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Electrical properties and alkali-pathways simulation of new mixed conductor Na$_{4}$Li$_{0.62}$Co$_{5.67}$Al$_{0.71}$(AsO$_4$)$_6$

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Abstract

Polycrystalline sodium lithium-cobalt-aluminum arsenate, Na$_{4}$Li$_{0.62}$Co$_{5.67}$Al$_{0.71}$(AsO$_4$)$_6$, was synthesized by solid state reaction route and characterized by infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The title material is a member of $\beta$-Xenophyllite family which show 3D anionic framework with interconnecting tunnels where alkali-ion are located. Dense ceramic with relative density of 97% is obtained after planetary grinding of the synthesized powder followed by optimal sintering at 1113 K. The effect of grinding on microstructure of sample is controlled by Scanning Electron Microscope (SEM). The electrical study using impedance spectroscopy, in the 443–773 K temperature interval, show interesting electrical performance of the dense ceramic: $\sigma_{333K} = \text{1.41} \times \text{10}^{-7}$ Scm$^{-1}$ and the activation energy $E_a = \text{0.449}$ eV. The alkali migration pathways in the anionic framework were simulated using Bond Valence Site Energy (BVSE) model to correlate structure with electrical properties of the studied material. The calculation results were compared to other $\beta$-Xenophyllite materials.

1. Introduction

Extensive search have focused on developing new materials or modifying existing ones by substitution or doping to study their properties. Phosphates and arsenates of monovalent metals and transitions consider a promising field for various applications [1–8]. Essentially, the introduction of monovalent ions in phosphates and arsenates can lead to materials with interesting properties, in particular ionic conduction [9].

According to this approach, mixed phosphates and arsenates of cobalt and alkali metals are studied. These materials have a remarkable structural richness: olivine structure [10–12], zeolitic structure [13], alluaudite structure [14], melilite structure [11, 15, 16], etc. In relation to their structures, these materials have several physico-chemical properties: ionic conduction [16], ion exchange [9, 11], etc. Xenophyllite, Na$_4$Fe$_6$(PO$_4$)$_6$, is a rare mineral phosphate adopting a structure with hexagonal tunnels in which sodium ions are located. It is recently tested as anode material for sodium batteries [17].

Other arsenate materials belonging to the same structural type have been synthesized [18–24]. Especially, LiCoAsO$_4$ arsenate with olivine structure [25] shows interesting electrochemical properties. Where, Li-ions was reversibly deinserted/inserted from/into material at average voltages of 4.8 and 4.6 V respectively. In addition, the delithiated material maintaining the olivine structural framework.

The electrical measurements of cobalt arsenate compounds show interesting electrical performance such as Ag$_8$Co$_7$(AsO$_4$)$_6$, Na$_4$Co$_5$Al$_2$(AsO$_4$)$_6$, and Na$_4$Co$_7$(AsO$_4$)$_6$ which are classified as fast electrical conductors [18–20].

In this context, this paper is dedicated to the synthesis of the Na$_4$Li$_{0.62}$Co$_{5.67}$Al$_{0.71}$(AsO$_4$)$_6$ material as polycrystalline powder then as dense ceramic. Qualitative and quantitative analyzes were carried out to confirm the composition and purity of the studied material: x-ray Diffraction, FT-IR, SEM, EDX and ICP-MS. The
electrical properties were investigated using impedance spectroscopy. The BVSE simulation of the alkali-ions in the anionic framework of Na₄Li₀.₆₂Co₅.₆₇Alₐ₇Na₆ are carried out in order to correlate structure with electrical properties and to compare results to other isostructural arsenates: Na₄Co₄(CO₁.₆₃Al₀.₉₁)(AsO₄)₆ and Na₄Co₇(AsO₄)₆.

2. Experimental and computational methods

2.1. Synthesis
The title material was synthesized by solid-state reaction method at atmospheric air and pressure. A mixture of Na₂CO₃ (Sigma-Aldrich, ≥99.5%); Li₂CO₃ (Sigma-Aldrich, ≥99.0%), (Co(CH₃COO)₂.4H₂O (Merck, 99.9%); Al₂O₃ (Sigma-Aldrich, 99.0%), As₂O₃ (Merck, 99%) is finely ground in an agate mortar in molar proportions Na: Li: Co: Al: As = 4: 0.62 : 5.67 : 6. First, the mixture placed in platinum crucible has been heated at 673 K for 24 h to ensure evaporation of acetate; carbonate and water. After cooling followed by a second grinding, the residue was heated at 1043 K for 3 days. The mixture was cooled slowly to room temperature. Pink polycrystalline powder was obtained.

2.2. Characterizations of Na₄Li₀.₆₂Co₅.₆₇Alₐ₇Na₆
The Fourier-Transform Infrared (FT-IR) spectrum of the Na₄Li₀.₆₂Co₅.₆₇Alₐ₇Na₆ material was recorded using Bruker FT-IR IFS 66 spectrophotometer over the range 500–1200 cm⁻¹, at room temperature. KBr was added to the sample and shaped as cylindrical pellet.
X-Ray Diffraction pattern of the polycrystalline powder was recorded at room temperature in the 2θ = [5°–80°] with step of 0.02° using Bruker D8 diffractometer operating with Cu anticathode Kα (λ = 1.5406 Å) equipped by secondary monochromator.
A qualitative energy dispersive x-ray (EDX) spectroscopy analysis was used to identify the elements present in the polycrystalline sample. The EDX analysis was performed using a JSM 6301 microscope.
The morphologies of the crystalline powder and pellets were controlled using Scanning Electron Microscopy SEM JEOL 6340.
The Na, Li, Co, Al, As elements of the synthesized powder were quantified using Inductively Coupled Plasma Mass Spectrometry (ICP-MS; Perkin Elmer model) operate NexION-300X software. The duration of acquisition is 1000 ms. A Helium collision cell was used to eradicate polyatomic interferences.
Impedance spectroscopic measurements were performed via 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 measurements were preceded by a pretreatment of the sample in order to reduce the mean particle size of the synthesized powder. In fact, mechanical grinding during 100 min was carried out using FRISCH planetary micromill pulverisette 7. The polycrystalline sample is shaped as cylindrical pellet using uniaxial press. The pellet was sintered in air at an optimal temperature of 1113 K for 2 h with 5 K min⁻¹ heating and cooling rates. The geometric factor of the dense ceramic is g = e/S = 0.812 cm⁻³ where e and S are the thickness and surface of pellet, respectively. After the control of the microstructure and determining the density of the pellet, the last step before beginning the electrical measurements is the metallization. To ensure good contact between the two faces of the pellet and the two measurement electrodes, a gold metal layer was deposited using a SC7620 Mini Sputter Coater. The faces of the pellet were previously coated with a metallic layer of gold (about 36 nm). The sample was placed between two platinum electrodes. These are connected by platinum cables (to ensure good electrical contact) to the frequency response analyzer (HP 4192 A) controlled by a microcomputer.
The Bond Valence Site Energy (BVSE) model [26, 27] has been used to simulate the alkali migration in the 3D anionic framework. In fact, the BVSE model is the current expansion of BVS model developed by Pauling (1929) [28] to describe the formation of inorganic materials. The BVSE model was improved by Brown & Altermatt 1985 [29] followed by Adams 2001 [30], ensuing in the expression (1) for an:

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

\(s_{A-X}\): individual bond-valence; \(R_{A-X}\): distance between counter-ions A and X; \(R_0\) and \(b\): fitted constants, \(R_0\): the length of a bond of unit valence.
Since 1999, the BVS model was used in the of cation motion simulation in the anionic framework by following the valence unit as a function of migration distance [31]. In 2011, The valence units was related to potential energy scale and electrostatic interactions treated by Adams [26, 27]. The BVSE was used with success to simulate the transport pathways of monovalent cations (Na⁺; K⁺ and Ag⁺) in NaCo₂As₃O₁₀ [32].
3. Results and discussion

3.1. Infrared spectroscopy
The IR spectrum of the title compound, recorded in the domain where are situated the principal vibrations, is shown in figure 1. The assignment of different vibrational bands of \( MO_4 \), AsO_4 and \( M'O_6 \) groups (\( M = \text{Co/Li}; M' = \text{Co/Co/Al} \)) based on previous work \[36–38\], is shown in table 1.

| Wave number (cm\(^{-1}\)) | Assignment  |
|---------------------------|-------------|
| 887 \( \nu_3 \) (AsO\(_4\)) | Na\(_4\)Co\(_{5.67}\)Al\(_{0.71}\)(AsO\(_4\))\(_6\) |
| 802–777 \( \nu_3 \) (M'\(O_4\)) | Na\(_4\)Li\(_{0.62}\)Co\(_{5.67}\)Al\(_{0.71}\)(AsO\(_4\))\(_6\) |
| 675 \( \nu_1 \) (M'O\(_6\)) | Na\(_4\)Co\(_{5.67}\)Al\(_{0.71}\)(AsO\(_4\))\(_6\) |
| 607 \( \nu_1 \) (M'O\(_6\)) | Na\(_4\)Co\(_{5.67}\)Al\(_{0.71}\)(AsO\(_4\))\(_6\) |
| 503–532 \( \nu_2 \) (M'O\(_6\)) | Na\(_4\)Co\(_{5.67}\)Al\(_{0.71}\)(AsO\(_4\))\(_6\) |
| 471 \( \nu_4 \) (AsO\(_4\)) | Na\(_4\)Co\(_{5.67}\)Al\(_{0.71}\)(AsO\(_4\))\(_6\) |
| 411 \( \nu_4 \) (M'O\(_6\)) | Na\(_4\)Co\(_{5.67}\)Al\(_{0.71}\)(AsO\(_4\))\(_6\) |

4. X-ray diffraction and structural characteristic of Na\(_4\)Li\(_{0.62}\)Co\(_{5.67}\)Al\(_{0.71}\)(AsO\(_4\))\(_6\)
X-ray diffraction (XRD) pattern of the studied material recorded in the 10°–70° range with step of about 0.02°, at room temperature is illustrated in figure 2. The powder diffraction pattern is indexed using dicvol software (Boultif & Louer, 2004) \[39\]. The Rietveld method has been used to verify the purity of the powder using the crystallographic data previous work \[22\] operate JANA2006 software (Petricek, Eigner, Dusek, & Cejchan, 2016). The final agreement factors are \( R_p = 0.049 \), \( Rwp = 0.065 \), and \( GOF = 1.16 \). No additional peaks have been detected. The final Rietveld plot is presented in figure 2.

The structural study conducted in our previous work previously showed us that the prepared material Na\(_4\)Li\(_{0.62}\)Co\(_{5.67}\)Al\(_{0.71}\)(AsO\(_4\))\(_6\) has characteristics favorable to the mobility of the alkali-ions such as: cations located in tunnels with large sections, partial occupations of cationic sites, the relatively high thermal agitation of these ions (figure 3). Therefore, it is interesting to carry out a electrical study of the titled maerial.
3.3. Morphology and microstructure control by SEM and EDX analysis

The SEM micrograph of the synthesized powder is shown in figure 2(a). It confirms the good crystallinity of the prepared powder. The mean grain size is about 5 μm. As for the chemical composition, the EDX analysis on SEM confirmed the presence of sodium, cobalt, aluminum, arsenic and oxygen elements (figure 4(a)). We note that the lithium element does not appear in the EDX spectrum. In this case a quantitative analysis can confirm the material composition like the ICP-MS technique.

After the synthesis of the crystalline powder, and before starting the electrical measurements, the powder has undergone a planetary milling treatment with a duration of 100 min and a sintering at suitable temperature, the relative density of the ceramic increases by 83% to 97%. The maximum densities obtained were reached for a total grinding time of 100 min. There is no more remarkable variation after two other grinding sequences of 10 min. The sample densification was controlled by SEM micrographs. Figures 4(b) and (c) show sintered pellet before and after mechanical grinding, respectively. In fact, we move from a relatively porous material (figure 4(b)) to a dense ceramic (figure 4(c)).

3.4. Quantitative analysis using ICP-MS

After polycrystalline powder preparation and XRD characterization (figure 1), the sample was analyzed by inductively coupled plasma mass spectrometry ICP-MS in order to approve the adopted chemical composition. The measured mass and the mass percentage values of the Na, Li, Co, Al, As elements contents in 0.50000 g of the powder are grouped in table 2. The ICP-MS analysis approves the element contents of the Na₄Li₀.₆₂Co₅.₆₇Al₀.₇₁(AsO₄)₆ formula. In fact, the weight percentages of the Na, Li, Co, Al and As elements are 7.167%; 0.335%; 26.042% 1.493% and 35.035%, respectively. The weight and the weight percentage of the oxygen can be deduced as being the remainder of...
0.5000 g of mass and the remaining mass percentage of 100%. The deduced oxygen weight and the percentage weight are 149634.7089 (±0.0007) mg and 29.928 % (±0.001%), respectively. Consequently, the quantitative analysis by ICP-MS confirmed that the composition of the material is exactly that of the initial fraction of the starting reactants described in the experimental section Na: Li: Co: Al: As = 4: 0.62 : 5.67 : 6 (ie the nominal formula Na₂₄Li₆Co₆.6₅Al₆.7₁(AsO₄)₆).

### Table 2. Measured mass and percentage mass values of elements on 0.50000 g powder of Na₄Li₀.₆₂Co₅₆₇₇₁(AsO₄)₆.

| Element | Measured weight (μg) | Weight percentage (%) (±0.001) |
|---------|----------------------|-------------------------------|
| Na      | 35835.3791 (±0.0003) | 7.167                         |
| Li      | 1676.9925 (±0.0003)  | 0.335                         |
| Co      | 130211.2843 (±0.0005)| 26.042                        |
| Al      | 7465.2176 (±0.0007)  | 1.493                         |
| As      | 175176.4176 (±0.0006)| 35.035                        |
| total   | 350365.2911 (±0.0007)| 70.072                        |

sample weight = 0.50000 g; M_w of Na₂₄Li₆Co₆.₆₂₇₁(AsO₄)₆ = 1283.07664 g mol⁻¹.

3.5. Electrical properties

The electrical properties of the Na₄Li₀.₆₂Co₅₆₇₁Al₆.₇₁(AsO₄)₆ sample were determined via complex impedance spectroscopy technique. The electrical measurements were carried out in the frequency range 5Hz–13 MHz. The

Figure 4. EDX spectrum and SEM micrographs of (a) polycrystalline powder (b) sintered pellet before grinding (c) sintered pellet after grinding of Na₄Li₆Co₅₆₇₁(AsO₄)₆.
normalized impedance spectra recorded on Na$_4$Li$_{0.62}$Co$_{5.67}$Al$_{0.71}$(AsO$_4$)$_6$ ceramic at 160 °C–445 °C are showed in figure 5.

Z-View software [40] was used to simulate the Nyquist plots which fitted as an equivalent circuit consisting of R/CPE. R is the resistance while CPE presents an empirical impedance function described in equation (2).

$$Z(\omega)_{\text{CPE}} = \frac{1}{C(j\omega)^p}; \quad (-1 \leq p \leq 1)$$  

C: true capacitance; $\omega$: frequency; p: parameter ($-1 \leq p \leq 1$)
The electrical parameters values achieved from the equivalent circuit in the temperature range 160–445 °C are summarized in Table 3. Where, the resistivity \( \rho = \frac{R}{k} \) is extracted from the refinement of each contribution which the geometric factor of the cylindrical pellet \( g( cm^{-1}) = \frac{e}{S}(e = \text{ thickness}; S = \text{ surface}) \).

The conductivity increases from \( 0.14 \times 10^{-4} \text{ S cm}^{-1} \) at 160 °C to \( 9.78 \times 10^{-4} \text{ S cm}^{-1} \) at 445 °C (Table 3). Although, the absolute conductivity value of the Al/Li-substituted title material at 320 °C (\( \sigma = 2.64 \times 10^{-4} \text{ S cm}^{-1} \)) is greater

![Figure 7. Projection in ab plane of unit cells of (a) Na\textsubscript{4}Co\textsubscript{4}(Co\textsubscript{1.63}Al\textsubscript{0.91})(AsO\textsubscript{4})\textsubscript{6}; (b) Na\textsubscript{4}Co\textsubscript{7}(AsO\textsubscript{4})\textsubscript{6}, and (c) Na\textsubscript{4}Li\textsubscript{0.62}Co\textsubscript{5.67}Al\textsubscript{0.71}(AsO\textsubscript{4})\textsubscript{6} showing the 1D infinite pathways of migration of Na\textsuperscript{+} ions along [100] direction with coordination polyhedra and without coordination polyhedra.](figure7.png)
The activation energy are 0.583 eV; 0.786 eV and 0.611 eV for Na₄Co₅.6₃Al₀.9₁
using the 3DBVSMAPPER computer program.

Compared to previous works, the activation energy of the studied material is lower than that of Na₄Co₇
that of Na₄Co₇
direction with diamond bases form show smaller section dimensions than the tunnels along
the isostructural materials Na₄Co₇
The BVSE simulation model was used to de
3.6. Alkali transport pathways simulation
The BVSE simulation model was used to define the alkali-ion transport pathways in the anionic frameworks of
the isostructural materials Na₄Co₇(AsO₄)₆ [20]; Na₄Co₅.6₃Al₀.9₁(AsO₄)₆ [26] and Na₄Li₀.6₂Co₅.6₇Al₀.7₁(AsO₄)₆ using the 3DBVSMAPPER computer program.

Investigation of isosurfaces connecting sodium ion sites in the unit cells of isostructural materials show that
the sodium can move along the [100] direction and form 1D infinite pathways (figure 7) while the calculated
activation energy are 0.583 eV; 0.786 eV and 0.611 eV for Na₄Co₅.6₃Al₀.9₁(AsO₄)₆; Na₄Co₇(AsO₄)₆ and
Na₄Li₀.6₂Co₅.6₇Al₀.7₁(AsO₄)₆, suggest fast ionic conductivity of this type of materials.

The BVS analyses are in agreement with the suggestions deduced from the structural studies [20, 26]: the
most likely conduction pathways of the monoarsenates are in the [100] direction which is the direction of the
tunnels. The dimensions of the hexagonal sections of tunnels along [100] direction of the three compounds are
shown in figure 8(a). These canals are delimited by two CoO₆ octahedra, two MO₆ or CoO₆ octahedra and two
AsO₄ tetrahedra. These sections are the largest and therefore more favorable to the movement of sodium cations.
The b direction appears less conducive than [100] direction. In fact, the windows (figure 8(b)) according to [010]
direction with diamond bases form show smaller section dimensions than the tunnels along [100] direction;
which explains that the migration of the sodium ions are favorable according to the direction [100].

On the other hand, the crystallographic studies [20, 25] show that the substitution of cobalt by aluminum
allows to increase the unit cell parameters and the dimensions of the tunnel sections. In fact, the volume of the
unit cell of Na₄Co₇(AsO₄)₆ is V = 1019.65(16) Å³ which is lower than those of Na₄Co₅.6₃Al₀.9₁(AsO₄)₆
(V = 1033.2(6) Å³) and Na₄Li₀.6₂Co₅.6₇Al₀.7₁(AsO₄)₆ (V = 1033.3(2) Å³); this may explain that the activation
energy values of aluminum materials, Na₄Co₅.6₃Al₀.9₁(AsO₄)₆ and Na₄Li₀.6₂Co₅.6₇Al₀.7₁(AsO₄)₆, are lower than that of Na₄Co₇(AsO₄)₆. In fact, sections tunnels along a direction in Na₄Co₅.6₃Al₀.9₁(AsO₄)₆ and
Na₄Li₀.6₂Co₅.6₇Al₀.7₁(AsO₄)₆ arsenates are of the same order: 4.463–4.819 Å and 4.463–4.818 Å, respectively.
The tunnel sections along a direction in Na₄Co₇(AsO₄)₆ are the lowest: 4.636–4.730 Å.
The conduction pathways simulation shown that the Li/Al-sub Na₄Li₀.₆₂Co₅.₆₇Al₀.₇₁(AsO₄)₆ and the Al-sub Na₄Co₅.₆₃Al₀.₉₁(AsO₄)₆ materials have electrical performances more interesting than the parent material Na₄Co₇(AsO₄)₆. In fact, the substituted materials have activation energies lower than that of Na₄Co₇(AsO₄)₆. However, the activation energy of the studied material is relatively higher than that of Na₄Co₅.₆₃Al₀.₉₁(AsO₄)₆. While, electrical measurements have shown that the studied material is more conductive than Al-sub material. This can be explained by the fact that the BVSE model does not take into account the electronic conductivity which may be due to the presence of several degrees of oxidation in the same crystallographic site. Indeed, in the studied material, in addition to site occupied by Co²⁺ and Al³⁺, another site is occupied by both cobalt and lithium ions Co²⁺/Li¹⁺. This double oxidation in the same site can create an electronic conductivity that will increase the value of the total conductivity: ionic and electronic.

4. Conclusion

The title compound, Na₄Li₀.₆₂Co₅.₆₇Al₀.₇₁(AsO₄)₆, has been synthesized as polycrystalline powder by solid-state method. The powder composition has been confirmed by qualitative analysis XRD followed by quantitative analysis, ICP-MS. This structure, isostructural to Na₄Co₅.₆₃Al₀.₉₁(AsO₄)₆ and Na₄Co₇(AsO₄)₆, presents a 3D open anionic framework facilitating one-dimensional Na⁺ ionic conductivity. The substitution of cobalt by aluminum reduces the activation energy of Na conductivity, as determined by impedance spectroscopy and supported by BVSE calculations. Overall, our study suggests that tuning of the Na₄Li₀.₆₂Co₅.₆₇Al₀.₇₁(AsO₄)₆ crystal structure geometry by doping can further improve Na ionic conductivity and thus rate capability of Na₄Co₇(AsO₄)₆ based cathodes.

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