Abstract: A new member of sodium metal diphosphate-diarsenate, \( \text{Na}_2\text{CuP}_{1.5}\text{As}_{0.5}\text{O}_7 \), was synthesized as polycrystalline powder by a solid-state route. X-ray diffraction followed by Rietveld refinement show that the studied material, isostructural with \( \beta\)-\( \text{Na}_2\text{CuP}_2\text{O}_7 \), crystallizes in the monoclinic system of the \( C2/c \) space group with the unit cell parameters \( a = 14.798(2) \, \text{Å} \); \( b = 5.729(3) \, \text{Å} \); \( c = 8.075(2) \, \text{Å} \); \( \beta = 115.00(3) \, ^\circ \). The structure of the studied material is formed by \( \text{Cu}_2\text{P}_4\text{O}_{15} \) groups connected via oxygen atoms that results in infinite chains, wavy saw-toothed along the [001] direction, with \( \text{Na}^+ \) ions located in the inter-chain space. Thermal study using DSC analysis shows that the studied material is stable up to the melting point at 688 \( ^\circ \text{C} \). The electrical investigation, using impedance spectroscopy in the 260–380 \( ^\circ \text{C} \) temperature range, shows that the \( \text{Na}_2\text{CuP}_{1.5}\text{As}_{0.5}\text{O}_7 \) compound is a fast-ion conductor with \( \sigma_{350 \, ^\circ \text{C}} = 2.28 \times 10^{-5} \, \text{S cm}^{-1} \) and \( \text{Ea} = 0.6 \, \text{eV} \). \( \text{Na}^+ \) ions pathways simulation using bond-valence site energy (BVSE) supports the fast three-dimensional mobility of the sodium cations in the inter-chain space.

Keywords: diphosphate-diarsenate; crystal structure; electrical properties; transport pathways simulation

1. Introduction

The research exploration of new inorganic materials with open framework constructed of polyhedra sharing faces, edges and/or corners forming 1D channels, 2D inter-layer spaces or 3D networks where cations are located, is currently an area of intense activity including several disciplines, in particular solid-state chemistry. In particular, alkali metal phosphates were found to have various applications because of their electric, piezoelectric, ferroelectric, magnetic, and catalytic properties [1–4]. Among those, the families of materials with the melilite structure [5], the olivine structure [6] and the natrium super ionic conductor (NaSICON) structure [7], attracted attention for their ionic conduction and exchange of ions [6,7].

More recently, in a series of studies arsenate analogs have been synthesized [8–10]. But, until today phosphate compounds are more studied as cathodes [11,12] compared to arsenate and this is perhaps due to the toxicity of arsenic III (\( \text{As}_2\text{O}_3 \)). However, the oxide of arsenic V (\( \text{As}_2\text{O}_5 \)) is less toxic. In addition, the introduction of arsenic into a structure changes its physical and chemical properties.
and even toxicity. On the other hand, the comparison of the electrochemical properties of LiCoPO_{4} and LiCoAsO_{4} both with olivine structure and close unit cell parameters, shows reversible (de)intercalation from/into material at average voltages of 4.8 and 4.6 V, respectively for LiCoAsO_{4} [10] and a voltage average of 2.5–5 V for LiCoPO_{4} [11].

The Na_{2}MP_{2}O_{7} systems (M = transition metal) [13,14] have a layered structure with the layers [MP_{2}O_{7}]^{2n-} and the sodium cations localized in the interlayer space, which favors high ionic conductivity. We recently investigated the effect of the substitution of P by As with a larger ionic radius for ionic conductivity and showed the improvement of ionic conductivity for Na_{2}CoP_{1.5}As_{0.5}O_{7} [15], which has an electrical conductivity value of \( \sigma_{290 \, ^{\circ}C} = 7.91 \times 10^{-5} \, \text{S cm}^{-1} \) and an activation energy \( E_{a} = 0.56 \, \text{eV} \) compared to Na_{2}CoP_{2}O_{7} (\( \sigma_{300 \, ^{\circ}C} = 2 \times 10^{-5} \, \text{S cm}^{-1} ; E_{a} = 0.63 \, \text{eV} \)) [13].

In our search for new polyanion oxides of sodium and transition metals, the exploration of the Na_{2}O-CuO-P_{2}O_{5}-As_{2}O_{5} crystallographic systems allowed us to isolate a new member of di-phosphate arsenates, Na_{2}CuP_{1.5}As_{0.5}O_{7}, in the polycrystalline powder form. In this paper, characterizations and physicochemical studies of the new member of sodium copper diphosphate-diarsenate material, Na_{2}CuP_{1.5}As_{0.5}O_{7}, and a comparison with other previous works encountered in the literature will be presented.

2. Materials and Methods

A mixture of Cu(NO_{3})_{2}.25H_{2}O, NH_{4}H_{2}PO_{4} and Na_{2}HAsO_{4}.7H_{2}O in the molar ratio Na:Cu:P:As equal to 2:1:1.5:0.5 was placed in a porcelain crucible and heated to 350 °C for 24 h to eliminate the volatile products H_{2}O, NO_{2}, and NH_{3}. The obtained powder was ground manually using agate mortar and shaped as cylindrical pellets by a uniaxial press. The obtained pellets were heated to 600 °C. After 72 h, the sample was cooled slowly at a rate of 10 °C/h down to room temperature. After grinding finely, a blue polycrystalline powder was obtained.

X-ray powder diffraction (XRD) was used to control and ensure the purity of the obtained powder. The analysis was carried out using XRD-6000 (Shimadzu, Japan) with graphite monochromator (Cukα, \( \lambda = 0.154178 \, \text{nm} \)) and a scan range of 2\( \theta \) = 10°–70° with step of about 0.02°. The structure was refined using the Rietveld method by the means of the GSAS computer program [16] (EXPGUI, Gaithersburg, Maryland, USA). The crystallographic data of Na_{2}CuP_{2}O_{7} [17] was used as a starting set. The obtained structural model was confirmed by the Charge Distribution CHARDI model of validation. The CHARDI calculation was done by using the CHARDI2015 computer program (Nespolo, IUCR) [18].

FTIR spectrometer (Agilent Technologies Cary 630 model) was used to allow a direct indexation of the peaks on a spectral range in wave numbers ranging from (1300–400 cm\(^{-1})\). Differential scanning calorimetry (DSC), with the SDT Q600 model, was used to study the thermal behavior of the obtained and prepared sample. In fact, the device contains two crucibles, one as a reference and the other contains the sample to be analyzed. These two crucibles are heated to 750 °C at a rate of 10 °C/min. The thermal analysis was carried out under a nitrogen atmosphere to avoid the reaction of the sample with the oxygen in the air.

Energy-dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM, Thermo Fisher Scientific model), were used to identify the present elements and the microstructure of the studied material, respectively.

The electrical measurements were preceded by pretreatment of the sample in order to densify the measured sample by reducing the mean particle size of the synthesized powder. Mechanical grinding for 100 min was carried out using the FRISCH planetary micromill pulverisette 7. The polycrystalline sample was shaped as a cylindrical pellet using a uniaxial press. The pellet was sintered in air at an optimal temperature of 610 °C for 2 h with 5 °C/min heating and cooling rates. The geometric factor of the dense ceramic is \( g = e/S = 0.793 \, \text{cm}^{-1} \) where e and S are the thickness and face area of pellet, respectively. Gold metal electrodes ~36 nm thick were deposited using a SC7620 mini sputter coater.
The sample was then placed between two platinum electrodes that were connected by platinum cables to the frequency response analyzer (HP 4192A) which was controlled by a microcomputer.

Impedance spectroscopic measurements were performed via the Hewlett-Packard 4192-A automatic bridge supervised by HP workstation. Impedance spectra were recorded with 0.5 V AC-signal in the 5 Hz–13 MHz frequency range.

The bond-valence site energy (BVSE) model [19,20] was used to simulate the alkali migration in the 3D anionic framework. The BVSE model is the latest extension of the bond-valence sum (BVS) model developed by Pauling [21] to describe the formation of inorganic materials. The BVS model was improved by Brown & Altermatt [22] followed by Adams [23], resulting in the expression:

$$ s_{A-X} = \exp\left(\frac{R_0 - R_{A-X}}{b}\right) $$

(1)

where $s_{A-X}$ is individual bond-valence, $R_{A-X}$ is the distance between counter-ions A and X, $R_0$ and $b$ are fitted empirical constants, and $R_0$ is the length of a bond of unit valence.

The BVSE model was extensively used in the cation motion simulation in the anionic framework by following the valence unit as a function of migration distance [24]. The valence unit was also recently related to potential energy scale and electrostatic interactions [19,20]. The BVSE method was used with success to simulate the transport pathways of monovalent cations (Na$^+$; K$^+$ and Ag$^+$) in numerous materials including Na$_2$CoP$_1.5$As$_{0.5}$O$_7$[15], Na$_{1.14}$K$_{0.86}$Co$_2$O$_7$[25] and Ag$_{3.68}$Co$_2$(P$_2$O$_7$)$_2$[26]. The BVSE calculations were performed using the SoftBV [27] code and the visualization of isosurfaces was carried out using VESTA3 software (version 3, Koichi Momma and Fujio Izumi, 2018).

3. Results and Discussion

3.1. X-ray Powder Diffraction

The crystallographic study was started by a simple comparison between the XRD pattern of the prepared materials in the Na$_2$O-CuO-P$_2$O$_5$-As$_2$O$_5$ system and those of the previous studies of diphasphate Na$_2$MP$_2$O$_7$[5,7,14,28,29] and Na$_2$CoP$_1.5$As$_{0.5}$O$_7$[15]. In this case, only the Na$_2$CuP$_1.5$As$_{0.5}$O$_7$ diffractogram showed a similarity with that of the β-Na$_2$Cu$_2$P$_2$O$_7$ diphasphate[17]. It crystallizes in the monoclinic system of the C2/c space group. This result prompted us to make a precise refinement using the Rietveld method which was implemented into the GSAS computer software [16]. The final agreement factors are Rp = 5.4% and Rw = 6.9%. No additional peaks were detected. The final Rietveld plot is presented in Figure 1. The unit cell parameters obtained from the Rietveld refinement are $a = 14.798(2)$ Å; $b = 5.729(3)$ Å; $c = 8.075(2)$ Å; $\beta = 115.00(3)^\circ$ (Table 1). The details of the crystallographic data, data collection and final agreement factors are given in Table 2. The atomic coordinates and isotropic displacement parameters are listed in Table 3. The main bond distances are given in Table 4. The charge distribution analysis and the bond-valence computation are summarized in Table 5.

| Parameter | Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ (Current Work) | β-Na$_2$Cu$_2$P$_2$O$_7$ [30] |
|-----------|-----------------------------------------------|-------------------------------|
| $a$ (Å)   | 14.798(2)                                    | 14.728(3)                     |
| $b$ (Å)   | 5.729(3)                                      | 5.698(1)                      |
| $c$ (Å)   | 8.075(2)                                      | 8.067(1)                      |
| $\beta$ (°) | 115.00(3)                                    | 115.15(1)                     |
| $V$ (Å$^3$) | 620.43(3)                                     | 612.80(2)                     |
Figure 1. Results of the Rietveld refinement of the powder of Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ based on XRD data.

Table 2. Structure refinement results of the Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ compound.

| Crystallographic Data                  |
|----------------------------------------|
| Empirical Formula                      | Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ |
| Formula Weight; $\rho_{\text{cal}}$    | 305.44 g mol$^{-1}$; 3.220 g cm$^{-1}$ |
| Crystalline System; Space Group        | Monoclinic, C2/c |
| Unit Cell Dimensions                   | $a = 14.8688$ (8), $b = 5.7591$ (3), $c = 13.5957$ (7) $\beta = 147.2406$ (12) |
| Volume; Z                              | $V = 629.97$ (6) Å$^3$; 4 |

| Data Collection                        |
|----------------------------------------|
| Diffractometer                         | Bruker D8 ADVANCE |
| Wavelength                             | $\lambda_{\text{Cu K}\alpha} = 1.54056$ Å |
| Temperature                            | 298 (2) K |
| Angle Range                            | $4.91^\circ$–$69.91^\circ$ |
| Step Scan Increment ($^\circ$2$\theta$) | 0.02$^\circ$ |
| Counting Time                          | 2 s |

| Refinement                              |
|----------------------------------------|
| Angle Range                            | $4.91^\circ$–$69.91^\circ$ |
| $R_p$                                  | 0.054 |
| $R_{\text{wp}}$                        | 0.069 |
| $R_{\text{exp}}$                       | 0.043 |
| $R(F^2)$                               | 0.05117 |
| Goodness of Fit $\chi^2$               | 2.592 |
| No. of Data Points                     | 3251 |
| No. of Restraints                      | 18 |
| Profile Function                       | Pseudo-Voigt |
| Background                             | Chebyshev function with 20 terms |
Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$).

|      | x    | y    | z    | U$_{iso}$ | Occ. (<1) |
|------|------|------|------|-----------|-----------|
| Cu1  | $\frac{1}{4}$ | $\frac{1}{4}$ | $\frac{1}{4}$ | 0.0123 (12) |           |
| P1/As1 | 0.5112 (2) | 0.5884 (5) | 0.6563 (3) | 0.0065 (14) | 0.75/0.25 |
| Na1  | 0.3211 (5) | 0.8919 (9) | 0.2991 (5) | 0.004 (2)   |           |
| O1   | 0.6590 (6) | 0.4179 (9) | 0.7999 (6) | 0.006 (2)   |           |
| O2   | 0.5389 (4) | 0.7622 (10) | 0.6011 (6) | 0.006 (2)   |           |
| O3   | 0.8432 (6) | 0.0371 (12) | 0.9916 (5) | 0.041 (5)   |           |
| O4   | $\frac{1}{2}$ | 0.7267 (9) | $\frac{3}{4}$ | 0.018 (5)   |           |

Table 4. Main bond distances (Å) in the coordination polyhedra for Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$.

| Bond           | Distance (Å) |
|----------------|--------------|
| Cu1—O1$^{iii}$ | 1.9938 (3)   |
| Cu1—O1$^x$    | 1.9938 (3)   |
| Cu1—O3$^{iii}$| 1.9247 (3)   |
| Cu1—O3$^x$    | 1.9247 (3)   |
| Na1—O1$^i$    | 2.3985 (4)   |
| Na1—O1$^{vi}$ | 2.6566 (4)   |
| Na1—O2$^{vi}$ | 2.5780 (4)   |

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

Table 5. Charge distribution analysis of cation polyhedra in Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$.

| Cation | q(i) | sof(i) | Q(i) | CN(i) | ECoN(i) | $d_{av}$(i) | $d_{med}$(i) |
|--------|------|--------|------|-------|---------|-------------|--------------|
| Cu1    | 2.000 | 1.96   | 4    | 3.96  | 1.955   | 1.959       |              |
| M1     | 5.000 | 5.03   | 4    | 3.88  | 1.544   | 1.552       |              |
| Na1    | 1.000 | 0.98   | 6    | 5.47  | 2.400   | 2.443       |              |

q(i), formal oxidation number; Q(i), computed charge; sof(i), site occupation factor; $d_{av}$(i), arithmetic average distance; $d_{med}$(i), weighted average distance; CN, coordination number; ECoN(i), effective coordination number.

By comparing the unit cell parameters of the studied material with those of β-Na$_2$CuP$_2$O$_7$, the P/As substitution effect increases the volume of the unit cell (Table 1), which is explained by the distance of As—O bonds being greater than that of P—O.

3.2. Infrared Spectroscopy

The IR absorption spectrum of the studied Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ material is shown in Figure 2. The spectrum shows the presence of the series of distinct bands attributed to asymmetric and symmetrical valence vibrations of the P-O-P and As-O-As bridges. These bands are characteristic of the pyrophosphate (P$_2$O$_7$)$^{4-}$ and diarsenate (As$_2$O$_7$)$^{4-}$ groups (Table 6) [30] and similar to those of the Li$_2$CuP$_2$O$_7$ spectrum [31].
Figure 2. FT-IR spectrum (1300–500 cm\(^{-1}\)) of Na\(_2\)CuP\(_{1.5}\)As\(_{0.5}\)O\(_7\).

Table 6. Proposed assignment of the vibration bands of Na\(_2\)CuP\(_{1.5}\)As\(_{0.5}\)O\(_7\).

| Attribution | Wave Number (cm\(^{-1}\)) |
|-------------|---------------------------|
| \(\nu_{as} (PO_3)\) | 1188                      |
| \(\nu_{as} (PO_3)\) | 1164                      |
| \(\nu_{as} (AsO_3)\) | 1100                      |
| \(\nu_s (PO_3)\) | 1064                      |
| \(\nu_s (PO_3)\) | 1025                      |
| \(\nu_s (AsO_3)\) | 994                       |
| \(\nu_{as} (POP)\) Stretching Vibrations | 901                      |
| \(\nu_{as} (AsOAs)\) Stretching Vibrations | 841                      |
| \(\nu_s (POP)\) Stretching Vibrations | 814                      |
| \(\delta_{as} (PO_3)\) Deformation Modes | 694                      |
| \(\delta_s (PO_3)\) Deformation Modes | 653                      |

3.3. DSC Thermal Analysis

In order to determine the thermal stability of the studied compound, the DSC analysis was used in the range from room temperature to 750 °C. The analysis result is illustrated in Figure 3. An endothermic peak was observed at 688 °C. This peak corresponds to the melting point of our compound. While, an exothermal peak is shown at 743 °C, after the fusion, probably corresponds to the oxidation of fractions of Cu\(^{2+}\) to Cu\(^{3+}\) in the obtained liquid phase. Overall, the thermal analysis
via DSC shows that Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ material is stable up to a temperature of 674 °C. The sharpness of the endothermic peak in the DSC analysis suggests good crystallinity of our synthesized powder.

![DSC curve of Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$](image)

**Figure 3.** DSC curve of the Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ compound.

Here we can also compare the thermal stability of Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ to that of the recently studied Co analog Na$_2$CoP$_{1.5}$As$_{0.5}$O$_7$. The Cu material is stable from room temperature to the melting temperature, which is around 688 °C. In contrast, the Na$_2$CoP$_{1.5}$As$_{0.5}$O$_7$ material undergoes a phase transition at a temperature of 675 °C before melting at ~700 °C. This shows that the Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ material is more stable than the Na$_2$CoP$_{1.5}$As$_{0.5}$O$_7$ material [15].

### 3.4. SEM Microstructure and EDX Analysis of Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$

Energy-dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM) analysis were used to confirm the chemical composition and examine polycrystalline morphology, respectively (Figure 4). The EDX analysis of the polycrystalline powder revealed the presence of the expected elements, i.e., sodium, copper, phosphorus, arsenic, and oxygen. The micrograph on SEM of the sample shows agglomeration of uniform parallelepiped crystallites. The mapping elemental analysis of Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ confirmed the uniform distribution of the constituent elements (Figure 5).

![EDX analysis and SEM micrograph of Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$](image)

**Figure 4.** (a) EDX analysis and (b) SEM micrograph of the Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ sample.
3.5. Crystal Structure Description

The structural unit of Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ is presented in Figure 6. It contains two P$_2$O$_7$ units connected by a vertex with two CuO$_4$ of square planar geometry. The charge neutrality of the structural unit is ensured by four sodium ions (Na$^+$).
The Cu$_2$P$_4$O$_{15}$ groups of the structural unit are bound by oxygen peaks to result in infinite chains and are wavy saw-toothed along the [001] direction (Figure 7). The Na$^+$ ions are located in the inter-chain space.

Other projections of the structure of Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ according to the [100] and [001] directions are shown in Figure 8.
The true capacitance was calculated from the pseudo-capacitance according to the following relationships:

\[ C = \frac{1}{\omega_0 (RA)^{1/p}} = \frac{1}{\omega_0 (RC)^{1}} \]

(3)

Figure 8. Projections of the Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ structure along the (a) [100] and (b) [001] directions.

The structure of our material differs from that of the allotropic form $\alpha$-Na$_2$CuP$_2$O$_7$ [17], which has a two-dimensional anionic framework formed by the connection of vertices of PO$_4$ tetrahedra, and CuO$_5$ polyhedra.

Compared to the sodium cobalt diphosphate-diarsenate Na$_2$CoP$_{1.5}$As$_{0.5}$O$_7$ investigated recently by Marzouki et al. [15], we notice that despite a similar composition, Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ crystallizes in a different structure type. Indeed, the cobalt material crystallizes in the tetragonal system of the P4$_2$/mm space group with the unit cell parameters $a = 7.764(3)$ Å, $c = 10.385(3)$ Å. In contrast, the studied material Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$, crystallizes in the monoclinic system of the C2/c space group with the unit cell parameters $a = 14.798(2)$ Å, $b = 5.729(3)$ Å, $c = 8.075(2)$ Å; $\beta = 115.00(3)^\circ$. The difference is undoubtedly determined by the preference of the Jahn–Teller active $d^9$ Cu$^{2+}$ to adopt square coordination (Figure 6).

3.6. Electrical Properties: Effect of P/As Doping

The prepared pellet of the Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ compound was sintered at 550 °C for 2 h with a 5 °C/min heating and cooling rate. The relative density of the obtained pellet is $D = 88\%$. The thickness and surface of the pellet are $e = 0.36$ cm and $S = 0.454$ cm$^2$, respectively. The electrical measurements of the obtained sample were carried out using complex impedance spectroscopy in the temperature range of 260–380 °C. The recorded spectra are shown in Figure 9.

The best fits of impedance spectra were obtained when using a conventional electrical circuit $R_g$/CPE$^g$-$R_{gb}$/CPE$^{gb}$, where CPE are constant phase elements (Figure 9a) and subscripts g and gb indicate bulk grain and grain boundary contribution, respectively:

\[ ZCPE = \frac{1}{A(\omega)^p} \]

(2)
Figure 9. Impedance spectra of Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ recorded in a temperature range of 240–360 °C in air. The refined calculated model is shown in (a) the Nyquist and (b) Bode planes.

The electrical parameter values calculated at different temperatures are shown in Table 4. The values of the capacities $C_{gk}$ and $C_{gbk}$ are approximately $10^{-11}$ and $10^{-10}$ Fcm$^{-1}$ for the bulk and grain boundaries, respectively [15]. In fact, with a relative density of $D = 88\%$, the conductivity of the prepared sample (Table 7) increases from $0.35 \times 10^{-5}$ Scm$^{-1}$ at 260 °C to $3.13 \times 10^{-5}$ Scm$^{-1}$ at 380 °C. On the other hand, the 12% porosity of our sample prompted us to estimate the conductivity values of the fully dense sample of Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ using the empirical formula proposed by Langlois and Coeuret [32]:

$$\sigma = \frac{1 - P}{4} \sigma_d$$  \hspace{1cm} (4)

where $\sigma$ and $\sigma_d$ are the electrical conductivity of porous and dense samples, respectively. $P$ is the porosity of the sample.
Table 7. Electrical parameters values of equivalent circuits of Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ determined by impedance spectroscopy at 260–380 °C.

| T (°C) | T (K) | $R_g$ ($10^4$ Ω) | $A_g$ ($10^{-10}$ F s$^{-1}$) | $C_{g,k}$ ($10^{-11}$ F cm$^{-1}$) | $R_{gb}$ ($10^4$ Ω) | $A_{gb}$ ($10^{-10}$ F s$^{-1}$) | $C_{gb,k}$ ($10^{-10}$ F cm$^{-1}$) | Rt ($10^4$ Ω) | $\rho_t$ ($10^4$ Ω cm) | $\sigma$ ($10^{-5}$ S cm$^{-1}$) | $\sigma_d$ ($10^{-5}$ S cm$^{-1}$) |
|--------|-------|------------------|-------------------------------|----------------------------------|-------------------|-------------------------------|----------------------------------|-------------|----------------|---------------------|-------------------|
| 260    | 533   | 5.54             | 2.1                           | 2.0                              | 17.04             | 1.7                           | 1.7                              | 22.58       | 28.58          | 0.35                | 1.59              |
| 290    | 563   | 2.70             | 3.4                           | 3.3                              | 7.82              | 1.8                           | 1.70                             | 10.52       | 13.32          | 0.75                | 3.41              |
| 320    | 593   | 1.43             | 3.4                           | 3.3                              | 4.18              | 1.5                           | 1.5                              | 5.61        | 7.10           | 1.41                | 6.41              |
| 350    | 623   | 1.21             | 3.4                           | 3.3                              | 2.26              | 1.4                           | 1.3                              | 3.47        | 4.39           | 2.28                | 10.36             |
| 380    | 653   | 1.01             | 8.4                           | 8.0                              | 1.51              | 1.2                           | 1.2                              | 2.52        | 3.19           | 3.13                | 14.23             |
This correction has been used in previous works such as Na$_2$CoP$_{1.5}$As$_{0.5}$O$_7$ [15]. Taking into account the porosity factor $P = 0.12$, the conductivity value of dense material will be $\sigma_d = (4\sigma/0.88)$. The conductivity values of dense sample calculated at different temperatures are summarized in Table 7. In this case, the experimental conductivity of $3.5 \times 10^{-6}$ S cm$^{-1}$ corresponds to the corrected value of $1.59 \times 10^{-5}$ S cm$^{-1}$ at 260 °C.

The curve $\ln (\sigma \times T) = f (1000/T)$ is linear (Figure 10), satisfying the Arrhenius law $\ln \sigma_T = \ln \sigma_0 - Ea/kT$ ($k$ = Boltzmann constant). The activation energy calculated from the slope of this curve is $Ea = 0.60$ eV.

![Linear fit](image)

**Figure 10.** Arrhenius plot of the conductivity of the Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ sample.

The electrical investigation of the studied material shows that the activation energy, which is unaffected by porosity and thus easier to use for comparison, decreases for Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ compared to that of Na$_2$CuP$_2$O$_7$ [33], i.e., 0.60 eV and 0.89 eV, respectively. Consequently, the effect of P/As substitution increases the electrical conductivity of the parent material Na$_2$CuP$_2$O$_7$ at lower temperatures [33]. Overall, a comparison of the conductivity values of the studied material Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ (at $T = 350$ °C, $\sigma_D = 88\% = 2.28 \times 10^{-5}$ S cm$^{-1}$; $\sigma_d = 2.28 \times 10^{-4}$ S cm$^{-1}$ and $Ea = 0.60$ eV) with those found in the literature shows that our material can be classified among the fast ionic conductors as shown in Table 8.

**Table 8.** Activation energies of ionic conductivity for some sodium-ion materials.

| Material                          | Activation Energy (eV) | Temperature Range (°C) | Ref.           |
|----------------------------------|------------------------|------------------------|----------------|
| Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$  | 0.60                   | 260–380                | current work   |
| Na$_2$CoP$_{1.5}$As$_{0.5}$O$_7$  | 0.56                   | 240–360                | [15]           |
| Na$_{1.14}$K$_{0.86}$CoP$_2$O$_7$| 1.34                   | 360–480                | [24]           |
| Na$_{2.84}$Ag$_{1.16}$Co$_2$(P$_2$O$_7$)$_2$ | 1.36               | 510–630                | [34]           |
| NaCo$_2$As$_3$O$_{10}$           | 0.48                   | 160–410                | [35]           |
| Na$_4$Co$_{0.63}$Al$_{0.91}$(AsO$_4$)$_6$ | 0.56              | 400–550                | [36]           |
| Na$_2$Co$_2$(MoO$_4$)$_3$        | 1.20                   | 180–513                | [37]           |
3.7. BVSE Simulation: Na$^+$ Migration Pathways in Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$

The BVSE calculation revealed in addition to the equilibrium site Na1, the presence of two interstitials sites (i1 to i2) and ten saddle points (s1 to s10) (Table 9). Thus, there are ten local pathways as shown in Table 10. Figure 11 shows the position of equilibrium sites and interstitial sites in the unit cell.

Table 9. Bond-valence sites energies and positions of equilibrium site (Na1), interstitial sites (i1 and i2) and saddle points (s1 to s10).

| Site | x     | y     | z     | Energy (eV) |
|------|-------|-------|-------|-------------|
| Na1  | 0.185 | 0.611 | 0.701 | 0.000       |
| i1   | 0.524 | 0.875 | 0.424 | 0.288       |
| i2   | 0.262 | 0.194 | 0.986 | 0.715       |
| s1   | 0.560 | 0.125 | 0.632 | 0.354       |
| s2   | 0.226 | 0.083 | 0.215 | 0.466       |
| s3   | 0.006 | 0.389 | 0.250 | 0.550       |
| s4   | 0.125 | 0.528 | 0.069 | 0.602       |
| s5   | 0.250 | 0.250 | 0.000 | 0.749       |
| s6   | 0.173 | 0.431 | 0.958 | 0.870       |
| s7   | 0.714 | 0.208 | 0.583 | 0.960       |
| s8   | 0.821 | 0.708 | 0.375 | 1.260       |
| s9   | 0.190 | 0.333 | 0.653 | 1.289       |
| s10  | 0.167 | 0.361 | 0.833 | 1.643       |

Figure 11. Unit cell of the title compound showing the position of the equilibrium site Na1 and the interstitial sites (i1 and i2).

Table 10. Local transport pathways in the anionic framework, energetic barrier (eV) and hop distance (Å).

| Local Path | Site 1 | Saddle | Site 2 | Barrier (eV) | Hop Distance (Å) |
|------------|-------|--------|-------|-------------|------------------|
| 1          | i1    | s1     | Na1   | 0.354       | 1.904            |
| 2          | Na1   | s2     | Na1   | 0.466       | 3.119            |
| 3          | i1    | s3     | i1    | 0.261       | 4.145            |
| 4          | i1    | s4     | Na1   | 0.602       | 2.593            |
| 5          | i2    | s5     | i2    | 0.033       | 0.955            |
| 6          | i2    | s6     | i1    | 0.582       | 2.922            |
Figure 11 shows that the migration along the $b$ direction does not involve any interstitial sites, and the diffusion occurs from the equilibrium site Na1 to its symmetry image, with a jump distance of approximately 3.119 Å and with an activation energy of approximately 0.466 eV (Figure 12a).

Along the $c$ direction, Figure 11 shows that the sodium moves from the Na1 position to the interstitial sites i2 then to i1 to reach the equivalent Na1 site (Figure 12b) with an activation energy along this direction of approximately 0.96 eV (Figure 12b).

### Table 10. Cont.

| Local Path | Site 1 | Saddle | Site 2 | Barrier (eV) | Hop Distance (Å) |
|------------|--------|--------|--------|-------------|------------------|
| 7          | i2     | s7     | Na1    | 0.960       | 3.282            |
| 8          | i1     | s8     | Na1    | 1.260       | 3.168            |
| 9          | Na1    | s9     | i1     | 1.289       | 3.168            |
| 10         | i2     | s10    | i1     | 1.355       | 3.956            |
Consequently, based on the BVSE calculations, the fast ionic conductivity observed for the material can be explained by the three-dimensional mobility of Na$^+$ ions in the inter-ribbon space, likely with more favorable diffusion along the b-axis.

4. Conclusions

A new quaternary oxide Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ was identified in the Na$_2$O-CuO-P$_2$O$_5$-As$_2$O$_5$ system. It crystallizes in the monoclinic C2/c space group and is isostructural to β-Na$_2$CuP$_2$O$_7$. The partial substitution of P appears to be beneficial for ionic conductivity as the material exhibits lower activation energy of 0.6 eV vs. 0.89 eV for the parent β-Na$_2$CuP$_2$O$_7$. According to the impedance spectroscopy performed on the 88% dense pellet, the bulk ionic conductivity reaches the value of 2.28 $10^{-5}$ Scm$^{-1}$, which allows Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ to classify as a fast ion conductor. The bond-valence site energy

**Figure 12.** Variation of energy as a function of the reaction coordinate along the (a) $b$-direction, (b) $c$-direction and (c) $a$-direction.

Along the $a$ direction, the sodium atoms pass through the following sites: Na1-i1-i1-Na1-i2. The activation energy along this direction is approximately 0.96 eV (Figure 12c). Thus, the activation energy of the title compound for 1D and 3D ionic conductivity is approximately 0.466 eV and 0.96 eV, respectively. Figure 13 shows the isosurfaces of conduction pathways.

**Figure 13.** Isosurfaces of conduction showing the polyhedral of coordination and the 3D ionic conductivity pathways transport of sodium in Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$. 

A new quaternary oxide Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ was identified in the Na$_2$O-CuO-P$_2$O$_5$-As$_2$O$_5$ system. It crystallizes in the monoclinic C2/c space group and is isostructural to β-Na$_2$CuP$_2$O$_7$. According to the impedance spectroscopy performed on the 88% dense pellet, the bulk ionic conductivity reaches the value of 2.28 $10^{-5}$ Scm$^{-1}$, which allows Na$_2$CuP$_{1.5}$As$_{0.5}$O$_7$ to classify as a fast ion conductor. The bond-valence site energy.
calculations suggest that the Na\(^+\) diffusion is three-dimensional with some preference for transport along the \(b\) axis.

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