ material are shown in **Figure 6**. We have used the Zview software [21] to fit these curves. The bulk ohmic resistance relative to each experimental temperature is deduced from complex impedance diagrams. It is the intercept Z0 on the real axis of the zero phase angle extrapolation of the highest frequency curve. The resistivity parameters R for this compound vary with temperature according to Arrhenius-type laws. The $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$ impedance diagrams show only one typical semicircle arc with a spike at lower frequencies. The best fit is obtained when we used an equivalent circuit composed of a resistor, R connected in parallel with a constant phase element, CPE (**Figure 7**) [22]. No additional blocking effect could be evidenced at lower frequencies ($f \leq 20$ Hz). Values of electric parameters calculated for $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$ compound, at different temperatures, after fitting are illustrated in **Table 4**.

A linear plots of log (σT(S.K·cm^{-1})) vs. 10^3/T (K^{-1}) is represented in **Figure 8**. The conductivity value σ at 683 K is 2.61 × 10^{-7} S·cm^{-1} and the activation energy deduced from the slope is Ea = 1.368 eV (**Figure 8**). Compared to the activation energies observed in $Na_2CoP_2O_7$ material (E_a = 0.63 eV) [8], in $NaAgZnP_2O_7$ (E_a = 0.76 eV) [23], in $Na_2PbP_2O_7$ (E_a = 0.90 eV) [24] and $Ag_2PbP_2O_7$ (E_a = 0.78 eV) [25], $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$ exhibit a low electric conductivity.

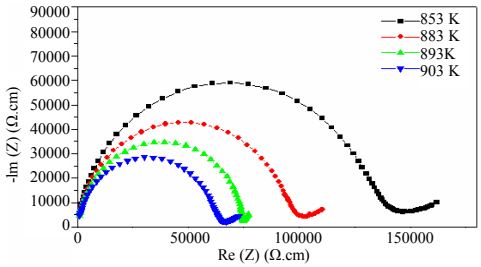


Figure 6. Impedance spectra recorded on $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$ sample over the temperature ranges 853 - 903 K.

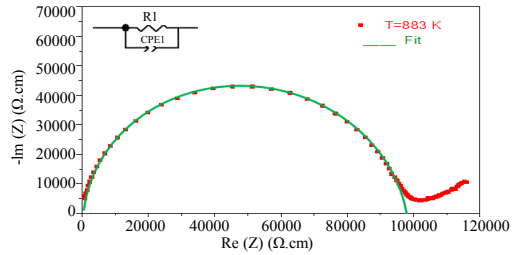


Figure 7. Impedance spectra recorded on $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$ sample over the temperature ranges 853 - 903 K.

Data from the structural study of $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$ compound show that the monovalent cations are located in 3 types of tunnels whose section dimensions are illustrated in **Figure 9**. In the [100] direction, the Na^+ and $(Na/Ag)^+$ ions are located in a tunnel of hexagonal section with maximum section equal to 4.671 (6) Å (**Figure 9(a)**). The other tunnel contains the Na^+ and Ag^+ ions. The smaller sections of these tunnels in this direction are 3.699 (3) Å and 3.460 (5) Å which are inferior to 2 (r_o^{2-} + r_{Na}^+) = 5.18 Å and 2 (r_o^{2-} + r_{Ag}^+) = 5.40 Å according to Shannon [26]. Furthermore, in the *b* direction, the tunnel of hexagonal section (**Figure 9(b)**) contains a bottleneck of small width equal to 2.917 (3) Å. It is smaller also than twice the sum of ray r_o^{2-} = 1.42 Å and r_{Na}^+ = 1.18 Å (5.18 Å) for Na^+ and 2 (r_o^{2-} + r_{Ag}^+) = 5.40 Å for Ag^+ according Shannon [26]. These geometric factors are causing a low mobility of the cations (Ea >1 eV).

4. Conclusion

In the summary, in this work we have synthesized a new diphosphate compound of composition $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$ by solid state reaction. This material was characterized by X-ray diffraction. The sample crystallized in triclinic symmetry with P-1 space group (Z = 2)

Table 4. Electrical values of the equivalent circuit parameters calculated for $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$ sample at different temperatures.

T (K)	R (×10^5 Ω·cm)	C (×10^{-12} F)	P	σ (×10^5 S·cm^{-1})
783	6.51	8.0	0.9	0.12
813	3.09	8.7	0.9	0.25
853	1.08	10.9	0.9	0.73
883	0.77	11.8	0.9	1.02
893	0.59	8.4	0.9	1.33
903	0.50	9.9	0.9	1.57

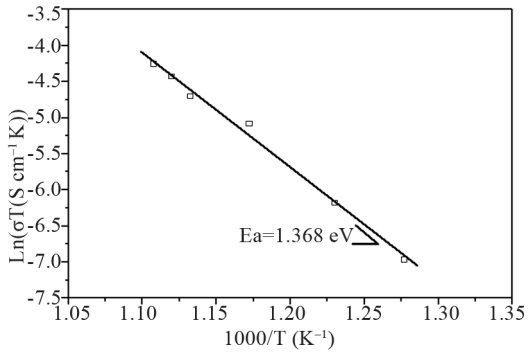
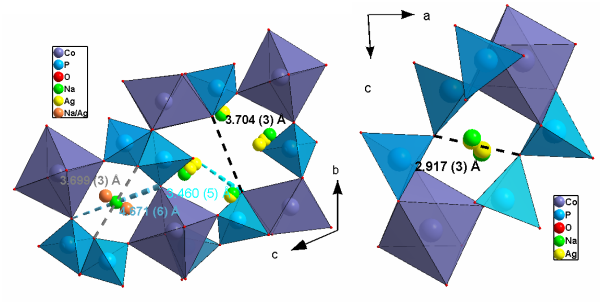


Figure 8. Conductivity Arrhenius plots of $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$ sample.



(a) (b)

Figure 9. Dimensions of the tunnel sections in $(Na_{0.71}Ag_{0.29})_2CoP_2O_7$ structure.

and the unit cell parameters are a = 6.4170(3) Å, b = 9.4510 (2) Å, c = 10.9350(3) Å, α = 115.240(2)˚, β = 80.190(3)˚ and γ = 106.810(2)˚. The structure of this material has an open framework having different interconnecting tunnels running along [100] and [010] where the Na^+ and Ag^+ ions are located. The electrical properties of the title compound are investigated using complex impedance spectroscopy. Impedance measurements (frequency/temperature ranges 13 MHz - 5 Hz/783 - 903 K) show $(Na_{0.71}$ $Ag_{0.29})_2CoP_2O_7$ a low electrical conductor being the conductivity 2.61 × 10^{-7} S·cm^{-1} at 683 K and the activation energy is 1.368 eV.

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