

UNIVERSITÉ DU QUÉBEC À TROIS-RIVIÈRES

SYNTHÈSE ET CARACTÉRISATION DE PHOSPHATES DE MÉTAUX DE TRANSITION
DE TYPE $\text{Na}_{2+2x}\text{Co}_{8-y}\text{M}_z(\text{PO}_4)_6$ COMME COMPOSANTS POUR BATTERIES IONS SODIUM

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COMME EXIGENCE PARTIELLE DU
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**“Tout obstacle renforce la détermination.
Celui qui s’est fixé un but n’en change pas. ”**

Léonard de Vinci

**“L'énergie est ce lien invisible qui relie
tout ; les matériaux nous fournissent la preuve”**

DuongLab

Résumé

Nous présentons dans cette thèse, la synthèse et la caractérisation des nouveaux phosphates de métaux de transition de formule $\text{Na}_{2+2x}\text{Co}_{8-y}\text{M}_z(\text{PO}_4)_6$ pouvant être utilisés comme composants dans les batteries ion sodium.

La première série de ces phosphates de métaux de transition est constituée de nouveaux composés pour $x = 0$, $y = z = 2$ et $M = \text{Mn}, \text{Ni}$, conduisant aux composés $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ et $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ qui ont été synthétisés à l'état solide aux températures respectives 800 et 850 °C pour une durée de 10 h chacun. L'affinement de Rietveld des diagrammes de diffraction des rayons X des poudres de ces composés a confirmé que ces composés sont isostructuraux, cristallisant dans le système monoclinique (groupe d'espace $P2_1/n$). Ces phases sont pures et ne montrent aucune présence de pics de phase secondaire. L'analyse microstructurale a révélé que les particules, dont la taille varie entre 1 et 10 μm , ont une composition homogène. Les résultats de la spectroscopie photoélectronique à rayons X (SPX) ont montré que tous les métaux de transition sont dans un état d'oxydation +2 et que les états d'oxydation de Na, P et O sont respectivement +1, +5 et -2. Les énergies des bandes interdites (E_g) pour $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ et $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ basées sur les spectres de réflectance diffuse UV-vis ont été estimées à 1,78 et 1,86 eV, respectivement. La conductivité ionique totale des deux composés est dans la gamme de $2,29 \times 10^{-5}$ – $1,21 \times 10^{-3}$ S/cm et $2,29 \times 10^{-5}$ – $6,58 \times 10^{-4}$ S/cm de 674 (400 °C) à 874 K (600 °C), respectivement.

La deuxième série de ces composés est $\text{Na}_{2+2x}\text{Co}_{8-y}\text{M}_z(\text{PO}_4)_6$ ($x = 0.5$, $y = 1$, $z = 0$), conduisant à un nouveau matériau polycristallin de formule $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$. Ce composé a été synthétisé à l'état solide (ST) et sol-gel (SG), il a été caractérisé par la diffraction des rayons X sur poudre. Les résultats de l'affinement de Rietveld ont confirmé que ce composé cristallise dans le système

monoclinique avec comme groupe d'espace $P2_1/n$. Les images de microscopie électronique à balayage (MEB) ont montré les particules sous forme d'agrégats avec une taille de grain allant de 8 à 35 μm et de 1 à 20 μm , respectivement pour $\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-ST}$ et $\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-SG}$. La spectroscopie de rayons X à dispersion d'énergie, et la cartographie confirment la présence des éléments Na, Co, P, O et leur distribution homogène dans les échantillons. Les résultats de la spectroscopie photoélectronique à rayons X indiquent que les états d'oxydation de ces éléments sont +1, +2/+3, +5 et -2, respectivement pour le Na, Co, P et O. Les bandes interdites optiques de $\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-ST}$ et $\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-SG}$ ont été estimées à 1,79 eV et 1,78 eV, respectivement, sur la base des spectres de réflectance diffuse UV-vis. La conductivité ionique est de $3,7 \times 10^{-4}$ S/cm à 300 °C et $6,53 \times 10^{-2}$ S/cm à 450 °C pour ces deux composés.

La dernière étude sur $\text{Na}_{2+2x}\text{Co}_{8-y}\text{M}_z(\text{PO}_4)_6$ ($x = 0, y = z = 8$) a conduit au phosphate de sodium tétra manganèse, $\text{NaMn}_4(\text{PO}_4)_3$. Le composé a été préparé à l'état solide à 900 °C pendant 10 h. La phase obtenue a été caractérisée par une analyse de diffraction des rayons X sur poudre (PXRD). Les affinements de Rietveld ont confirmé que l'échantillon cristallin préparé était pur et a une structure hexagonale (groupe d'espace R-3). Aucune phase secondaire n'a été observée. La morphologie de la poudre obtenue a été étudiée par microscopie électronique à balayage (MEB), donnant la taille moyenne des grains d'environ 7 μm . L'analyse élémentaire de la poudre a été réalisée par spectroscopie de rayons X à dispersion d'énergie (EDS), confirmant l'homogénéité de l'échantillon. Les spectroscopies Raman et infrarouge à transformée de Fourier (FTIR) montrent des bandes caractéristiques des liaisons P-O du groupe fonctionnel $(\text{PO}_4)^{3-}$. L'énergie de la bande interdite optique de 1,57 eV a été estimée à partir de la réflectance diffuse en utilisant la fonction de Kubelka-Munk et la relation de Tauc. Les coordonnées chromatiques de l'échantillon indiquent que le $\text{NaMn}_4(\text{PO}_4)_3$ peut être un candidat pour un matériau émetteur bleu-violet. Le

$\text{NaMn}_4(\text{PO}_4)_3$ peut être potentiellement utilisé comme phosphore rouge pour les diodes électroluminescentes blanches. Ses propriétés diélectriques présentent le comportement d'un matériau conducteur ionique. Le tracé de Nyquist montre un seul demi-cercle qui mène à trois circuits RC parallèles, mettant en exergue la présence de grains, les limites de grains et l'interface matériau-électrode où le comportement électrique dominant se produit dans les limites de grains.

Mots-clés: $\text{Na}_2\text{Co}_8(\text{PO}_4)_6$, $\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$, $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$, $\text{Na}_2\text{Co}_{8-x}\text{Mn}_x(\text{PO}_4)_6$, Phosphates, diffraction des rayons X, affinement de Rietveld, bandes interdites optiques, impédance, matériaux semi-conducteurs, état solide, sol-gel, fonction de Kubelka-Munk, relation de Tauc, propriétés diélectriques.

Abstract

In this thesis, we report the synthesis and characterization of several transition metal phosphates of the formula $\text{Na}_{2+2x}\text{Co}_{8-y}\text{M}_z(\text{PO}_4)_6$ that can be used as materials for sodium ion batteries.

The first series consists of new $\text{Na}_{2+2x}\text{Co}_{8-y}\text{M}_z(\text{PO}_4)_6$ compounds ($x = 0$, $y = 2$, $z = 2$ and $M = \text{Mn}$, Ni), leading to the $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ which were synthesized by a solid-state method at 800 and 850 °C for 10 h, respectively. Rietveld refinement of the X-ray powder diffraction patterns confirmed that both compounds are isostructural, crystallizing in a pure phase in the monoclinic system with $P2_1/n$ space group. These phases show no evidence of secondary phase peaks. Microstructural analysis revealed that the particles, ranging in size from 1 to 10 μm , have a homogeneous composition. X-ray photoelectron spectroscopy (XPS) results showed that all transition metals are in their +2-oxidation state and the oxidation states of Na, P, and O are +1, +5, and -2, respectively. The band gap energies (E_g) for $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ based on the UV-vis diffuse reflectance spectra were found to be 1.78 eV and 1.86 eV,

respectively. The total ionic conductivity of the two compounds is in the range of 2.29×10^{-5} – 1.21×10^{-3} S/cm and 2.29×10^{-5} – 6.58×10^{-4} S/cm from 674 (400 °C) to 874 K (600 °C), respectively.

The second study was based on $\text{Na}_{2+2x}\text{Co}_{8-y}\text{M}_z(\text{PO}_4)_6$ ($x = 0.5$, $y = 1$, $z = 0$) leading to a new $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ polycrystalline material which was synthesized by solid-state (ST) and sol-gel (SG) methods and characterized by X-ray powder diffraction to resolve the structure. Rietveld refinement results confirmed that this compound crystallizes in the monoclinic system with $P2_1/c$ space group. Scanning electron micrographs showed the particles as aggregates with grain size between 8 to 35 μm and 1 to 20 μm , respectively for $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG. Energy dispersive X-ray spectroscopy, and mapping confirm the presence of Na, Co, P, O elements and their homogeneous distribution in the samples. X-ray photoelectron spectroscopy results indicate that the oxidation states of elements are +1, +2/+3, +5, and -2, for Na, Co, P, and O, respectively. Optical band gaps of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG were estimated to be 1.79 eV and 1.78 eV, respectively, based on UV-vis diffuse reflectance spectra. The ionic conductivity is 3.7×10^{-4} S/cm at 300 °C and 6.53×10^{-2} S/cm at 450 °C.

Another study on $\text{Na}_{2+2x}\text{Co}_{8-y}\text{M}_z(\text{PO}_4)_6$ ($x = 0$, $y = z = 8$) led to sodium tetra manganese phosphate, $\text{NaMn}_4(\text{PO}_4)_3$. The obtained phase was characterized by powder X-ray diffraction (PXRD) analysis. Rietveld analysis refinements confirmed that the prepared crystalline sample was pure and had a hexagonal structure (space group R-3). No secondary phases were observed. The morphology of the obtained powder was studied by scanning electron microscopy (SEM), giving the average grain size of about 7 μm . Elemental analysis of the powder was performed by energy dispersive X-ray spectroscopy (EDS), confirming the homogeneity of the sample. Raman and Fourier transform infrared (FTIR) spectroscopies show characteristic bands of P-O bonds of the $(\text{PO}_4)^{3-}$ functional group. The optical band gap energy of 1.57 eV was determined for the

sample from the diffuse reflectance using the Kubelka-Munk function and the Tauc relation. The chromatic coordinates of $\text{NaMn}_4(\text{PO}_4)_3$ indicate that it may be a candidate for a blue-violet emitting material. $\text{NaMn}_4(\text{PO}_4)_3$ can potentially be used as a red phosphor for white light emitting diodes. Its dielectric properties exhibit the behavior of an ionic conducting material. The Nyquist plot is displayed as a single semicircle leading to three parallel RC circuits, highlighting the presence of grains, grain boundaries and the material-electrode interface where the dominant electrical behavior occurs in the grain boundaries.

Keywords: Phosphates, $\text{Na}_2\text{Co}_8(\text{PO}_4)_6$, $\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$, $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$, $\text{Na}_2\text{Co}_{8-x}\text{Mn}_x(\text{PO}_4)_6$ diffraction des rayons X, Rietveld refinement, Optical bandgaps, Impedance, Semiconductor's materials, solid-state, sol-gel, Kubelka–Munk function, Tauc's relation, dielectric properties.

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Liste des abréviations

Abréviations	Explication
SG	Sol-gel
ST	Solid-state
LIBs	Lithium-ion batteries
NIBs	Sodium-ion batteries
PXRD	Powder X-ray Diffraction
TGA	Thermogravimetric Analysis
DTA	Differential Thermal Analysis
XRD	X-ray Diffraction
FTIR	Fourier transform infrared
SEM	Scanning Electron Microscopy
EDS	Energy Dispersive Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
kN	Kilonewtons
SPS	Spark Plasma Sintering
EIS	Electrochemical Impedance Spectroscopy
AC	Alternating current
DC	Direct current

HTF	High Temperature Furnace
ICSD	Inorganic Crystal Structure Database
VESTA	Visualization for Electronic and Structural Analysis
DRS	Diffuse Reflectance Spectroscopy
CCT	Calculate Color Temperature
CIE	Commission Internationale de l'éclairage
eV	Electron Volt
μm	Micromètre
Å	Angstrom
CIF	Crystallographic Information File
UV-Vis	Ultraviolet-Visible
a.u	Arbitrary Units

Curriculum vitae personnel

Pendant ma thèse de doctorat, j'ai publié deux articles en tant que premier auteur et j'ai un article soumis et un autre en instance de soumission. Un article en tant que co-auteur dans la revue de renommée mondiale a été publié. Un autre article en tant que co-auteur dans la revue de renommée mondiale est en instance de soumission Au total, depuis mes études universitaires, j'aurai six articles.

1. Nzaba Madila EE, Rousselot S, Rioux M, Dollé M, Duong A. Comparative studies of synthesis, structure, optical properties and conductivity of the monoclinic phases $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$. *Solid State Sciences*. 2021;2:106779. <https://doi.org/10.1016/j.solidstatesciences.2021.106779>.
2. Nzaba Madila EE, Yasmine Benabed, Prabhjyot Kaur, Rousselot S, Rioux M, Dollé M, Duong A. Synthesis of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ by sol-gel and solid-state methods. *Journal of Solid state chemistry*, Journal of Solid State Chemistry. 314 (2022) 123338. <https://doi.org/10.1016/j.jssc.2022.123338>.
3. Erman Eloge Nzaba Madila, Amina Lahrichi, Youness El Issmaeli, Malak Slaoui, Love Karan Rana, Taj-dine Lamcharfi, Adam Duong. Investigation of structural, optical, dielectric, and electrical properties of $\text{NaMn}_4(\text{PO}_4)_3$ with fillowite-type structure. Cet article est en instance de soumission encore.
4. Erman Eloge Nzaba Madila, Yasmine Benabed, Youness El Issmaeli, Amina Lahrichi, Steeve Rousselot, Mickael Dollé, Adam Duong. Effects of Manganese Doping in the Monoclinic $\text{Na}_2\text{Co}_8(\text{PO}_4)_6$ -Compound: $\text{Na}_2\text{Co}_{8-x}\text{Mn}_x(\text{PO}_4)_6$ ($0 \leq x \leq 4$). Cet article est déjà soumis.

Chapitre 1: Introduction

1. Contexte et justification

D'une part, les réserves mondiales de pétrole sont limitées et, d'autre part, son utilisation dans la production d'énergie s'accompagne d'un certain nombre de problèmes environnementaux. L'augmentation du prix des combustibles fossiles, du réchauffement de la planète et des problèmes de pollution, sont à l'origine de la réduction ou du remplacement des combustibles fossiles par le développement de nouvelles sources d'énergie qui sont en vogue aujourd'hui. Un autre aspect est qu'avec la guerre en Ukraine, la dépendance de certains pays du monde au pétrole et au gaz russes, et l'augmentation excessive des prix des hydrocarbures causée par les sanctions internationales contre la Russie, il est important de penser aux énergies propres d'une part, et d'autre part, des énergies susceptibles d'être accessibles à tous[1–3].

Les recherches sont orientées ces dernières années de manière à pouvoir répondre à ces situations. L'enjeu est d'utiliser des énergies « propres », renouvelables et capables de générer des puissances élevées. Les énergies solaire et éolienne peuvent répondre aux problèmes évoqués précédemment, mais la transformation et le stockage de l'énergie constituent les problèmes majeurs dans la mise en application des énergies renouvelables[4–7]. Cela est causé par leur incapacité à assurer une production constante d'électricité. Les batteries rechargeables sont des dispositifs importants pour stocker l'énergie électrique.

Au cours des trois dernières décennies, de grands progrès ont été réalisés dans l'application des batteries lithium-ion (LIBs), générant un changement sociétal finalement reconnu par l'attribution du prix Nobel de chimie 2019 à Whittingham, Goodenough et Yoshino[8]. s. Récemment, les batteries sodium-ion (NIBs) ont suscité beaucoup d'intérêt en raison de l'abondance naturelle et du coût du sodium et de leurs propriétés chimiques proches de celles des LIBs[9]. Par conséquent, les NIBs sont considérées comme une alternative prometteuse et

réalisable aux LIBs, notamment pour les applications stationnaires. Les activités de recherche sur les batteries sodium-ion se développent dans le monde entier mais nécessitent encore beaucoup de recherche fondamentale et appliquée[4,10–18].

La découverte des propriétés électrochimiques très intéressantes du phosphate de fer lithié LiFePO_4 [19–23] a ouvert la voie à la recherche de nouveaux hôtes d'insertion à base de polyanions [13,24–46][47,48]. Les phosphates de métaux de transition du lithium et du sodium avec des structures de type olivine de LiMPO_4 et NaMPO_4 ($M = \text{Mn, Fe, Co}$ et Ni) respectivement, ont attiré un intérêt significatif de la recherche comme matériaux de cathode pour les batteries de haute puissance avec un potentiel pour alimenter les véhicules électriques [24,28,30,39,49–55]. La conception et la synthèse de nouveaux matériaux cathodiques constituent l'un des défis à relever pour développer des NIBs durables et sûres.

Afin de diminuer la production de gaz à effet de serre et la pollution atmosphérique, l'énergie produite à partir de batteries constitue une technique propre et adéquate qui permet de réduire à long terme l'utilisation de combustibles fossiles. Une batterie est un dispositif de puissance capable de convertir l'énergie chimique en énergie électrique. Les batteries sont principalement classées en deux groupes : les piles primaires et les piles secondaires. Les piles primaires sont généralement jetables et non rechargeables. Par conséquent, une fois déchargées, elles sont mises au rebut car les matériaux utilisés dans les piles primaires ne peuvent pas revenir à leur forme initiale, la réaction chimique n'étant pas facilement réversible. Les piles secondaires sont connues comme des piles rechargeables, c'est-à-dire qu'elles peuvent être rechargées plusieurs fois après chaque décharge en appliquant un courant électrique pour inverser la réaction chimique qui se produit pendant la décharge, ce qui rend la pile réutilisable[4,56].

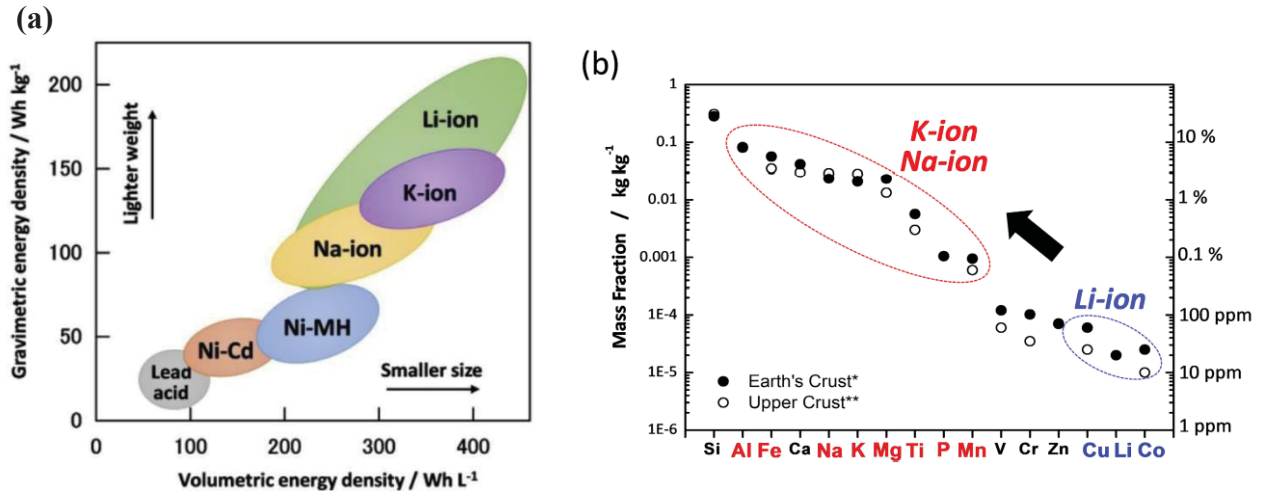


Figure 1 (a) Comparaison de la densité énergétique des technologies de batteries commerciales dans le passé (plomb-acide, Ni- Cd), du présent (Ni-MH, Li-ion) et du futur (Na-ion et K-ion) et (b) Abondance des éléments dans la croûte terrestre[57–59].

2. Problématiques

Le lithium est présentement l'élément alcalin le plus habituellement utilisé dans les batteries. Les batteries à base d'ions lithium sont très performantes en densité d'énergie volumétrique et gravimétrique, comparées aux autres types de batteries rechargeables, comme le montre la figure 1a [58,59], mais leurs utilisations présentent des inconvénients. Le lithium est un élément coûteux en raison de son abondance limitée sur la croûte terrestre et aussi, son extraction a un impact environnemental. Bien que le lithium soit largement distribué dans la croûte terrestre et dans les mers, l'abondance du lithium est inférieure à 20 ppm dans la croûte terrestre, comme le montre la figure 1b. De plus, les ressources en lithium sont pratiquement limitées en Amérique du Sud, en Australie, en Chine et aux États-Unis. D'autre part, le cobalt est un métal indispensable pour les technologies propres de nouvelle génération, et est aussi un métal stratégique et critique utilisé dans de nombreuses applications civiles, industrielles et

militaires. Actuellement, la principale utilisation du cobalt se trouve dans les électrodes des batteries lithium-ion (LIB)[60]. Seulement, l'industrie des produits électroniques et automobiles doit vérifier la provenance du cobalt utilisé pour la fabrication de piles et de batteries, car le cobalt est un minerai trop souvent extrait dans des conditions dangereuses et parfois par des enfants dans les mines sauvages artisanales en RDC[61,62].

3. Solutions possibles

À l'inverse du lithium, le sodium et le potassium sont également répartis uniformément dans le monde et sont les éléments les plus abondants sur la Terre. En outre, aucun alliage avec l'aluminium n'est électrochimiquement formé avec le sodium et le potassium ; par conséquent, la feuille d'aluminium est disponible comme collecteur de courant (bipolaire) des électrodes négatives et positives des batteries Na-ion et K-ion, contrairement aux batteries Li-ion. Comme le lithium, le cuivre et le cobalt ne sont pas des éléments essentiels, le coût des matériaux est inférieur pour les batteries aux ions Na et K [13–15,37,63]. Une alternative captivante consisterait à l'utilisation du sodium car le sodium présente en conséquence les mêmes propriétés chimiques car les deux (Li et Na) sont sur une même colonne du tableau périodique. Un autre aspect plus intéressant est que le sodium est disponible en quantité nettement plus importante. C'est pourquoi les batteries sodium-ion (NIBs) sont en train de devenir une alternative à faible coût aux batteries lithium-ion (LIBs) les plus modernes. La chimie sodium-ion présente des avantages considérables par rapport à celle du lithium-ion. Les sources de sodium sont très répandues et ses précurseurs sont peu coûteux[64]. Les électrodes positives sont constituées de matériaux dont la structure doit assurer une mobilité des cations[37].

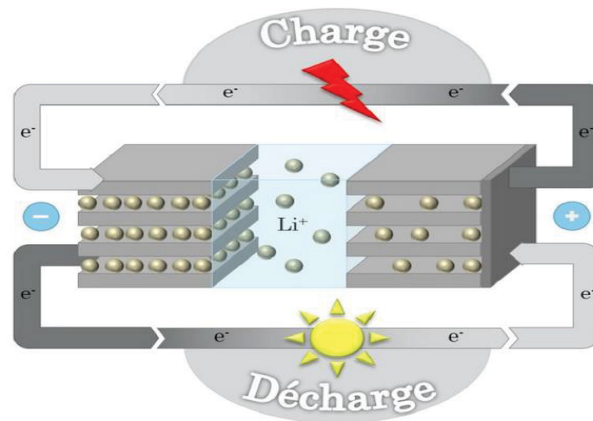


Figure 2 Fonctionnement d'une batterie Li-ion[65].

Ces dernières années, les composés phosphatés ont attiré une grande attention et un intérêt de recherche de longue date en raison de leur propriété structurale unique et de leurs diverses applications. Selon la disposition d'attachement des groupes P-O, les phosphates peuvent être groupés en trois classes: les orthophosphates, les pyrophosphates et les polyphosphates. La structure orthophosphate comporte un tétraèdre PO_4 isolé, le pyrophosphate comporte un dimère P_2O_7 et la structure polyphosphate comprend un multimère isolé $[\text{P}_n\text{O}_{3n+1}]$, ou une chaîne $[\text{PO}_3]_\infty$ ou un anneau $[\text{P}_n\text{O}_{3n}]$ ($n \geq 3$)[66]. En outre, ces groupes P-O complexes et diversifiés et les polyèdres métal-O introduits dans les cristaux forment différentes unités structurales en partageant des atomes d'oxygène, ce qui conduit à la richesse et au caractère unique du type de structure des matériaux phosphatés. Ces types de structure cristalline riches et uniques ont contribué à une large gamme d'applications des matériaux phosphatés, tels que les matériaux fluorescents[67], les catalyseurs[68], les batteries[28,30,38,39,69–73], les diélectriques[74–77], les lasers[78], l'optique non linéaire[79], etc.

L'association des polyèdres de métaux de transition et des entités tétraédriques telles que les phosphates ou les silicates offre généralement des possibilités de produire des structures

possédant des tunnels larges permettant une mobilité aisée des ions sodium. L'exploitation du système Na-Co-P-O a permis de synthétiser un nombre important de cobaltophosphates de sodium. La capacité qu'ont les phosphates de manganèse, de cobalt et de nickel à former un réseau ouvert provient des diverses coordinations du manganèse divalent, cobalt divalent et nickel divalent, donnant soit des tétraèdres, des octaèdres, des pyramides tétraogonales ou des pyramides trigonales. Ces composés sont largement exploités pour leur excellente conductivité ionique[80–82].

Depuis la découverte des propriétés électrochimiques très intéressantes de LiFePO_4 [35,83], la recherche de nouveaux matériaux d'insertion à base de polyanions est intense[35,37,40,84–87]. Les phosphates des métaux de transition lithium et sodium de structure olivine, LiMPO_4 et NaMPO_4 ($M = \text{Mn, Fe, Co et Ni}$), ont suscité un intérêt considérable pour la recherche en tant que matériaux de cathode pour batteries[49,88,89].

4. Objectif de la thèse

L'objectif de cette thèse est de synthétiser puis caractériser les nouveaux phosphates de métaux de transition de types $\text{Na}_{2+2x}\text{Co}_{8-y}\text{M}_z(\text{PO}_4)_6$ pouvant être utilisés comme composants (cathode, anode ou électrolyte) dans les batteries ions sodium. D'une part, nous avons essayé de substituer partiellement le cobalt par le nickel et le manganèse dans le phosphate de cobalt et de sodium suivant $\text{Na}_2\text{Co}_8(\text{PO}_4)_6$. D'autre part, nous avons aussi effectué une substitution totale (Cas de $\text{Na}_2\text{Co}_8(\text{PO}_4)_6 = \text{NaCo}_4(\text{PO}_4)_3$). Ceci, pour des raisons de coût puisque le cobalt est en effet unique parmi les métaux de base car son approvisionnement est dominé par un seul pays, la République démocratique du Congo (RDC). En effet, la RDC produit environ 60 % du cobalt mondial, et aucun autre pays ne produit plus de 6 %[90,91]. En raison de prix élevé et de toxicité liés à l'élément cobalt, une partie des ions Co^{2+} ont été substitués par les

ions Ni^{2+} et Mn^{2+} (Cas du deuxième chapitre), pour améliorer les propriétés conductrices. Pour cela, nous avons tentés d'incorporer une partie de nickel et de manganèse dans ce réseau. D'autre part, nous avons procédé à la réduction du cobalt dans $\text{Na}_2\text{Co}_8(\text{PO}_4)_6$. Pour cela, le composé $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ (Cas du troisième chapitre) avait été obtenu, et dérive du groupe de composés $\text{Na}_{2+2x}\text{Co}_{8-y}(\text{PO}_4)_6$ (pour $x = 0,5$ et $y = 1$), dont les phases ont été obtenues par deux méthodes de synthèse: la synthèse à l'état solide et la méthode sol-gel. Cette optique qui consiste toujours à réduire la quantité du cobalt dans nos composés est motivé par le fait que 60 % du cobalt mondial émane de la République démocratique du Congo (RDC). Ainsi, les conditions d'extraction du cobalt sont assez critiquées car elles se font dans les mines sauvages artisanales dans lesquelles on fait travailler des enfants (voir figure 3)[92–94].



Figure 3 Le Congo, le travail des enfants et votre voiture électrique[92].

Après les synthèses par la voie solide (l'état solide) et la voie liquide (sol-gel) de tous les composés, la diffraction des rayons-X (DRX), la microscopie électronique à balayage (MEB), la spectroscopie de dispersion d'énergie (EDS), l'analyse thermogravimétrique (ATG), l'analyse spectroscopique photoélectronique à rayons X (XPS), la spectroscopie d'Impédance électrochimique (SIE), la spectrophotométrie en Réflectance Diffuse (SRD) ont été utilisées pour la caractérisation des matériaux synthétisés.

Ce travail est donc subdivisé en cinq chapitres :

- ❖ Le premier chapitre concerne l'introduction ;
- ❖ Le deuxième parle des études comparatives de la synthèse, de la structure, des propriétés optiques et conductrices des phases monocliniques $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ et $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$;
- ❖ Le troisième est axé sur la synthèse de $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ par les méthodes sol-gel et à l'état solide;
- ❖ Le quatrième s'intéresse de l'étude des propriétés structurelles, optiques, diélectriques et électriques de $\text{NaMn}_4(\text{PO}_4)_3$ avec une structure de type Fallowite.
- ❖ Le dernier chapitre s'occupe de la conclusion et les perspectives.

5. Matériaux pour batteries ions Na

5.1. Les matériaux d'électrodes positives

Les matériaux d'électrodes positives sont des matériaux qui peuvent réagir réversiblement avec le sodium à un potentiel haut et présentent une capacité spécifique élevée. Ils doivent également posséder une bonne réversibilité de telle sorte que de nombreux cycles puissent être réalisés sans perte de capacité. Ainsi, ces matériaux, doivent répondre à un certain nombre de critères comme:

- Le choix du matériau d'électrode positive est très important selon l'usage dans une batterie rechargeable Na métal ou dans une batterie Na-ion. Dans les cas des batteries au Na rechargeables, comme on utilise du Na métallique à l'anode, le matériau d'électrode peut ne pas contenir de Na. Alors que, pour les batteries Na-ion le matériau d'électrode positive doit contenir le Na.

- Il faut que la structure du matériau hôte soit capable d'accueillir les ions Na^+ et être stable après leur restitution. La variation des paramètres de la structure doit aussi être minimale pour le maintien d'une longue tenue de cyclage.
- Ils doivent avoir un potentiel élevé par rapport à l'électrode négative pour conduire à une densité d'énergie.
- Une grande conductivité électronique et un grand coefficient de diffusion chimique des ions Na sont nécessaires pour réduire la résistance interne de la batterie.
- Une stabilité chimique de la cathode et de l'électrolyte pour une durée de cyclage plus longue.
- Un très faible coût du matériau d'électrode positive, non toxique et facile à synthétiser[4].

Il existe principalement trois catégories de matériaux d'électrodes positives, dont les oxydes de métaux de transition lamellaires, les oxydes de structure spinelle et les structures polyanioniques.

5.1.1. Les oxydes de métaux de transition lamellaires

Ce sont des matériaux dont la structure est composée de feuillets d'oxygène avec un empilement ABCABC séparés alternativement par des couches de métaux de transition et des couches de lithium ou de sodium. Comme le carbone graphite, les chalcogénures de métaux de transition (TaS_2 , TiS_2 , MoS_2) ou bien des matériaux du types LiMO_2 et NaMO_2 (M= Mn, Fe, Co, Ni), présentent une structure en feuillets, une structure maintenue par de fortes liaisons ioniques et qui sont liés entre eux par des liaisons faibles de type Van der Waals permettant l'intercalation de l'ion Li^+ ou Na^+ puis son extraction dans un « mouvement de respiration ». Le LiCoO_2 est parmi la catégorie de ces matériaux d'électrode positive le plus

communément utilisé dans les batteries au lithium rechargeable commerciales. Il a été rapporté pour la première fois par Mizushima et al. en 1980 (Figure 2)[95].

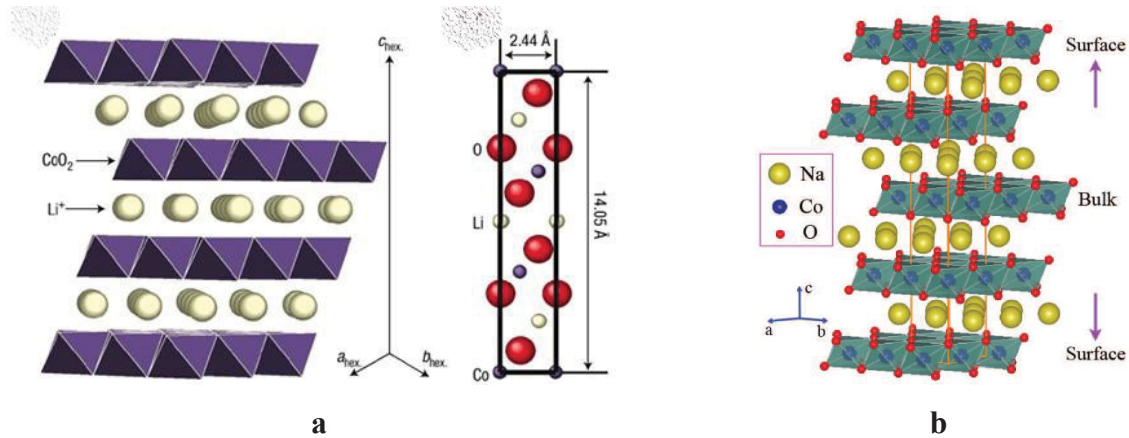


Figure 4 (a, b) La structure des oxydes de métaux de transition lamellaires[96,97].

Plusieurs matériaux d'oxydes de métaux de transition lamellaires ont été étudiés de manière intensive, et les plus connus sont LiCoO_2 et LiNiO_2 . Mais pour des causes des inconvénients liés à la sécurité de la batterie, à la pollution et au coût du cobalt, LiCoO_2 ne peut pas être le parfait matériau d'électrode positive bien qu'il soit présent dans la majorité des batteries commerciales. La meilleure manière était de remplacer le cobalt par le nickel, ce qui conduisit au composé LiNiO_2 , ceci afin d'améliorer ces trois points (la sécurité de la batterie, la pollution et le coût). LiNiO_2 est isostructural à LiCoO_2 et semble présenter de meilleures potentialités pour le remplacer, car moins coûteux pour des performances électrochimiques toujours élevées. Malgré sa capacité spécifique plus élevée que le composé au Co, LiNiO_2 présente plus de désordre cationique et est thermiquement instable après deintercalation. Ce désordre est causé par les ions Ni qui occupent des sites situés dans les couches formées par les ions lithium ce qui empêche leur intercalation et deintercalation au cours du cyclage. Le degré du désordre dépend fortement de la méthode de synthèse. Des études ont montré qu'une

substitution cationique partielle des ions nickel était un bon moyen pour conserver une structure lamellaire et de bonnes propriétés électrochimiques[4,98].

5.1.2. Les structures de type spinelle

La structure spinelle possède une structure cristalline commune de type AB_2O_4 où A est un cation en site tétraédrique (entouré de 4 oxygènes) et B, deux cations en sites octaédriques (entouré de 6 oxygènes). Les composés ayant une structure spinelle ont trouvé de nombreuses applications pratiques. Ils sont des bons matériaux d'électrode positives. À l'opposé des oxydes de métaux de transition lamellaires, les structures de types spinelles ont des tunnels qui donnent une diffusion tridimensionnelle des ions Li^+ ou Na^+ [4,99,100].

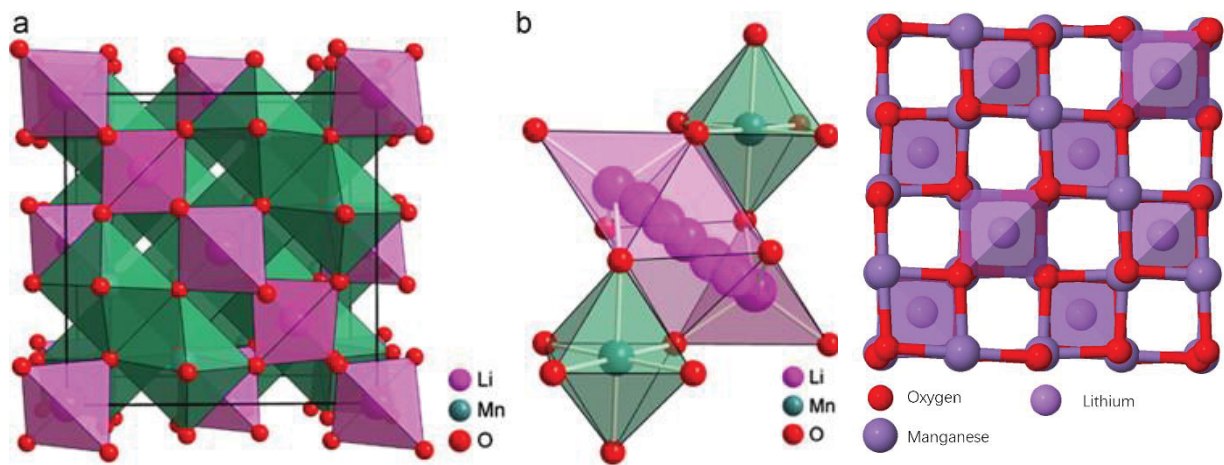


Figure 5 La structure de $LiMn_2O_4$ [101].

5.1.3. Les structures polyanioniques

Les structures polyanioniques constituent une nouvelle classe de matériaux d'électrode positive qui offrent des perspectives captivantes comme une meilleure stabilité thermique, et en fonction des matériaux utilisés, un coût moins élevé et une toxicité moindre. Ces matériaux ont la forme $(XO_4)^{y-}$ ($X = S, P, Si, As, Mo, W$) et possèdent souvent des liaisons M-O-X. L'effet inductif des groupements $(XO_4)^{y-}$ avec de forte liaison covalente X-O, augmente les potentiels d'oxydoréduction grâce à la forte polarisation entre les ions oxygène et le cation M qui ainsi diminue la covalence de la liaison M-O[4,80–82,102].

Les composés à base de fer ayant une structure NASICON ou olivine sont les plus étudiés de toute la large variété des structures polyanioniques. Constituée d'octaèdres MO_6 (avec $M = Fe, Nb, Ti$ et V) reliés par les sommets à des tétraèdres XO_4 (avec $X = S, P, As, W$ et Mo), la structure NASICON est tridimensionnelle et offre une grande mobilité des ions lithium ou sodium. Les travaux de Goodenough *et al.* sur la phase $LiFePO_4$ utilisée comme matériau de cathode ont démontré que ce matériau présente d'intéressantes performances électrochimiques. $LiFePO_4$ est de type olivine et est constitué de couches d'octaèdres FeO_6 reliés entre eux par les sommets et de chaînes d'octaèdres LiO_6 reliés entre eux par les arêtes (figure 5). Ces chaînes sont reliées entre elles par des tétraèdres PO_4 qui créent une structure tridimensionnelle stable. $LiFePO_4$ est le phosphate de fer le plus étudié en tant qu'électrode positive parce qu'il possède de nombreux avantages [35,42,103–106]:

- Une capacité spécifique théorique élevée de 170 mAh/g.

- Un potentiel moyen de 3.5 V vs. Li^+/Li
- Une bonne stabilité au cours du cyclage grâce à la bonne stabilité du matériau dans les électrolytes organiques courants.
- Une absence de toxicité et un prix de revient réduit grâce à l'abondance de l'élément fer comparé au cobalt.

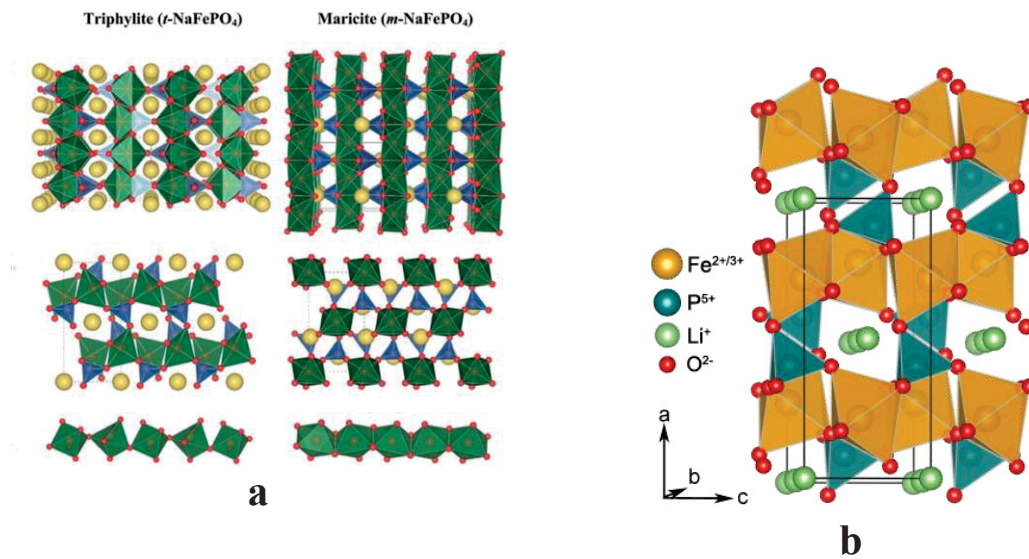


Figure 6 La structure de (a) NaFePO_4 et (b) LiFePO_4 [42,106].

5.2. Matériaux d'électrodes négatives

D'une part, une très grande variété de matériaux a été rapportée comme potentiels matériaux d'électrode positive. D'autre part, très peu de matériaux ont été identifiés comme matériaux d'électrode négative. Parmi ces derniers, nous avons: Le carbone (par exemple, le carbone dur (hard carbon) ou le carbone mou (soft carbon) [17,107,108], les oxydes de métaux de transition (par exemple, $\text{Na}_{0.66}\text{Li}_{0.22}\text{Ti}_{0.78}\text{O}_2$)[109], les

alliages[16,110] et les phosphates de métaux de transition (par exemple, NaTiOPO_4)[111].

5.2.1. Le carbone

Les carbones durs ont un immense potentiel en tant que matériaux d'anode pour les batteries Na-ion, car les intercalaires de graphène expansé et les nanovoïdes entre les fragments aromatiques empilés de manière aléatoire peuvent accueillir une quantité substantielle de sodium. Cependant, la grande capacité irréversible au cours du premier cycle reste un problème important en termes de technologie de batterie praticable[112]. La figure 7 représente le schéma d'une cellule de batterie Na-ion avec une anode en carbone dur[113]. Les différences entre les carbones durs, les carbones mous et le graphite ont été examinées dans la littérature[114]. En plus des propriétés mécaniques, les carbones durs sont "plus durs" que les deux autres formes de carbone. Une définition plus spécifique est que ces matériaux en carbone sont des matériaux de qualité supérieure ne pouvant pas être graphitisés, même à très haute température (plus de 3000 °C), alors que les carbones mous correspondent aux matériaux carbonés que l'on peut graphitiser[115].

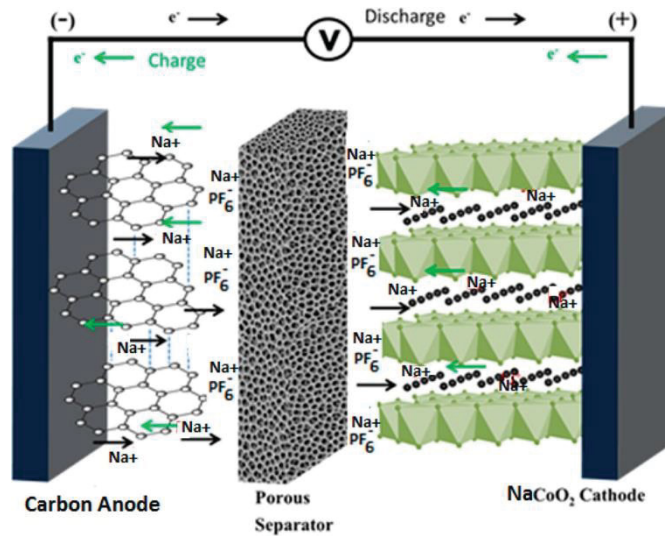


Figure 7 Représentation schématique d'une cellule de batterie Na-ion avec une anode en carbone dur[113].

5.2.2. Les oxydes de métaux de transition et les phosphates de métaux de transition

En dehors du carbone, les oxydes de métaux de transition et les phosphates de métaux de transition ont aussi fait l'objet d'une recherche en tant que matériaux d'électrode négative pour les batteries sodium-ion. Ceux-ci peuvent être divisés en deux catégories : les matériaux de conversion et les matériaux d'insertion. Il est difficile de prévoir si l'oxyde de métal de transition présentera, dans une batterie sodium-ion, un mécanisme de conversion ou d'insertion mais il semblerait que les métaux de transitions avec un remplissage faible de la couche 3d (Ti,V) conduisent préférentiellement à un mécanisme d'insertion[18,73,116–120],[121].

5.3. Matériaux d'électrolyte

Ils comprennent les électrolytes liquides, les électrolytes polymères et les électrolytes céramiques.

Les électrolytes liquides sont des solutions d'un sel de sodium ou de lithium dans des solvants organiques. Il existe de nombreux sels de sodium utilisés dans différents types de batteries sodium-ion. Le sel de sodium le plus habituellement utilisé dans les électrolytes liquides est le NaPF_6 . Les électrolytes liquides ont des très bonnes conductivités, la principale limite est celle des solvants inflammables qui peuvent présenter des risques pour la sécurité. Par conséquent, des efforts considérables sont dirigés vers des électrolytes ininflammables[122–125].

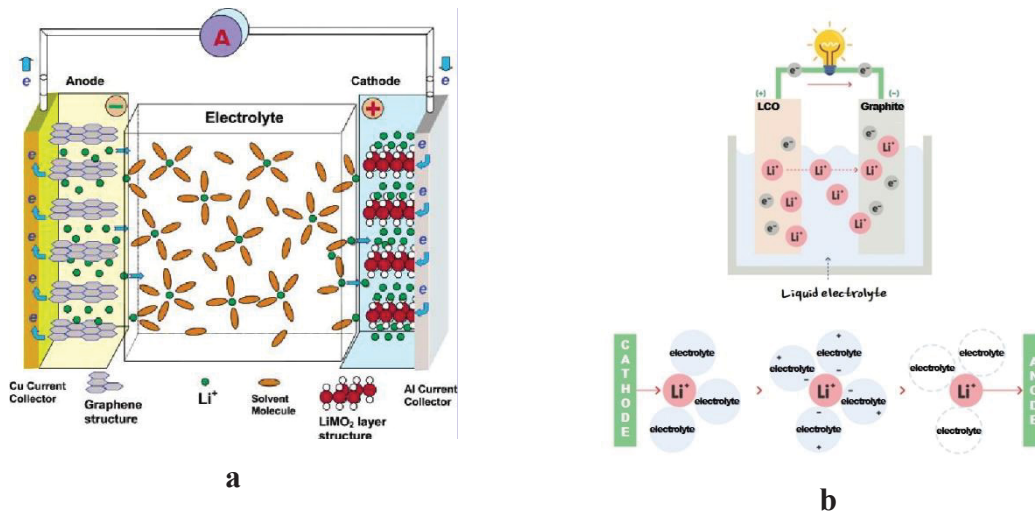


Figure 8 (a, b) Représentation schématique d'une cellule de batterie avec l'électrolyte liquide.

Les avantages des électrolytes polymères comprennent l'amélioration des propriétés de sécurité, la stabilité dimensionnelle et la capacité à empêcher la formation de dendrites de

sodium en raison de leur faible volatilité et de leur haute viscosité. En outre, les électrolytes polymères sont attrayants pour les conceptions de batteries flexibles, mais des conductivités plus élevées sont indispensables pour les applications à température ambiante[126–128].

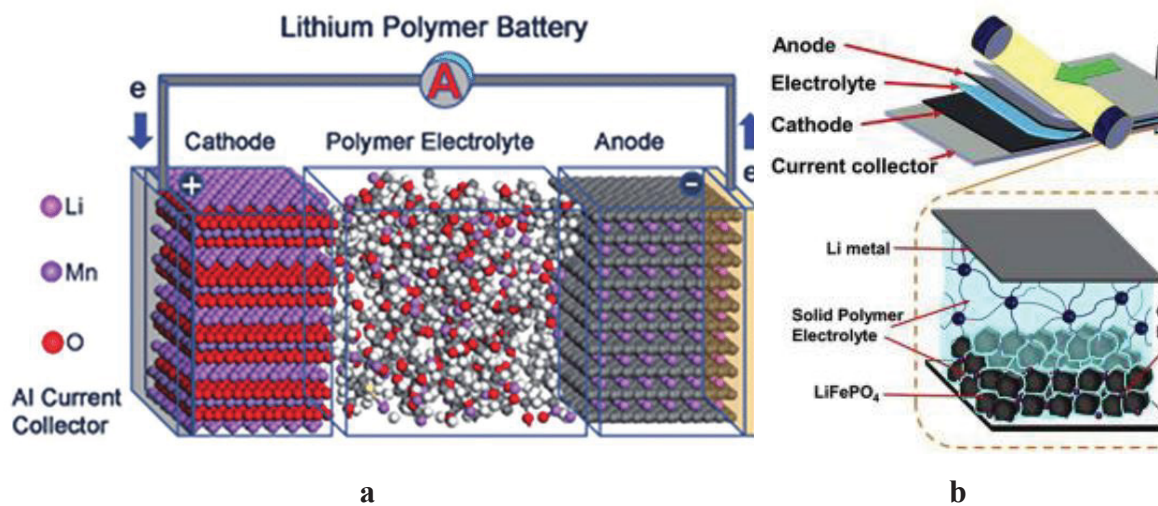
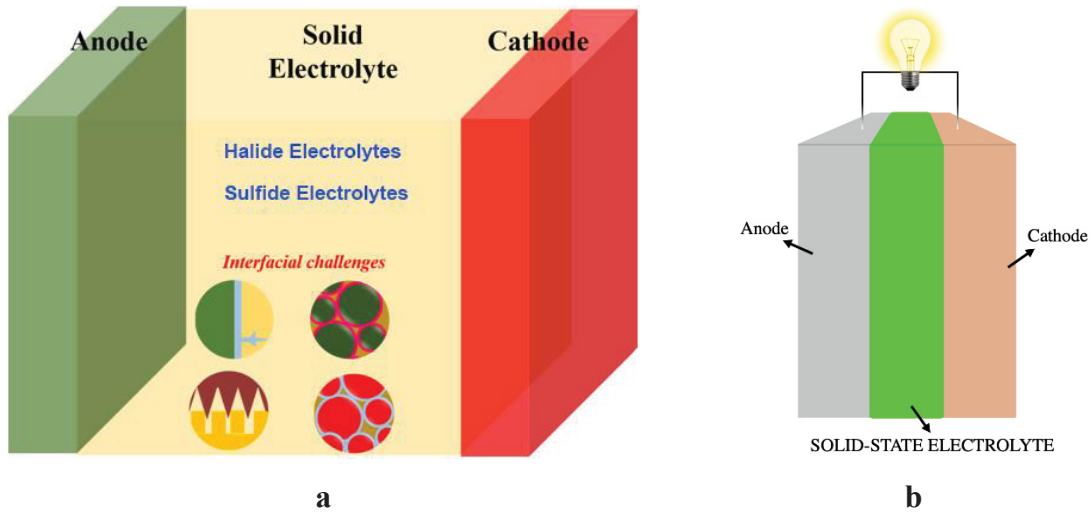


Figure 9 (a, b) Représentation schématique d'une cellule de batterie avec l'électrolyte polymère.

Dans le but d'améliorer la conception des batteries sodium-ion ainsi que leur sécurité et leur durabilité, les électrolytes céramiques ont été largement étudiés au cours des dernières décennies. Les électrolytes solides présentent de nombreux avantages, tels que l'absence de fuite d'électrolyte, l'élimination des problèmes du liquide, l'amélioration des transitions de phase à basse température, la facilité de la miniaturisation, ainsi qu'une très bonne adaptation à des températures élevées et à des environnements agressifs. Toutes les

batteries sodium-ion à l'état solide ont montré une excellente stabilité de stockage et une très longue durée de vie[129–133].



6. Techniques expérimentales

6.1. Synthèse des phases

Il existe plusieurs procédés dans la littérature pour la synthèse des matériaux qui sont: la réaction à l'état solide, la mécanosynthèse, la synthèse par combustion, la méthode sol-gel, la synthèse par coprécipitation, la méthode hydrothermale, etc.... Dans notre cas, nous nous sommes intéressés à la réaction à l'état solide et à la méthode sol-gel car ce sont les plus courantes, et aussi les plus accessibles pour la synthèse des phosphates de métaux de transition.

6.1.1. Synthèse à l'état solide

Dans la chimie du solide, la synthèse par réaction à l'état solide est l'une des méthodes les plus utilisées. Il s'agit d'un traitement thermique entre deux ou plusieurs substances sous forme solide qui sont intimement mélangées. Les réactifs, qui peuvent être des oxydes et/ou des carbonates sous forme des poudres, sont pesés en quantités stœchiométriques et mélangés soigneusement par broyage dans un mortier. La cinétique de la réaction sera facilitée par l'obtention d'un mélange solide homogène composé des particules à faible taille. La poudre est ensuite soumise à des traitements thermiques successifs jusqu'à l'obtention d'une phase pure (une seule phase). En général, les traitements se font à des températures proches de 1000 °C et, l'avantage de cette technique est qu'elle est assez facile et rapide à réaliser, car elle ne nécessite aucune préparation antérieure des précurseurs. La granulométrie des particules joue un rôle très important sur la vitesse de la réaction et sur l'homogénéité du composé obtenu, car la diffusion à l'état solide est lente. On peut compenser ceci en faisant des broyages intermédiaires[82,134–136].

6.1.2. Synthèse par sol-gel

Le procédé sol-gel est parmi les méthodes utilisées pour la synthèse des matériaux. C'est une méthode spécialement bien adaptée à la fabrication de matériaux homogènes, sous forme de poudres et de films. Lors d'une synthèse par voie sol-gel, les précurseurs moléculaires contenus dans la solution de départ (« le sol ») polymérisent suivant divers mécanismes et forment un réseau d'oxydes (« le gel »). Une étape de séchage suivie de

traitements thermiques qui permet d'éliminer les composés organiques pour former le matériau oxyde inorganique. Cette technique présente de nombreux avantages. Parmi les plus significatifs, citons la très grande pureté et l'homogénéité des solutions liées au fait que les différents constituants sont mélangés à l'échelle moléculaire en solution, les contrôles de la porosité des matériaux et de la taille des nanoparticules, les traitements thermiques requis à basses températures ainsi que la synthèse de matériaux inaccessibles par d'autres techniques[4,137,138].

6.2. Techniques de caractérisation

Ce sont des techniques indispensables qui permettent d'étudier et comprendre des matériaux, en les caractérisant à l'aide des techniques de caractérisation appropriées. Dans notre cas, nous avons utilisés les techniques suivantes: L'Analyse Thermogravimétrique (ATG), la Diffraction des Rayon-X (DRX), les Spectroscopies Raman et infrarouge, la Microscopie Électronique à Balayage (MEB), la Spectroscopie de Dispersion d'énergie (EDS), l'analyse spectroscopique photoélectronique à rayons X (XPS), Spectrophotométrie en Réflectance Diffuse (SRD) et la Spectroscopie d'Impédance Electrochimique (SIE).

6.2.1. L'analyse thermogravimétrique (ATG)

C'est une technique de caractérisation qui mesure les changements de masse d'un échantillon en fonction de la température. Ces mesures se réalisent généralement dans

une atmosphère contrôlée, constituée d'azote ou d'air. Quand un matériau est chauffé, il peut perdre de la masse en raison de plusieurs processus comme le séchage ou les réactions chimiques qui libèrent des gaz. Une connaissance du comportement thermique d'un échantillon peut permettre de s'assurer, par exemple, qu'il est utilisé à une température assurant sa stabilité chimique[139,140]. Dans le cadre des études de cette thèse, l'appareil Diamond Pyris 6000 TGA/DTA de Perkin-Elmer a été utilisé dans la gamme de température comprise entre 30 °C et 850 °C en utilisant des creusets en aluminium sous flux de N₂ à une vitesse de chauffe de 20 °C /min. La précision de température de l'appareil est de $\pm 0,5$ °C.

6.2.2 La diffraction des rayons-X (DRX)

La DRX est une méthode mondialement utilisée pour reconnaître la nature et la structure des échantillons cristallisés. En effet, cette méthode ne s'applique qu'à des échantillons cristallins montrant les caractéristiques de l'état cristallin, c'est-à-dire un arrangement périodique, ordonné et dans des plans réticulaires tridimensionnels des atomes constitutifs. Les atomes s'organisent donc en plans réticulaires plus ou moins denses qui sont désignés par leurs coordonnées (h, k, l) dans un système de repérage de l'espace. La méthode permet ainsi clairement de différencier les produits amorphes (verres) des produits cristallisés. Ainsi, avec un rayonnement de longueur d'onde suffisamment petit, il est possible d'obtenir des diffractions par les plans réticulaires (de la même manière que les rayons lumineux sont diffractés par les petites fentes d'un réseau en optique). Cette réfraction est d'autant plus intense que le plan est « dense » c'est-à-dire riche en

atomes. Cette théorie a été élaborée concomitamment par W.L. Bragg et G.Wulff , c'est pourquoi on l'appelle la relation de Wulff-Bragg. Un faisceau de rayons X incident de longueur d'onde ne sera réfléchi par une famille de plan (h,k,l) que dans la mesure où il rencontre ces plans sous un certain angle dit angle θ de Bragg tel que[141–143]:

$$2d_{hkl} \sin \theta = n\lambda \quad (1)$$

Le diffractomètre Bruker D8 (rayonnement Cu-K α , géométrie θ -2 θ , monochromateur arrière) avec un mode de balayage pas à pas sur la plage 2 θ de 10-70°, en utilisant le rayonnement CuK α (1,5406 Å) sous une tension et un courant électrique de 40 kV et 100 mA, respectivement, et pendant une durée totale de mesure de 2 h, avec un pas de $\sim 0,006^\circ$ et une fente de divergence fixe de $0,3^\circ$ était utilisé pour les mesures de nos travaux.

6.2.3 Les spectroscopies Raman et infrarouge

Ce sont des techniques qui sont souvent bien adaptées pour l'obtention d'informations structurales sur certains matériaux. Ces techniques sont sensibles aux changements à courte distance intervenant par exemple dans les réseaux de tétraèdres, lors des changements de composition surtout. Dans ce contexte un certain nombre d'études Infrarouge et Raman sont réalisées sur les matériaux phosphatés[144]. Les spectres d'absorption FTIR et Raman de nos échantillons ont été enregistrés respectivement à l'aide d'un spectromètre FTIR Thermo 10 de 500 à 4000 cm⁻¹ et sur un spectromètre Thermoscientist Raman DXR3 avec une source laser verte (532 nm).

6.2.4 La microscopie électronique à balayage (MEB)

La MEB est une technique qui permet de visualiser la surface de structures massives, sur les échantillons qui apparaissent en volume. Un microscope électronique à balayage utilise un faisceau d'électrons très fin qui balaie, point par point, la surface de l'échantillon à observer. Le principe du balayage consiste à parcourir la surface de l'échantillon par lignes successives et à transmettre le signal recueilli via un détecteur à un écran cathodique dont le balayage est exactement synchronisé avec celui du faisceau incident[145]. La morphologie de nos échantillons a été caractérisée par le microscope X-max 20 mm² de Hitachi et le détecteur d'électrons secondaires d'un microscope électronique à balayage Hitachi modèle SU1510 fonctionnant à 30 keV. Le diamètre moyen des particules a été déterminé à l'aide du logiciel Image J®[146].

6.2.5 La spectroscopie de dispersion d'énergie (EDS)

L'EDS est une technique de caractérisation qui peut fournir une analyse élémentaire résolue spatialement à partir de zones aussi petites qu'un nanomètre de diamètre. L'impact du faisceau d'électrons sur l'échantillon produit des rayons X caractéristiques des éléments présents sur l'échantillon. L'analyse EDS peut être utilisée pour déterminer la composition élémentaire de points individuels, des balayages de lignes ou pour tracer la distribution latérale des éléments de la zone imagée[147,148]. Les compositions de nos échantillons ont été caractérisés par des analyses EDS utilisant la colonne EDX, l'instrument OXFORD, le microscope X-max 20 mm² de Hitachi et le détecteur

d'électrons secondaires d'un microscope électronique à balayage Hitachi modèle SU1510 fonctionnant à 30 keV.

6.2.6 L'analyse spectroscopique photoélectronique à rayons-X (XPS)

Cette technique est utilisée pour déterminer la composition atomique quantitative et la chimie. Il s'agit d'une analyse de surface technique avec un volume d'échantillonnage qui s'étend de la surface à une profondeur d'environ 50-100 Å. Ceci est utile aussi pour caractériser les couches minces en quantifiant les éléments au niveau de la matrice en fonction de la profondeur. La XPS est une technique d'analyse élémentaire. Ceci est unique en ce qu'il fournit également des informations sur l'état chimique des éléments détectés[149,150]. Les mesures XPS dans cette thèse ont été effectuées avec un VG Escalab 220i-XL équipé d'un analyseur hémisphérique et d'une source de rayons X à double anode. Les énergies de liaison ont été calibrées en utilisant du carbone de confinement (C 1s = 284,4 eV).

6.2.7 La spectrophotométrie en réflectance diffuse (SRD)

La Spectrophotométrie en Réflectance Diffuse (SRD) est une méthode de caractérisation des matériaux pour évaluer les bandes interdites optiques, bandes interdites directes et indirectes. Les bandes interdites des matériaux sont ensuite calculées en convertissant la réflectance en données d'absorption selon l'équation de Kubelka-Munk. Les bandes interdites sont estimées à l'aide du tracé de Tauc en utilisant l'équation[151–154]. Pour les travaux de cette thèse, une analyse par spectroscopie UV-vis à l'état solide a été

réalisée sur les pastilles de l'échantillon à température ambiante, en mode de réflectance diffuse, à l'aide d'un spectrophotomètre UV/Visible Agilent Cary 60.

6.2.8 La spectroscopie d'impédance électrochimique (SIE)

C'est une méthode qui est largement appliquée dans la littérature pour caractériser électrochimiquement des électrolytes solides. En effet, cette méthode permet de différencier et d'identifier les réponses relatives à l'électrolyte et aux électrodes pour donner suite à l'application d'une perturbation de tension alternative de fréquence variable et de faible amplitude autour d'un point de fonctionnement stationnaire. Ainsi, les inhomogénéités électriques dans les électrolytes céramiques, les interfaces électrode/électrolyte, les couches superficielles sur les verres, la ferroélectricité, le comportement de la résistance à coefficient de température positif et même la ferroélectricité sont autant d'exemples d'inhomogénéités qui peuvent tous être sondés, avec succès, en utilisant cette technique[143,155–158]. Les mesures d'impédance ont été enregistrées à l'aide d'un analyseur de réponse en fréquence Solartron 1260. Un signal alternatif de 100 mV d'amplitude avec une fréquence allant de 1 MHz à 100 mHz à différentes températures.

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Chapitre 2: Comparative studies of synthesis, structure, optical and conductivity of the monoclinic phases $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$

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2.1. Introduction

Le deuxième chapitre est intitulé '*Comparative studies of synthesis, structure, optical and conductivity of the monoclinic phases Na₂Co₆Mn₂(PO₄)₆ et Na₂Co₆Ni₂(PO₄)₆*'. Deux nouveaux composés, Na₂Co₆Mn₂(PO₄)₆ et Na₂Co₆Ni₂(PO₄)₆ ont été synthétisés par une méthode à l'état solide aux températures respectives 800 °C et 850 °C. L'analyse d'affinement de Rietveld des diagrammes de diffraction des rayons X de la poudre a confirmé que les deux composés sont iso-structuraux, et cristallisent dans le système monoclinique avec comme groupe d'espace $P2_1/n$. Les spectroscopies Raman et Infrarouge ont confirmé la présence des groupements phosphates PO₄. L'analyse microstructurale a révélé que les particules, dont la taille varie entre 1 et 10 µm, ont une composition homogène. Les résultats XPS ont montré que tous les métaux de transition sont dans leur état d'oxydation +2 et que les états d'oxydation de Na, P et O sont respectivement +1, +5 et -2. Les énergies des bandes interdites (E_g) pour Na₂Co₆Mn₂(PO₄)₆ et Na₂Co₆Ni₂(PO₄)₆ basées sur les spectres de réflectance diffuse UV-vis ont été trouvées à 1.78 eV et 1.86 eV, respectivement. La conductivité ionique totale des deux composés est dans la gamme de $2,29 \times 10^{-5}$ à $1,21 \times 10^{-3}$ S/cm et $2,29 \times 10^{-5}$ à $6,58 \times 10^{-4}$ S/cm de 674 à 874 K, respectivement.

2.2. Les points forts de ce travail

- Synthèse à l'état solide des composés Na₂Co₆Mn₂(PO₄)₆ et Na₂Co₆Ni₂(PO₄)₆ à 800 °C et 850 °C, respectivement.
- Confirmation des phases pures de Na₂Co₆Mn₂(PO₄)₆ et Na₂Co₆Ni₂(PO₄)₆ par l'affinement de Rietveld.

- Des études de spectroscopie Raman et infrarouge ont confirmé la présence des liaisons P-O du groupe fonctionnel $(\text{PO}_4)^{3-}$.
- Les bandes interdites optiques de $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ et $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ ont été calculées.
- Des études de spectroscopie d'impédance ont été réalisées.

2.3 Contribution des auteurs

- ❖ **Erman Eloge Nzaba Madilla:** Conceptualisation, méthodologie, analyse formelle, investigation, traitement des données, rédaction du premier projet, révision et édition.
- ❖ **Steve Rousselot:** Mesure et traitement des résultats d'impédance.
- ❖ **Maxime Rioux:** Préparation des échantillons pour les mesures d'impédance.
- ❖ **Mickael Dollé:** Rédaction - Révision et édition de l'article.
- ❖ **Adam Duong:** Visualisation, Supervision, Acquisition de financement, Rédaction-révision et édition.

2.4. Conclusion

En somme, l'objectif principal est de faire une étude comparative sur la synthèse et la caractérisation des composés $\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$ ($\text{M} = \text{Mn}, \text{Ni}$) dopés au manganèse et au nickel. Les composés $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ et $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ ont été synthétisés à l'état solide aux températures respectives 800 °C et 850 °C. Cette différence de température de 50 °C entre les deux composés, prouve qu'avec le composé $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$, il est possible d'économiser de l'énergie par rapport au composé $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$. Les

énergies des bandes interdites optiques (E_g) de ces deux composés, $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ et $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$, ont des valeurs respectives 1.78 eV et 1.86 eV. La conductivité ionique totale de ces deux composés à la même température 874 K (600 °C) montre que le composé $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ a une conductivité de $1,21 \times 10^{-3}$ S/cm alors que celle de $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ est de $6,58 \times 10^{-4}$ S/cm.



Comparative studies of synthesis, structure, optical properties and conductivity of the monoclinic phases $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$

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ABSTRACT

New compounds, $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ have been synthesized by solid-state method. Rietveld refinement analysis of the powder X-ray diffraction patterns confirmed that both are isostructural, crystallizing in a pure phase with monoclinic $P2_1/n$ space group and showed no evidence of secondary phase peaks. Microstructural analysis revealed that the particles, which size range between 1 and 10 μm , have a homogeneous composition. The XPS results showed that all transition metals are in their +2-oxidation state and the oxidation states of Na, P and O are +1, +5 and -2, respectively. The band gap energies (E_g) for $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ based on the UV-vis diffuse reflectance spectra were found to be 1.78 eV and 1.86 eV, respectively. The total ionic conductivity of the two compounds is in the range of 2.29×10^{-5} – 1.21×10^{-3} S/cm and 2.29×10^{-5} – 6.58×10^{-4} S/cm from 674 to 874 K, respectively.

1. Introduction

In the past two decades, great progress has been made in the application of lithium-ion batteries (LIBs), and the development in this field is still very intense and dynamic, leading to an ever-increasing risk of lithium shortage in the world due to its earth's limitation [1–3]. Recently, sodium-ion batteries (NIBs) have gained much more attention owing to the natural abundance and cost of sodium and the close chemical properties to that of the LIBs [2–7]. Therefore, NIBs are being considered as a promising and feasible alternative to LIBs, notably for stationary applications. Research activities on sodium-ion batteries are growing worldwide but still require a great deal of basic and applied research.

The discovery of the highly interesting electrochemical properties of lithium iron phosphate LiFePO_4 [9–11], opened the way to the search of novel polyanion-based insertion hosts [8,10–20]. Lithium and sodium-transition metal phosphates with olivine-type structures of LiMPO_4 and NaMPO_4 ($M = \text{Mn, Fe, Co}$ and Ni) respectively, have attracted significant research interest as cathode materials for high power batteries with potential to power electric vehicles [15,21–30]. Design and synthesis of new cathode materials are one of the challenging

tasks to develop sustainable and safe NIBs. In this present work, we proposed to prepare $\text{Na}_2\text{Co}_6(\text{PO}_4)_6$ materials type by partial substitution of Co atom with Mn and Ni atoms to reduce the cost and the toxicity but also to study the electrochemical properties of these compounds. Baies *et al.* reported a study of $\text{Na}_2\text{Co}_6(\text{PO}_4)_6$ materials which was synthesized as a single crystal. The compound crystallizes in the monoclinic $P2_1/n$ space group. They also showed that this compound is an ionic conductor above 600 K, due to the mobility of sodium along the b axis of the structure [21]. The materials synthesized have been characterized by powder X-ray diffraction (PXRD), Raman and infrared spectroscopies, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) to determine their structures.

2. Material and methods

2.1. Synthesis of $\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$ ($M = \text{Mn}$ or Ni)

$\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$ compounds ($M = \text{Mn}$ or Ni) were prepared by high temperature solid state reaction, using the Vulcan Model A-550 furnace.

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The temperature accuracy of the furnace is ± 25 °C. The starting chemicals, MnO (Alfa Aesar, 99.99%) for $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and NiO (Alfa Aesar, 99%) for $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ and the Na_2CO_3 (Alfa Aesar, 98%), Co_3O_4 (Alfa Aesar, 99.7%) and $\text{NH}_4\text{H}_2\text{PO}_4$ (Alfa Aesar, 98%) for both samples were weighted according to the stoichiometric ratio and mixed homogeneously in an agate mortar. Samples were ground and placed in an alumina crucible. Pure powders were obtained, after several intermediate thermal treatments and grindings, by prolonged final treatment at 800 and 850 °C, respectively for $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ held at these temperatures for 10 h and cooled to room temperature.

2.2. Powder X-ray diffraction (PXRD) measurements and Rietveld analysis

X-ray diffraction patterns were acquired on a D8 Bruker diffractometer (Cu-K α radiation, θ -2 θ geometry, back monochromator). Data were recorded in an angular range between 10° and 70°2 θ for a total measurement time of 2 h using a step size of $\sim 0.006^\circ$ and a fixed divergence slit of 0.3°. The presence of a nearly single-phase material was identified by a ICSD database match. The Phase purities and lattice parameters determinations were carefully monitored by using the Rietveld method as implemented in TOPAS V6 [22].

2.3. Simultaneous thermal analysis (TGA)

The thermogravimetric analysis (TGA) was carried out on the $\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$ (M = Mn or Ni) compounds by a thermogravimetric analyzer device Diamond Pyris 6000 TGA/DTA apparatus from PerkinElmer in the temperature range between 100 °C and 850 °C using aluminum crucibles under N_2 flow at a heating rate of 20 °C/min. The temperature accuracy of the device is ± 0.5 °C.

2.4. Raman and infrared spectroscopies studies

The Fourier transform infrared (FTIR) absorption spectra of $\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$ (M = Mn, Ni) samples were recorded with a Nicolet iS 10 Smart FT-IR Spectrometer in the range of 4000 to 400 cm^{-1} . To investigate the homogeneity of the samples, Raman data were collected from various areas on the powders of $\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$. Raman spectra of the $\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$ (M = Mn, Ni) powders were measured on a ThermoScientist Raman DXR3 spectrometer with a green laser source of excitation wavelength of 532 nm.

2.5. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

The morphology characteristics of the synthesized powder was obtained by means of scanning electron microscopy (SEM) analysis using the secondary electron detector of a Hitachi model SU1510 scanning electron microscope operating at 30 keV. The EDX measurements was made to determine the elementary topographic composition of the powder samples of composition $\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$ (M = Mn or Ni) compounds. The measurements were carried out using the column EDX, OXFORD instrument, X-max 20 mm² microscope from Hitachi. The powder samples were made of pellets. Pellets were prepared by uniaxially pressing the powder followed by a subsequent isostatic pressing at a pressure of 700 kN. Pellets were then sputtered with a thin layer of gold on both sides. The mean particle diameter was determined using ImageJ software [23].

2.6. Solid-state ultraviolet-visible (UV-vis) spectroscopy

To evaluate the optical absorption properties of $\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$ (M = Mn or Ni) compounds, the solid-state ultraviolet-visible (UV-vis) spectroscopy was performed on the powders samples (pellets) at room

temperature in a diffuse reflectance mode using a UV/Visible Agilent Cary 60 spectrophotometer. Pellets were prepared by uniaxially pressing the powder followed by a subsequent isostatic pressing at a pressure of 700 kN. The reflectance versus wavelength data was recorded over a wavelength range of 800 nm–200 nm. The bandgaps of these compounds were further calculated by converting reflectance to absorption data according to the Kubelka–Munk equation (3) [24]. The bandgaps were estimated by using the Tauc Plot using equation (4) [25,26].

$\frac{\alpha}{S} = \frac{(1-R)^2}{2R}$ (3) here R, α , and S are the reflectance, the absorption, and scattering coefficients, respectively. $(\alpha h\nu)^n = A(h\nu - E_g)$ (4) where α , h, and ν are absorption coefficient, Planck's constant, and frequency of light. A is a proportionality constant, and E_g is the bandgap. The value of constant n determines the nature of bandgap: n = 2 and n = 1/2 value suggest direct and indirect bandgap, respectively.

2.7. X-ray photoelectron spectroscopy (XPS)

The X-ray photoelectron spectroscopy (XPS) was carried out to confirm the elements and the chemical state of transition metal ion in the compounds. X-ray photoelectron spectroscopy (XPS) was performed in a VG Escalab 220i-XL equipped with hemispherical analyzer, applying a Twin Anode X-Ray Source. The binding energies were calibrated using containment carbon (C 1s = 284.4 eV).

2.8. Impedance spectroscopy analysis (ISA)

To study the ionic conductivity behavior of the compounds depending on the content of Co/Mn and Co/Ni in $\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$ samples, the electrochemical impedance spectroscopy (EIS) was performed. Spark Plasma Sintering (SPS) using a Dr. Sinter Lab Jr. series 632Lx SPS was used for the densification of pellets. 150 mg of the powder was loaded into a Grafoil coated graphite die ($\phi = 8$ mm) and pressed between two graphite punches. The die was placed inside the SPS chamber between two graphite spacers and uniaxially pressed at 100 MPa for 15 min to maximize particle cohesion. The sintering was performed up to 750 °C at a 50 °C/min heating rate with a dwell of 5 min before cooling down to room temperature at the system inertia. The resulting pellets were then heated to 750 °C under air for 12 h, to calcinate the remaining Grafoil from the pellet surface. The impedance measurements were recorded using a Solartron 1260 frequency response analyzer. An AC signal of 100 mV amplitude with a frequency ranging from 1 MHz to 100 mHz at different temperatures ranging from 524 to 874 K. The temperature was controlled using a Biologic High Temperature Furnace (HTF).

3. Results and discussions

3.1. Thermal analysis

Thermogravimetric (TG) measurements were performed on the precursor powder in the temperature range 100–850 °C to precise phase formation temperature of $\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$ (M = Mn or Ni) samples. The TG curves of $\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$ (M = Mn or Ni) samples are shown in Fig. 1. As can be seen in Fig. 1, the two TG curves look almost the same. Thus, after the weight losses, both curves seem to reach a limit. Their weight loss stops at around 700 °C, which confirms the formation temperature of $\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$. Therefore, the $\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$ powders were calcined in the temperature ranges from 700 to 850 °C for 10 h in air atmosphere.

3.2. Crystal structure, morphology and chemical composition

The powder X-ray diffraction patterns of $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ were recorded, and the phase, $\text{Na}_2\text{Co}_6(\text{PO}_4)_6$ [21] of the materials were identified by a ICSD database match. The matching

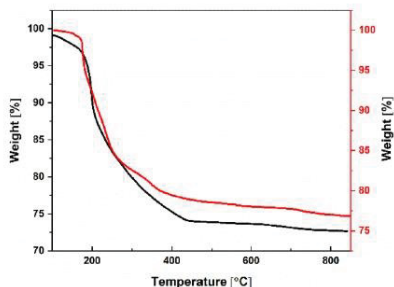


Fig. 1. TG curves of the mixed precursors for (black) $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and (red) $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

was further analyzed using the Rietveld method as implemented in TOPAS V6 [22]. The Rietveld analysis of $\text{Na}_2\text{Co}_6(\text{PO}_4)_6$ [21], $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ samples is displayed in Fig. 2.

The structure of $\text{Na}_2\text{Co}_6(\text{PO}_4)_6$ [21] was carried as the starting model for the main phase and was used for Rietveld refinement of $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$. The PXRDs recorded agree with that of the pattern of $\text{Na}_2\text{Co}_6(\text{PO}_4)_6$ in Ref. [21]. These are indexed with the monoclinic $P2_1/n$ space group. The profile factors which were found are less than 2% of existing patterns and refined patterns confirmed the goodness of refinement (Table 1) [27].

To confirm the purity of $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$, $\text{Na}_2\text{Co}_6(\text{PO}_4)_6$ was prepared by the solid-state reaction method at 900°C for 10 h. The phase formation of the prepared sample was confirmed by

Table 1

Number of parameters R-factors (%).

Samples	GOF	R_{exp}	R_{wp}	R_p
$\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$	1.05	3.52	3.69	2.93
$\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$	1.06	3.13	3.33	2.64
$\text{Na}_2\text{Co}_6(\text{PO}_4)_6$	1.12	1.05	1.18	0.94

PXRD with a D8 Bruker diffractometer (Cu-K α radiation, θ - 2θ geometry, back monochromator).

Fig. 2a shows the PXRD patterns of $\text{Na}_2\text{Co}_6(\text{PO}_4)_6$, $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$. It shows that all samples present similar diffraction patterns without impurity peaks. Indexation by a single monoclinic phase shows that peak positions agree well with ICSD database match of $\text{Na}_2\text{Co}_6(\text{PO}_4)_6$ [21].

Cell parameters of $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$, $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6(\text{PO}_4)_6$ [21] are given in Table 2. The structures of these compounds drawn using the Visualization for Electronic and Structural Analysis (VESTA) software [28] are shown in Fig. 3 and S1. Considering the ion sizes and the valence states, Mn^{2+} and Ni^{2+} ions are most likely occupying the Co^{2+} sites. The atomic coordinates were used to determine the structure of the series of $\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$ ($M = \text{Mn}$ or Ni) solid solutions. The position of the Mn and Ni atoms relative to Co in the different compounds is very difficult to determine with a laboratory XRD because these atoms have only one electron difference. The $\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$ ($M = \text{Mn}$ or Ni) solids show a layered structure like described by Baies et al. [21] and Hui Zhang et al. [29]. The details of Rietveld refinement and structural parameters of $\text{Na}_2\text{Co}_6(\text{PO}_4)_6$ [21], $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ are listed in Table S1, S2 and S3, respectively. The selected atoms distances are given in Table S4, S5 and S6 and their, the stacking of alternating layers can be $-\text{Co}(\text{PO}_4)-\text{Na}(\text{PO}_4)-\text{M}$ running along the crystallographic a -axis. The crystal

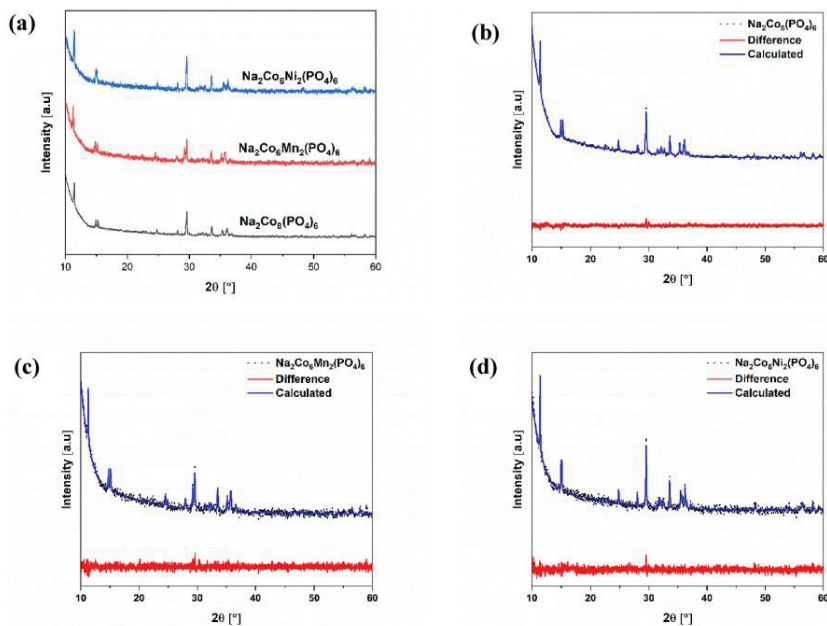


Fig. 2. (a) Comparison of PXRD patterns and their Rietveld refinements (b) $\text{Na}_2\text{Co}_6(\text{PO}_4)_6$, (c) $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and (d) $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$.

Table 2
Lattice parameters of $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$, $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$.

Parameters	Sample			
	$\text{Na}_2\text{Co}_6(\text{PO}_4)_6$ [21]	$\text{Na}_2\text{Co}_6(\text{PO}_4)_6$	$\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$	$\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a(Å)	6.339(1)	6.332(3)	6.359(9)	6.322(6)
b(Å)	9.867(1)	9.815(4)	9.788(13)	9.799(8)
c(Å)	15.301(2)	15.393(10)	15.565(3)	15.297(18)
β (°)	91.049(12)	91.830(7)	92.004(17)	90.70(12)
V(Å ³)	956	956.34(9)	968.3(3)	947.65(16)

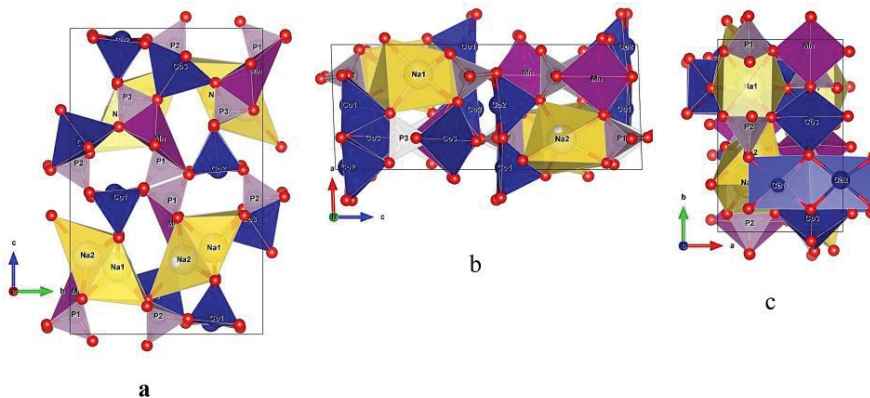


Fig. 3. Structure of $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$. (a)–(c) Projection along a , b and c -axis respectively. Conventions colour: PO_4 tetrahedra in purple, CoO_6 polyhedral in blue and NaO_6 in yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

structures comprise three-dimensional framework in the cobalt manganese phosphate and the cobalt nickel phosphate, respectively. In both compounds, the structure, $\text{Co}(1)\text{O}_5$ – $\text{Co}(3)\text{O}_5$ (pyramid), MnO_6 /NiO₆

(octahedron), and PO_4 (tetrahedra) form large six-sided tunnels along b -axis and three- or four-sided tunnels running along a -axis.

Based on the Rietveld refinement results, the unit cell volume in

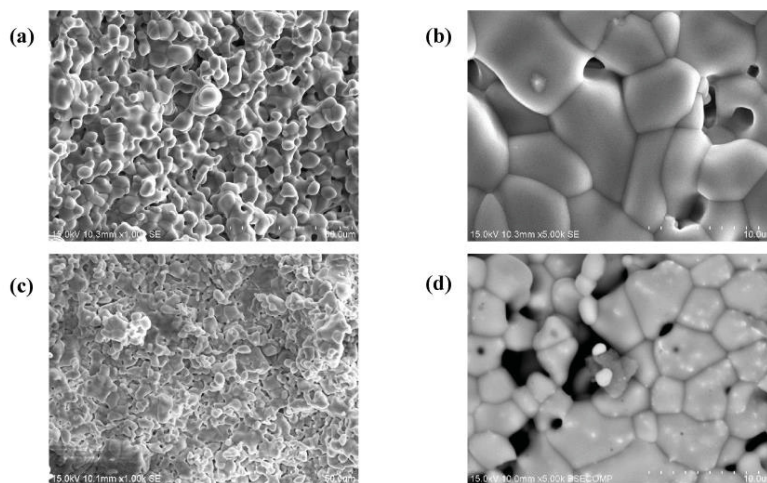


Fig. 4. SEM images with zooms areas showing the particle sizes of samples (a)–(b) $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and (c)–(d) $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$.

$\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ is bigger as compared to $\text{Na}_2\text{Co}_6(\text{PO}_4)_6$ [21] and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ samples (Table 2). This result is the consequence of smaller cell parameters a , c and β angle in the structures of the reference and Ni compounds. The bigger size of the Mn^{2+} ionic radius as compared to Co^{2+} and Ni^{2+} [30] can be used to explain the elongation of the unit cell parameters which induce an augmentation of the volume in $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$.

The morphology and particle size of the samples were determined by SEM. Fig. 4 show SEM micrographs of $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ which display uniform particle distributions in both samples.

However, for $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ the material is denser as can be seen in Fig. 4c-d. The spherical hollow particles have an average size between 1–10 μm and 1–6 μm for $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ respectively. These particles are micron-sized, which can increase the contact interface between the electrode and the electrolyte. Elemental analysis of the powders was carried out using energy dispersive X-ray spectroscopy (EDS). The EDS analysis confirms the presence of the Na, P, O, Co elements for both samples and Mn atoms for $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and Ni atoms for $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ (Fig. S3). The elemental mappings indicated that these elements are homogeneously distributed in the materials. The 1:3 ratio of M:Co (M = Mn or Ni) calculated using the EDS (Table 3) matches well with the chemical formula elucidated by XRD.

3.3. Raman and infrared spectroscopies

Fig. 5a displays the Raman spectra of $\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$ (M = Mn or Ni) samples. Series of Raman spectra took on different areas of the materials demonstrated that the composition of the polycrystalline phase is homogeneous for each sample (Fig. S4). The spectra of $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ reveals a band at 950 cm^{-1} and 949 cm^{-1} respectively which are attributed to the symmetric stretching mode of P–O bonds in $(\text{PO}_4)^{3-}$ units. The bands at the range of $960\text{--}1088\text{ cm}^{-1}$ in both samples can be assigned to asymmetric stretching modes of P–O bonds in $(\text{PO}_4)^{3-}$ units. The comparison of IR spectra of both Mn and Ni samples in Fig. 5b show that they have similar absorption bands between 1250 and 500 cm^{-1} . The bands between 900 and 600 cm^{-1} can be associated with the stretching vibrations of P–O bonds of PO_4 tetrahedra [31].

3.4. X-ray photoelectron spectroscopic analysis (XPS)

X-ray photoelectron spectroscopy (XPS) was employed to further investigate the elemental composition and chemical state of metal ions of $\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$ (M = Mn or Ni) samples. XPS spectra of the bulk samples are shown in Fig. 6, S5 and S6. The patterns for both materials are similar except for the extra peaks with the binding energy corresponding to Mn (II) 2p at $\sim 645.45\text{ eV}$ and Ni (II) 2p at $\sim 859.51\text{ eV}$ (see the inset in Fig. 6a and Fig. 6b) for $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ respectively. A summary of binding energy values of XPS peaks for both samples are given in Table 4 [32–35].

The oxidation states of sodium, cobalt, manganese, nickel, phosphorus, and oxygen were determined by the XPS analysis of $\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$ (M = Mn or Ni), leading to the following values: +1, +2, +2, +2, +5 and –2, respectively. XPS survey scan spectra of $\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$ (M = Mn or Ni) (Fig. 6) confirms the presence of Mn in $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$, Ni in $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ and Na, Co, P and O in both samples.

Table 3
Summary of EDS analysis of compounds $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$.

Sample	Element percentage (%)				
	O(%)	P(%)	Na(%)	Co(%)	Ni(%)
$\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$	56.4	16.2	5.6	16.5	5.4
$\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$	56.2	16.4	5.8	16.4	5.4

3.5. Optical and ionic conductivity properties

Diffuse-reflectance UV–vis spectra were recorded for $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ at room temperature (Fig. S7). The bands with maximum absorption were used to estimate the bandgaps. From the optical absorption edge study, the optical bandgap (Eg) of the Mn-doped compound, was found to be 1.78 eV. This value fit well with the brownish color (Figs. 7a and S8a). The Ni-doped one, presents a bandgap of 1.86 eV, which is in agreement with its purple-blue color (Figs. 7c and S8b).

For $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$, the values for direct and indirect bandgaps found from the Tauc plot method are 1.93 and 1.82 eV, respectively (Fig. 7b). Those for $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ are 1.92 and 1.88 eV, respectively. These bandgaps indicate that both materials can be classified as semiconductors.

Uniform Pellets of these samples are shown in Fig. S8. The measured geometric density was determined at 3.28 g/cm^3 for $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and 3.41 g/cm^3 for $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ reaching a compactness of 87.93 for Mn-doped and 89.50% for Ni-doped materials based on the calculated density of the crystal structure. Fig. 8a–b displays the Nyquist plots for both compounds recorded at 874 K. They exhibit high resistivity at room temperature like those described by Baies et al. [21]. Therefore, impedance measurements were made at high temperature. The Nyquist plots show either a semi-depressed semicircle or two semi-circles at high to medium frequencies. The high frequency semicircles observed for both samples represent the migration of the Na^+ ions within the bulk of the materials while the middle frequency range of the semicircle corresponds to the grain boundary contribution. At low frequencies, vertical line (capacitance), ascribed to the charge accumulation at the surface of the electrodes. This observation is usually expected in the case of typical ionic conductor material. Performing the measurement to lower frequencies could have evidenced this straight line. In contrast, an accumulation of points on Re(Z) axis would be seen for a mixed ionic-electronic conductor. Electronic resistances at room temperature using a Keithley 2400 source meter could not be measured though because the samples were too electronic resistive. Still the brownish color of materials, as shown in SI, points to a mix-electronic-ionic conduction.

Owing to the shape of the signal for both compounds, discriminating bulk from grain boundaries phenomenon is tricky. In the interest of comparison, total conductivity was fitted using the equivalent circuit shown in Fig. 8c. For that, it is possible to calculate the total ionic conductivity by using the following equation (5): $\sigma_T = \frac{L}{SR_T}$ (S/cm) (5).

where e , R_T and S are respectively, the thickness of the sample, the total resistance of the sample and the effective contact area of the sample with the electrode. The total conductivity values calculated can be seen in Fig. 8c, respectively for $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$. A straight line are found indicating an Arrhenius conduction mechanism typical for ceramics with ions hopping from site to site. The corresponding activation energies are calculated on the basis of the Arrhenius equation (6): $\sigma_T T = A \exp(-E_a/kT)$ (6).

At $400\text{ }^\circ\text{C}$, conductivities are in the range of 10^{-5} S/cm or lower are found for both materials. With increase of the temperature, these values increase up to $1.21 \times 10^{-3}\text{ S/cm}$ and $6.58 \times 10^{-4}\text{ S/cm}$ at $600\text{ }^\circ\text{C}$, respectively for Mn- and Ni-doped materials. The total activation energies were indeed calculated at 1099 and 911 meV for these two materials respectively.

For a deeper analysis, the bulk conductivity was fitted at high frequencies in the case of $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$, in order to dodge the impact of the processing, i.e. grain boundaries and sintering conditions, on the conductivity. Unfortunately, the semi-circles in the diagrams of $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ are much overlapped, making it hard to accurately separate the bulk from the grain boundaries contribution on the resulting total conductivity. Consequently, only the bulk conductivity of Mn-substituted sample is shown on Fig. 8d. It increases from $2.03 \times$

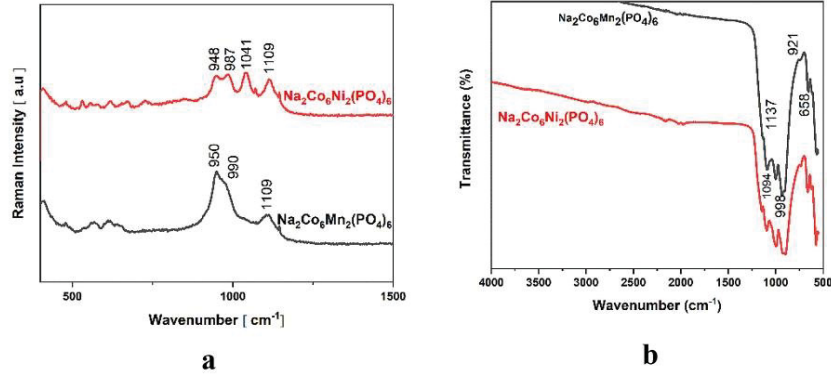


Fig. 5. (a) Raman and (b) Infrared spectra of Na₂Co₆M₂(PO₄)₆ (M = Mn or Ni).

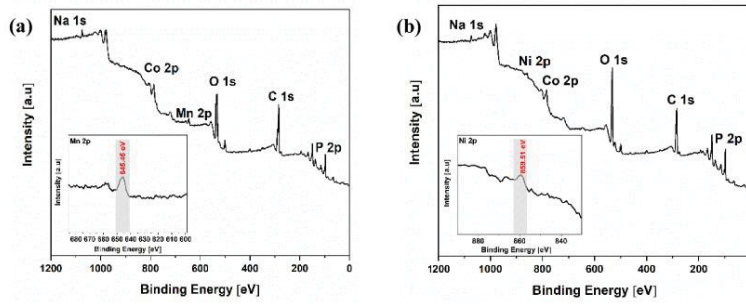


Fig. 6. Wide survey XPS spectra of (a) Na₂Co₆Mn₂(PO₄)₆ and (b) Na₂Co₆Ni₂(PO₄)₆.

Table 4

Binding energy values (eV) of XPS element peaks for Na₂Co₆Mn₂(PO₄)₆ and Na₂Co₆Ni₂(PO₄)₆.

Sample	Element									
	Mn	Co			Ni	O	P	Na		
	2p _{3/2}	2p _{1/2}	2p _{3/2}	2p _{1/2}	2p _{3/2}	1s	2p _{1/2}	2p _{3/2}	1s	
Na ₂ Co ₆ Mn ₂ (PO ₄) ₆	645.69	806.38	800.46	788.84	784.22	–	531.78	139	136.3	1073.72
Na ₂ Co ₆ Ni ₂ (PO ₄) ₆	–	807.7	802.66	790.68	786	857.72	531.61	–	138.04	1075.34

10⁻³ to 1.05 × 10⁻¹ S/cm with the rise of the temperature from 400 to 600 °C and an activation energy of 983 meV. These conductivities and activation energies are comparable to those from literature [21]. The ionic conductivity of Na₂Co₆(PO₄)₆ [21] is of the order of 10⁻⁶ S/cm at 300 °C. The ionic conductivity of our samples comparable to the values obtained by Baies *et al.* [21]. However, in terms of cost and toxicity, our samples are interesting because there is less cobalt atoms. Note that cobalt is more expensive than manganese and nickel. The ionic conductivity remains low compared to the best ionic conductors, on the order of 10⁻³ S/cm at room temperature, and the activation energy is somewhat high [36,37]. Nevertheless, considering the presence of Co in both compounds, and especially Mn in Na₂Co₆Mn₂(PO₄)₆ with potentially different electronic states, a proper treatment of the material, i.e., a reduction of the particle size, and a carbon coating similar to that used for the production of carbon-coated LiFePO₄ [38–41] could lead to a

new active electrode material for sodium batteries.

4. Conclusion

Na₂Co₆M₂(PO₄)₆ (M = Mn, Ni) were prepared by the solid-state method at 800 °C and 850 °C respectively. X-ray diffraction data confirmed that the samples were single phases with no detectable impurities and crystallized in the monoclinic structure with the space group P2₁/n. SEM indicate particle size distributions ranging between 1 and 10 μm, having a homogeneous composition in both materials. The optical bandgap investigation is 1.78 eV and 1.86 eV for Mn- and Ni-doped materials respectively which are in good agreement with the colors of the samples. The total conductivity for each compound suggests an ionic conduction mechanism. The range values are 2.29 × 10⁻⁵–2.29 × 10⁻³ S/cm and 2.29 × 10⁻⁵–6.58 × 10⁻⁴ S/cm from 674 to 874 K

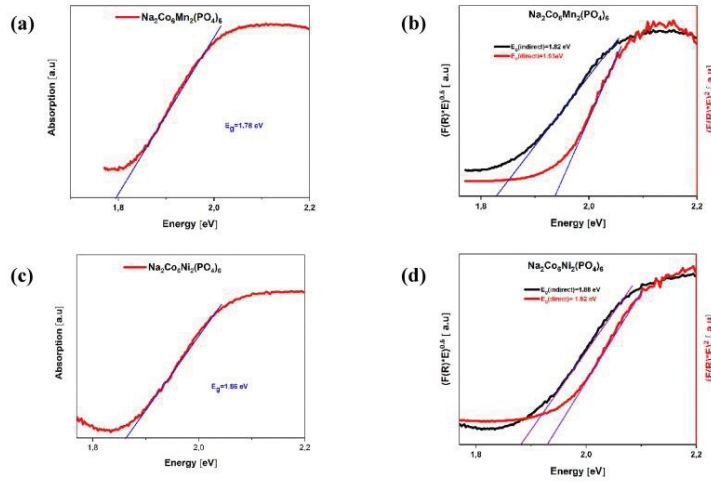


Fig. 7. Optical absorption spectrum and Tauc plots respectively for (a)–(b) $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and (c)–(d) $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$.

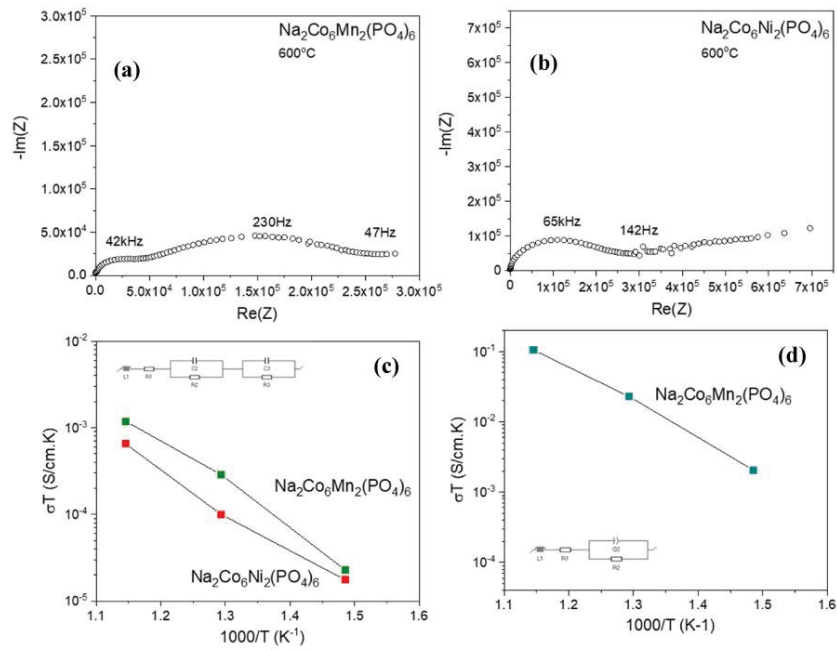


Fig. 8. (a)–(b) Nyquist plots of $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ respectively. (c) Arrhenius plots of the total conductivity for both samples and equivalent circuit used for its determination and (d) Arrhenius plots of the bulk conductivity of Mn-doped material with the equivalent circuit used.

for $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ respectively. Solid-state ultraviolet–visible spectroscopy (UV–vis) from the diffuse reflectance by using the Kubelka–Munk function and Tauc's relation and impedance studies indicate that both materials display interesting properties as semiconductors.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.solidstatedsciences.2021.106779>.

Author statement

Erman Eloge Nzaba Madilla: Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing first draft–review & editing. **Steeve Rousselot:** Impedance spectroscopy measurement and Software. **Maxime Rioux:** Sample preparation for Impedance study. **Mickael Dollé:** Writing–Reviewing and Editing. **Adam Duong:** Visualization, Supervision, Funding acquisition, Writing–review & editing.

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Chapitre 3: Synthesis of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ via sol-gel and solid-state methods

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3.1. Introduction

Le troisième chapitre intitulé ‘ Synthesis of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ via sol-gel and solid-state methods’, s’intéresse à la synthèse d’un nouveau composé, $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ par deux méthodes (l’état solide et sol-gel) respectivement aux températures respectives 800 °C pendant 10 h et 800 °C pendant 5 h. Les poudres obtenues ont été caractérisée par la diffraction des rayons-X et l’analyse de Rietveld a confirmé que les phases étaient pures. La présence des groupements phosphates par les spectroscopies Raman et Infrarouge a été confirmée. La microscopie électronique à balayage et la spectroscopie de dispersion d’énergie ont révélé respectivement, la distribution uniforme de la taille des particules et l’homogénéité de la composition dans les deux échantillons. Le troisième aspect de ce chapitre, montre à travers la spectrophotométrie en Réflectance Diffuse, en utilisant l’équation de Kubelka-Munk et les tracés de Tauc que ces composés sont des semiconducteurs. L’étude de l’impédance électrochimique sur ces composés, ont aidé d’évaluer la conductivité de ces composés.

3.2. Les points forts de ce travail

- Synthèse a l’état solide de $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ à 800 °C pendant 10 h.
- Synthèse par sol-gel de $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ à 800 °C pendant 5 h.
- Confirmation des phases pures de $\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-ST}$ et $\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-SG}$ par affinement de Rietveld.
- Des études de spectroscopie Raman et infrarouge ont été réalisées.
- Les bandes interdites optiques de $\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-ST}$ et $\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-SG}$ ont été calculées.

- Des études de spectroscopie d'impédance ont été réalisées.

3.3 Contribution des auteurs

- ❖ **Erman Eloge Nzaba Madila:** Conceptualisation, méthodologie, analyse formelle, investigation, Recueil de données, Logiciels, traitement des données, rédaction du premier projet, révision et édition.
- ❖ **Yasmine Benabed:** Préparation des échantillons pour les mesures d'impédance, révision et édition.
- ❖ **Prabhjyot Kaur:** Méthodologie, révision et édition.
- ❖ **Steve Rousselot:** Mesure et traitement des résultats d'impédance and logiciels, révision et édition.
- ❖ **Mickaël Dollé:** Rédaction- révision et édition.
- ❖ **Adam Duong:** Visualisation, Supervision, Acquisition de financement, Rédaction-révision et édition.

3.4. Conclusion

En résumé, le but principal était de faire une étude comparative sur la synthèse du composé $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ par deux techniques, l'état solide et sol-gel. Les phases $\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-ST}$ et $\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-SG}$ ont été obtenues respectivement aux températures respectives 800 °C pendant 10 h et 800 °C pendant 5 h. Cette différence de 5 h dans la synthèse est très utile non seulement pour économiser de l'énergie, mais aussi pour gagner en temps. Les énergies des bandes interdites optiques (E_g) de ces deux composés, $\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-ST}$ et $\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-SG}$, ont des valeurs respectives 1.79 eV et 1.78 eV.

La conductivité ionique totale de ces deux composés à la même température 300 °C montre que le composé $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ a une conductivité de l'ordre 10^{-4} S/cm alors que celle de $\text{Na}_2\text{Co}_8(\text{PO}_4)_6$ est de l'ordre 10^{-6} S/cm.



Synthesis of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ by sol-gel and solid-state methods

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ABSTRACT

A new polycrystalline material $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ has been synthesized by solid-state (ST) and sol-gel (SG) methods and characterized using powder X-ray diffraction (XRD) to solve the structure, which is found to crystallize in the monoclinic system with a $P2_1/n$ space group. Scanning electron micrographs showed the particles as aggregates with grain sizes ranging from 8 to 35 μm and 1 to 20 μm , for $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG, respectively. Energy-dispersive X-ray Spectroscopy (EDS) confirms the presence of Na, Co, P, O elements and their homogenous distribution in the samples. The X-ray photoelectron spectroscopy (XPS) results indicate that the oxidation states for these elements are Na(I), Co(II/III), P(V) and O(-II). The optical bandgaps of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG were estimated to be 1.79 eV and 1.78 eV, respectively, based on the UV-Vis diffuse reflectance spectra. The ionic conductivity for both samples is found to be 3.7×10^{-4} S/cm at 300 °C and 6.53×10^{-2} S/cm at 450 °C.

1. Introduction

The discovery of the properties of LiFePO_4 [1,2] compound as a cathode material in lithium-ion batteries (LIBs), marks the beginning of the research of new polyanionic materials [1–4]. LiFePO_4 belongs to the family of alkali (A) and transition metal (M) phosphates of the general formula AMPO_4 [5–12] which have been widely studied for their interesting electrochemical properties. By varying the type of A and transition metal (M) cation, and by appropriate chemical substitutions at the A and M positions in their crystal structures, the physical and chemical properties of these compounds can be improved. Thus, the AMPO_4 family of alkali (A) and transition metal (M) phosphates, emanates from another family of alkali (A) and transition metal (M) phosphates of general formula $\text{A}_{2-2x}\text{M}_{8-x}(\text{PO}_4)_6$ ($x = 2$). Fewer compounds of this group, $\text{A}_{2-2x}\text{M}_{8-x}(\text{PO}_4)_6$, have been studied, although in some cases they show the same properties as AMPO_4 . For example, in the case of the $\text{Na}_{2-2x}\text{Co}_{8-x}(\text{PO}_4)_6$ group, only three compounds have been studied, the $\text{Na}_2\text{Co}_8(\text{PO}_4)_6$ [13] (for $x = 0$), $\text{Na}_4\text{Co}_7(\text{PO}_4)_6$ [14] (for $x = 1$) and NaCoPO_4 [15–17] (for $x = 2$). In view of the above, one can note the difference between the $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ phase and the following known phases of NaCoPO_4 and $\text{Na}_2\text{Co}_8(\text{PO}_4)_6$. The monophosphate α - NaCoPO_4 , β - NaCoPO_4 and μ - NaCoPO_4 compounds crystallized in the orthorhombic ($Pnma$), hexagonal ($P6_3$) and monoclinic ($P2_1/n$) system, respectively

[18]. However, the crystal structure of $\text{Na}_2\text{Co}_8(\text{PO}_4)_6$ is monoclinic with $P2_1/n$ space group [13]. Thus μ - NaCoPO_4 , $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_8(\text{PO}_4)_6$ crystallize in a monoclinic structure with $P2_1/n$ space group. The comparison between our target compound, $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ and similar compounds is limited for the simple reason that the compound $\text{Na}_2\text{Co}_8(\text{PO}_4)_6$ for example has only been synthesized by single crystal and characterized by X-ray diffraction (XRD) and electrochemical impedance spectroscopy (EIS). The $\text{Na}_4\text{Co}_7(\text{PO}_4)_6$ compound was only synthesized using the hydrothermal method and characterized by XRD.

Rechargeable batteries are important devices for storing energy and are used in a multitude of devices including laptops, cell phones, cameras vehicles and so forth. Currently, lithium is the most widely used alkaline element in batteries. Although LIBs are efficient energetic technology, they suffer from several drawbacks such as the expensive nature of lithium which is due to its limited availability in the earth's crust and, in extraction causing environmental impact. One of the promising substitutes to overcome these shortcomings associated with LIBs is sodium-ion batteries (NIBs) which are cheap due to the great abundance of sodium and are environmentally friendly [3]. Besides, NIBs due to their high structural stability, have simple reaction mechanisms and high structural diversity [7,10,19–21]. Even though the development of research activities on NIBs is increasing worldwide, it still requires a lot of input in terms of fundamental and applied research on efficient novel

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sodium-based materials. Among others, the lithium and sodium transition metal phosphates of olivine-type materials structure, LiMPO_4 [10–12,22,23] and NaMPO_4 ($M = \text{Mn, Fe, Co}$ and Ni) [8,24], have attracted increasing attention and considerable research interest as cathode materials for rechargeable batteries. Studying phosphates as cathode materials can be justified by the strong P–O bond and the significantly larger electronegativity of $(\text{PO}_4)^{3-}$ groups which increases the structural stability of the electrode; and the ionic character of the M–O bonds [25]. The diminution of the covalent character of M–O linkage reduces the separation between the bonding and antibonding orbitals, giving rise to a higher cell potential that helps to boost the electrochemical performance of materials. So far, only a few Na–Co–P–O system-based materials such as $\text{Na}_2\text{Co}_8(\text{PO}_4)_6$ [13], $\text{Na}_4\text{Co}_7(\text{PO}_4)_6$ [14], $\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$ ($M = \text{Mn}$ or Ni) [26] and NaCoPO_4 [27], have been reported to have remarkable features such as open framework with large tunnels suggesting the possibility of high mobility for the sodium cations. In this study, we are interested in $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$, a new compound derived from the $\text{Na}_{2+2x}\text{Co}_{8-y}(\text{PO}_4)_6$ family (with $x = 0.5$ and $y = 1$), synthesized by sol-gel ($\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG) and solid-state ($\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST) methods. We have evaluated which of the synthesis methods (ST and SG) gives the best properties to the material required for NIBs. The two structures are elucidated by powder X-ray diffraction (PXRD) and Rietveld refinement. The structures of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG and $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST prove to belong to the monoclinic system. The electrochemical EIS measurement indicates that $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ prepared by both methods, behaves as an ionic conductor above 300 °C.

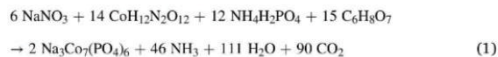
2. Experimental section

2.1. Synthesis procedure

All chemical reagents were purchased from commercial sources and used as received without further purification. The sodium cobalt phosphate powders were prepared by conventional solid-state and sol-gel methods using the Vulcan Model A-550 furnace. The temperature accuracy of the furnace is $\pm 25^\circ\text{C}$.

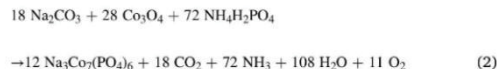
2.1.1. Synthesis of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG

In the sol-gel method, stoichiometric amounts of sodium nitrate, NaNO_3 (Sigma-Aldrich, $\geq 99.0\%$); cobalt(II) nitrate hexahydrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, 98%) and ammonium dihydrogen phosphate, $\text{NH}_4\text{H}_2\text{PO}_4$ (Alfa Aesar, 98%) were dissolved separately in de-ionized water and mixed thoroughly (eq. (1)). The solution was stirred continuously with gentle heating ($\sim 60^\circ\text{C}$) till a homogeneous solution was obtained. Citric acid solution was then added to the solution mixture which acted as a complexing and gelling agent. This was followed by stirring the solution for another 2–3 h after which it was poured on a china dish and heated on a water bath. Heating was continued till the formation of a thick gel at 80°C which was dried at 120°C in an oven to form a powder. The powder was then ground in a pestle mortar and calcined at 800°C for 5 h to produce the final homogeneous single phase of highly crystalline $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG.



2.1.2. Synthesis of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST

$\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ was also synthesized by solid-state method. A stoichiometric ratio of Na_2CO_3 (Alfa Aesar, 98%), Co_3O_4 (Alfa Aesar, 99.7%) and $\text{NH}_4\text{H}_2\text{PO}_4$ (Alfa Aesar, 98%) were ground in an agate mortar and then placed in a crucible. The powder mixture was annealed at 500°C for 5 h. After cooling to room temperature, the sample was reground and annealed a second time at 800°C for 10 h to produce $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST (eq. (2)).



2.2. Thermogravimetric analysis

Using a Perkin-Elmer TGA Diamond Pyris 6000, the thermal analysis of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ precursors (~ 4 mg) was performed, with a heating rate of $20^\circ\text{C}/\text{min}$ in the temperature range of 100 and 850°C in alumina crucibles under N_2 flow. The temperature accuracy of the device is $\pm 0.5^\circ\text{C}$.

2.3. Powder X-ray diffraction measurement and rietveld refinement

To determine the crystal structures of both compounds synthesized by solid-state and sol-gel methods, PXRD was performed using a Bruker D8 Advance diffractometer equipped with $\text{Cu-K}\alpha$ radiation. XRD patterns were collected between 10 and 60° in the 2θ configuration in a continuous scan mode with a step size of $\sim 0.006^\circ$ and a fixed divergence slit of 0.3° for a total measurement time of 2h. After identifying the presence of a nearly single-phase material by a match from the ICSD database, the analysis of the structure of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ using the XRD data was performed using the Rietveld method with the program TOPAS V6 [28].

2.4. Raman and Infrared spectroscopies studies

Raman and Fourier transform infrared (FTIR) absorption spectra of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ samples were recorded, respectively, using a Thermo-scientist Raman DXR3 spectrometer with a green laser source of excitation wavelength 532 nm and a Nicolet iS 10 Smart FT-IR spectrometer in the range of 4000 to 400 cm^{-1} .

2.5. Scanning electron microscopy and energy dispersive X-ray spectroscopy

The microstructure of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and SG was studied by SEM using the secondary electron detector of a Hitachi model SU1510 scanning electron microscope operating at 30 keV. The elemental topographic composition of the two samples was recorded using an EDS column, OXFORD instrument, Hitachi X-max 20 mm^2 microscope. The powder samples were made of pellets. Pellets were prepared by uniaxially pressing the powder followed by a subsequent isostatic pressing at a pressure of 700 kN. The particle size was determined using ImageJ [29].

2.6. X-ray photoelectron spectroscopy

The X-ray photoelectron spectroscopy (XPS) was carried out to evaluate the valence states of the metals/ions in solids. XPS was performed using a VG Escalab 220i-XL equipped with a hemispherical analyzer, applying a Twin Anode X-Ray Source. The binding energies were calibrated using containment carbon ($\text{C } 1s = 284.4$ eV).

2.7. Solid-state ultraviolet-visible spectroscopy

The optical absorption properties of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ compounds, were recorded at room temperature in a diffuse reflectance mode using a UV/Visible Agilent Cary 60 spectrophotometer by solid-state UV-Vis spectroscopy on pellets. Pellets were prepared by uniaxially pressing the powder followed by a subsequent isostatic pressing at a pressure of 700 kN. The reflectance versus wavelength data were recorded over a wavelength range of 800 nm– 200 nm. The bandgaps of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and SG were calculated by converting the reflectance to absorption according to the Kubelka–Munk equation (3) [30] and the bandgaps were estimated using the Tauc Plot following equation (4) [31,32].

$$\frac{\alpha}{S} = \frac{(1-R)^2}{2R} \quad (3)$$

here R , α , and S are the reflectance, the absorption, and scattering coefficients, respectively.

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (4)$$

where α , h , and ν are the absorption coefficient, Planck's constant, and frequency of light respectively. A is a proportionality constant, and E_g is the bandgap. The value of constant n determines the bandgap's nature: $n = 2$ and $n = 1/2$ value suggest direct and indirect bandgaps, respectively.

2.8. Electrochemical impedance spectroscopy

Spark Plasma Sintering (SPS) was used to densify $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and SG powders into pellets (Dr. Sinter Lab Jr. series 632Lx SPS). 150 mg of powder was loaded into a Grafoil coated graphite die ($\phi = 8$ mm) and pressed between two graphite punches. The die was placed inside the SPS chamber between two graphite spacers and uniaxially pressed at 100 MPa for 15 min to maximize particle cohesion. The sintering was performed up to 750 °C at a 50 °C/min heating rate with a dwell of 5 min before cooling down to room temperature at the system inertia. The resulting pellets were then heated to 750 °C under air for 12 h, to calculate the remaining Grafoil from the pellet's surface. EIS measurements were recorded using a Solartron 1260 frequency response analyzer. An AC signal of 100 mV amplitude was employed with a frequency ranging from 1 MHz to 100 MHz at different temperatures ranging from 300 to 450 °C. The temperature was controlled using a Biologic High Temperature Furnace (HTF).

3. Results and discussion

3.1. Thermal analysis

TGA was carried out on the precursor powders in a temperature range of 100 °C to 850 °C to monitor the phase formation temperatures. Fig. 1 shows the thermal behavior of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and SG. It is seen from Fig. 1 that the mass decreases as temperature increases which describe the decomposition processes of the mixture. It displays three discrete weight-loss steps up to 800 °C, and no further weight loss. The observed initial (from 100 to 200 °C) weight loss is attributed to the evaporation of residual water. The weight loss in the second temperature range from

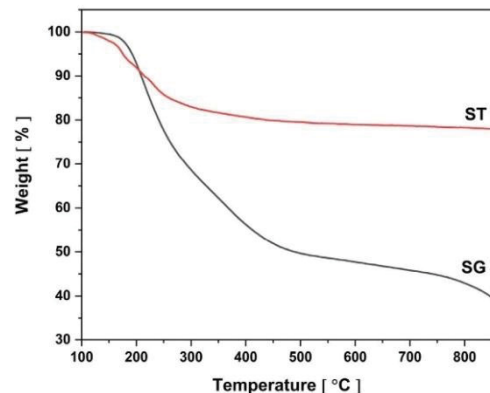


Fig. 1. TG curve of the precursor mix of (red) $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and (black) $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG.

200 to 400 °C is due to the decomposition of NH_3 . The weight loss in the third temperature range from 400 to 800 °C can be assigned to the release of oxides of carbon during the pyrolysis of citric acid [21,33]. Hence, we have calcined the precursors at 800 °C for 5h and 10 h respectively to prepare $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG and $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST.

3.2. Structural analysis

Samples named $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and SG respectively, were characterized by PXRD and refined by Rietveld (Fig. 2a and Fig. S1, respectively) to elucidate their structures, based on the structure of $\text{Na}_2\text{Co}_8(\text{PO}_4)_6$ [13].

X-ray powder diffraction patterns of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and SG were recorded, and results from these samples were used for phase identification using DIFFRAC.EVA [34] software. The presence of a nearly single-phase material, $\text{Na}_2\text{Co}_8(\text{PO}_4)_6$ phase was identified by ICSD database match. To more confirm this, the data were analyzed by using the Rietveld method as implemented in TOPAS V6 [28]. The structure of $\text{Na}_2\text{Co}_8(\text{PO}_4)_6$ [13] was chosen as the starting model for the main phase and was used for the Rietveld refinement of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and SG. The Rietveld analysis of the samples is shown in Fig. 2. The recorded PXRDs are in agreement with the model of $\text{Na}_2\text{Co}_8(\text{PO}_4)_6$ in Ref. [13].

All samples show similar diffraction patterns and crystallized in the monoclinic space group $P2_1/n$ like $\text{Na}_2\text{Co}_8(\text{PO}_4)_6$ [13] compound. Crystallographic data are provided in Table 1. According to the PXRD, the sol-gel method provides a pure phase material (Fig. 2a). The structure of the compound is represented using Visualization for Electronic and Structural Analysis (VESTA) [35] software (Fig. S2). A refinement of the data of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG with TOPAS6 software [36] confirms no additional peaks indicating the absence of impurities (black pattern Fig. 2b). However, an additional small peak (at about 30° in the 2θ configuration) appears in $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST pattern (red pattern, Fig. 2b) which is assigned to the $\text{Co}_2(\text{PO}_3)_4$ phase. After a rough refinement, the percentage of the main phase in $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST was found to be ~97.16 wt%, while $\text{Co}_2(\text{PO}_3)_4$ was ~2.84 wt%. $\text{Co}_2(\text{PO}_3)_4$ secondary phase found in the $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST sample is considered acceptable because the detection limit of phases in a mixture is generally in the range of 2-3 wt%, meaning that if the sample is thought to be pure by XRD, it is still possible for a small amount of secondary phases to be present below the detection limit of the technique [37]. Based on the Rietveld refinement results, the unit cell volume of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG was found to be smaller than that of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST (Table 1). As shown in Table 1, the variations of cell parameters a , b and c between the synthesized samples are relatively small. The refinement for both samples was stable and gave low R-factors, suggesting that single-phase $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and SG can be obtained under both methods (Table 1, more information on R factor can be seen [38]). The decrease of the cell volume in $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG is caused by the decrease of the cell parameters a , b and c as compared to $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST (Table 1). The monoclinic angle β decreases in both samples and remains close to 90° (Table 1). The atomic parameters of these compounds have been listed in Tables S1 and S2.

Thus, from Table 1, it is evident that there is a small difference in the lattice parameters obtained between $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and SG methods. This is because, even though the conditions for the SG process are optimized to obtain the almost single phase $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$, the optimized condition for the ST process could only minimize the secondary phases to certain limit. Thus, the same structural model leads to a small difference in lattice parameters.

3.3. Raman and Fourier-transform infrared spectroscopy

Raman data were collected from different areas on $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and SG (Fig. 3a), to confirm the homogeneity of the samples and the presence of $(\text{PO}_4)^{3-}$. All the Raman spectra obtained were similar (Fig. S3), which shows that the composition of the polycrystalline phases

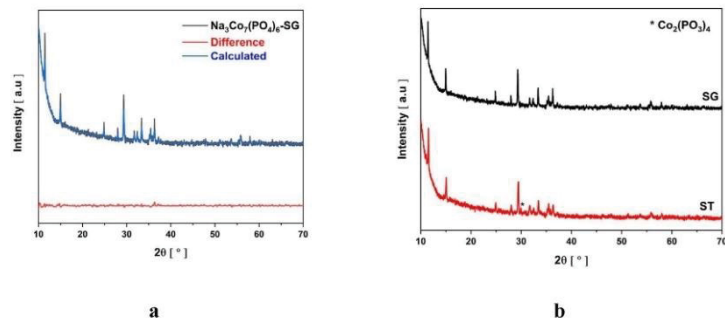


Fig. 2. (a) Rietveld refinement of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG, (b) Powder X-ray diffraction patterns of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG and $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST.

Table 1

Lattice parameters and Number of parameters R-factors (%) of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG, $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and $\text{Na}_2\text{Co}_6(\text{PO}_4)_6$.

Parameter	Sample		
	$\text{Na}_2\text{Co}_6(\text{PO}_4)_6^{\text{a}}$	$\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST	$\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a(Å)	6.339(1)	6.355(6)	6.348(4)
b(Å)	9.867(1)	9.916(8)	9.912(5)
c(Å)	15.301(2)	15.280(18)	15.270(11)
β (°)	91.049(12)	90.279(13)	90.172(9)
$V(\text{Å}^3)$	948.726	962.87(16)	960.92(10)
		GOF = 1.13	GOF = 1.10
		Rexp = 1.50	Rexp = 1.59
		Rwp = 1.68	Rwp = 1.75
		Rp = 1.33	Rp = 1.38

is homogeneous. The bands at 975 and 946 cm^{-1} can be attributed to the ν_1 symmetric stretching vibration of $(\text{PO}_4)^{3-}$. On the other hand, the bands in the range of 1030–1555 cm^{-1} in both samples could be attributed to the asymmetric stretching modes of P–O bonds in $(\text{PO}_4)^{3-}$ units. The others weak bands observed at 621 cm^{-1} and 844 cm^{-1} most likely correspond to the antisymmetric ν_3 stretching vibration of $(\text{PO}_4)^{3-}$ [39, 40]. FTIR were recorded to determine the main characteristics bonds in $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and SG (Fig. 3b). The comparison of both spectra shows that the samples have similar absorption bands. In both spectra, the absorption band between 1250 and 500 cm^{-1} can be associated with the stretching vibrations of P–O bonds of PO_4 tetrahedra [41].

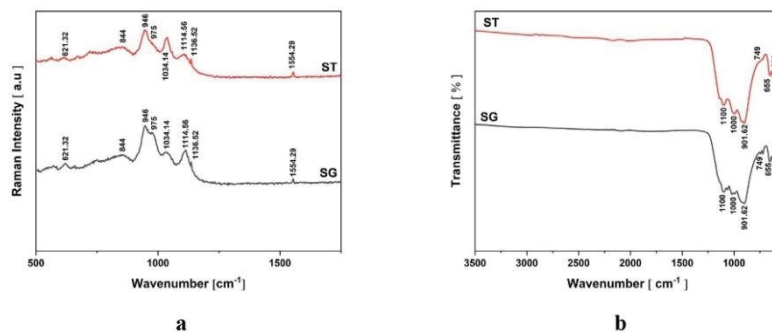


Fig. 3. (a) Raman and (b) Infrared spectra of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG and $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST.

3.4. Scanning electron microscopy and energy-dispersive X-ray spectroscopy

Fig. 4 shows the EDS mapping of Na, Co, P and O elements in $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and SG compounds. EDS mapping of Na, Co, P and O shows the homogeneous distribution of the elements across the two samples.

The elemental ratios of Na and, Co were found to be $\sim 2.8:6.7$ and $\sim 2.8:6.5$, respectively for $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and SG. The ratio Na:Co calculated using the EDS matches quite well with the chemical formula of both compounds. The SEM images obtained for $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ are presented in Fig. 5. For both compounds, aggregates consist of entangled particles on the surface. These aggregates are well defined specially in the encircled areas. The particle sizes for $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG (1–20 μm), Fig. 5c and d are smaller than those of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST (8–35 μm), Fig. 5a and b. This indicate that the sol-gel method allows the reduction of particle sizes and a better dispersion of the grains. Indeed, a small particle size can shorten the diffusion path of the inserted or deintercalated ions, which improves the intercalation process. Also, smaller particles provide a larger contact surface with the electrolyte and the conductive additive.

3.5. X-ray photoelectron spectroscopy

Fig. 6 shows the XPS patterns of the whole spectrum of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and SG samples. The narrow spectra of all the elements for these compounds are presented in Fig. S4 and Fig. S5.

The binding energy of the central Na(1s) level emission peak for

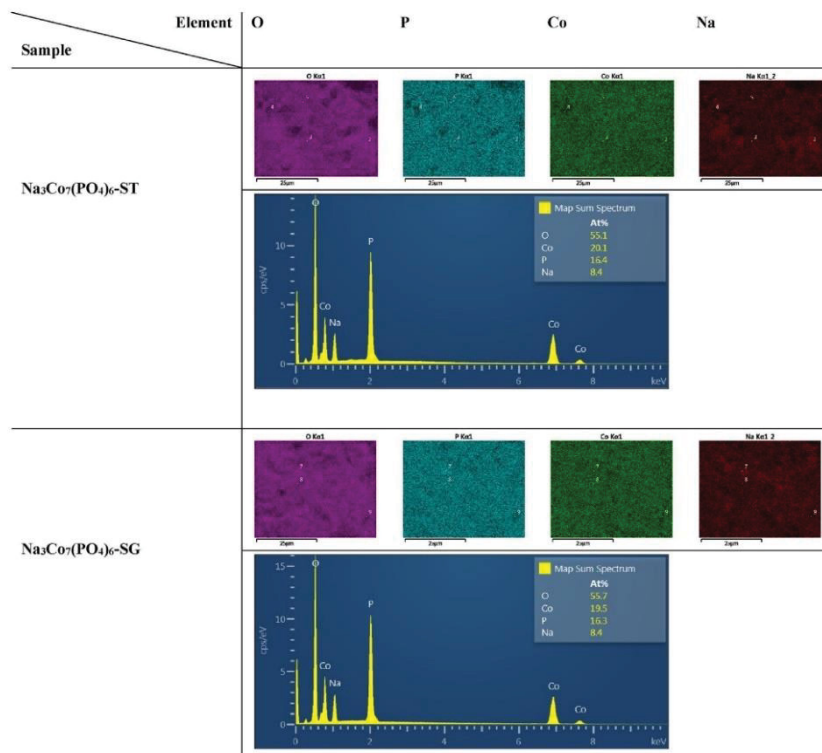


Fig. 4. EDS mapping (Na, Co, P and O) elemental distribution of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-ST}$ and -SG.

$\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-ST}$ and -SG compounds is located at 1075.50 eV and 1074.22 eV, respectively. These values are close to that of NaCl [42,43]. The Co2p region shows two intense peaks in both samples (ST and SG). For the ST sample, one peak at ~ 786 eV, and another at ~ 802 eV. For SG, one at ~ 784 eV and at ~ 800 eV, as well as the corresponding weak satellite peaks at higher energies (Figs. S4 and S5). According to the literature, the peaks at 786, 784, 800 and 802 eV are attributed to Co^{2+} ions. The other weak peaks are attributed to Co^{3+} in the normal sites of the $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ structure. Due to the annealing temperature, the peaks corresponding to Co^{3+} and Co^{2+} ions are slightly shifted to higher energies. This may indicate a release of the defective sites on the surface. This proves that for both compounds, ST and SG, Co presents Co^{3+} and Co^{2+} ions in the following way: $6x(\text{Co}^{2+})$ and $1x(\text{Co}^{3+})$, suggesting that the most intense peaks should be associated with Co^{2+} . For $\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-ST}$ and $\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-SG}$ samples, the P(2p) spectrum shows that the binding energy is located at 138 eV and 136 eV, respectively. These energies can be assigned to the $(\text{PO}_4)^{3-}$ group of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$. Finally, in our case the oxidation state of oxygen in the material was deduced by knowing the oxidation state of Na, Co and P. This leads to the O^{2-} ions of the $(\text{PO}_4)^{3-}$ group [39,40,44,45,47,48].

3.6. Optical and ionic conductivity properties

Diffuse-reflectance spectroscopy (DRS) UV-vis measurements were carried out on $\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-ST}$ and -SG at room temperature to estimate

their bandgaps. After running the optical absorption measurement, the optical bandgap (E_g) of these materials were found to be 1.79 eV and 1.78 eV respectively. Their direct and indirect bandgaps were also estimated by using Tauc's plot as shown in Table 2. From the analysis (Fig. 7) and the values reported in Table 2, a slight variation in the E_g value is observed as a function of the chosen transition of the two compounds synthesized by the sol-gel and the solid-state methods.

This small variation is mainly observed in the direct and indirect bandgaps of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-ST}$ and -SG. The compound synthesized by sol-gel exhibits slightly smaller values compared to the solid-state method. However, both materials have small values of optical, direct and indirect bandgaps energies which is attributed to semiconductors.

As the conductivity plays a vital role to estimate the electrochemical performance, we study the Na-ion conductivity using EIS on both $\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-ST}$ and -SG. The Nyquist plots and the fitted curves are shown in Fig. 8. At low temperatures (from 25 to 300 °C), the samples are too resistive and hence impedance cannot be measured. Above 300 °C, it was possible to measure the electrochemical impedance for both samples. The Nyquist plots recorded at 350, 400 and 450 °C for both materials show a depressed semicircle at high frequencies, followed by a tail at low frequencies. Typically, inorganic ionic conductors present in these EIS Nyquist diagrams two semi-circles at different frequency ranges that correspond to the bulk resistance at high frequencies and to the grain boundary resistance at mid-range frequencies. The tail observed at lower frequencies is attributed to the accumulation of sodium ions on the

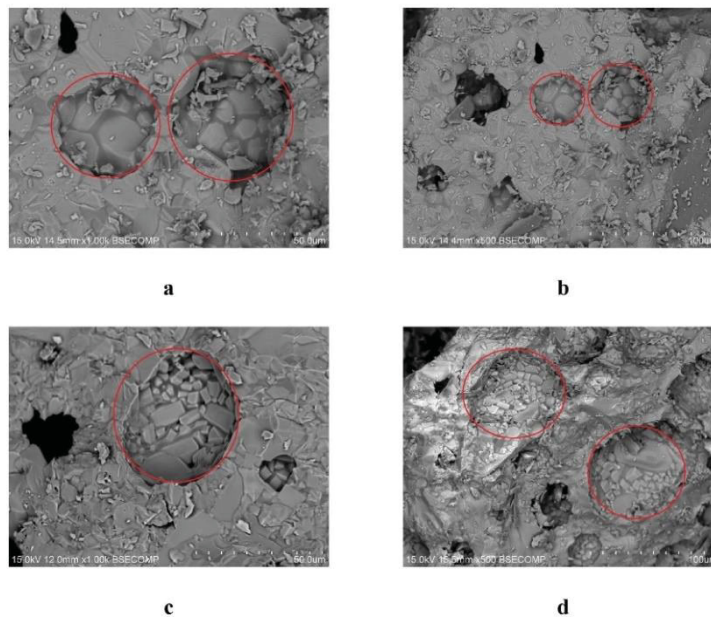


Fig. 5. SEM images of (a, b) $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and (c, d) $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG.

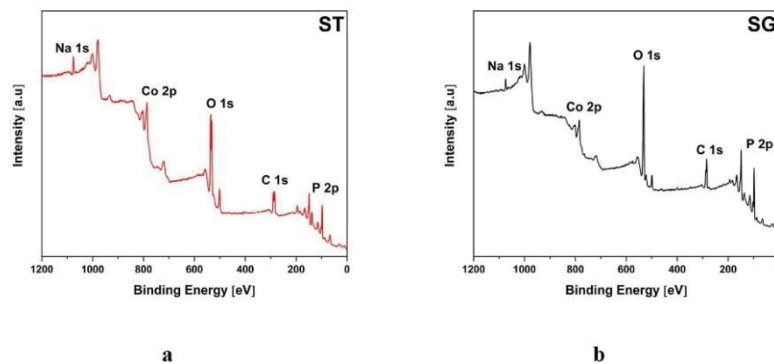


Fig. 6. XPS patterns of the whole spectrum of (a) $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and (b) $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG.

Table 2
Experimental bandgap energy values (E_g) obtained from different graphic methods for $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and -SG.

Sample	Method		
	Optical bandgap(eV)	Direct bandgap(eV)	Indirect bandgap(eV)
$\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST	1.79	1.87	1.75
$\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG	1.78	1.77	1.72

electrode. For $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG samples, the grain boundary contribution at mid-frequencies is negligible compared to that of the bulk at high frequencies as seen in Fig. 8a. However, this is not true for $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST samples. Indeed, for $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST the bulk resistance is accompanied by a clear contribution from the grain boundaries in the medium frequency range before the tail at lower frequencies as shown in Fig. 8b. The grain boundaries contribution is even more visible at lower temperatures. Eventually, the absence of a significant grain boundary contribution in the SG case clearly indicates the benefit from this synthesis method compared to the synthesis via ST reaction.

As the aim of the present study is to report the synthesis of a new

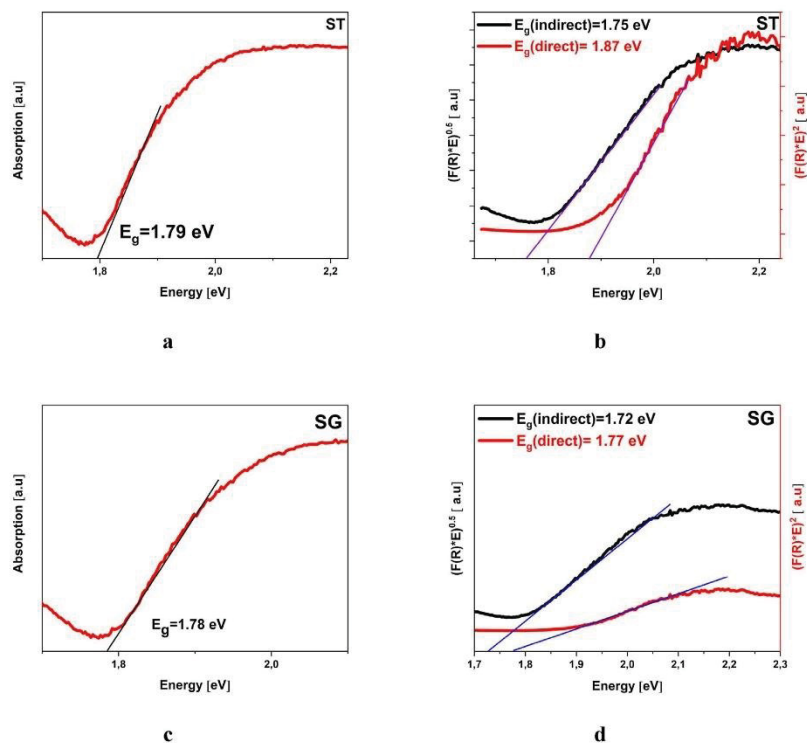


Fig. 7. (a) Optical absorption spectrum and (b) Tauc plot for $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST. (c) Optical absorption spectrum and (d) Tauc plot for $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG.

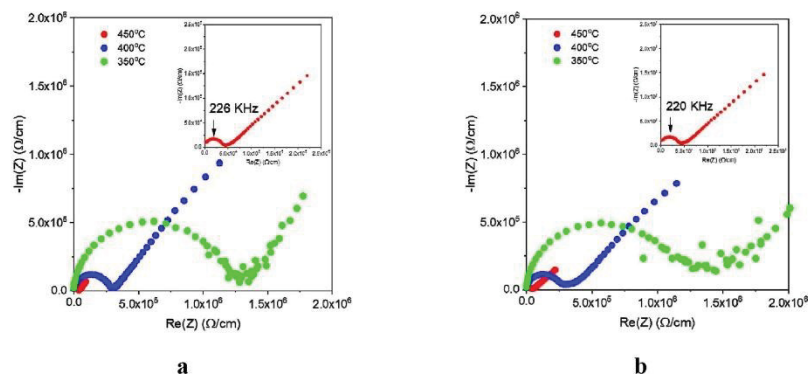


Fig. 8. Nyquist plots of impedance recorded between 350 and 450 °C for $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ (a) -SG and (b) -ST.

sodium conducting compound, the following discussion is focused on the bulk conductivity, *i.e.* related solely to the crystal structure of the material without interference brought about by the synthesis of the material. The bulk ionic conductivity (σ_b) is derived from the value of the resistance ascribed from the high frequency part of the diagrams modeled using the

appropriate equivalent circuit. The following equation is then used for the determination of the bulk conductivity (5).

$$\sigma_T = \frac{e}{SR_b} \quad (S/cm) \quad (5)$$

Table 3
Conductivity of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG at different temperatures.

Temperature	Conductivity (S/cm^{-1})			
	300 °C	350 °C	400 °C	450 °C
$\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST	1.94×10^{-4}	7.56×10^{-4}	4.25×10^{-3}	2.94×10^{-2}
$\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG	1.76×10^{-4}	8.70×10^{-4}	4.25×10^{-3}	3.59×10^{-2}

where e , R_b and S are, the thickness of the sample, the resistance associated to the bulk of the sample and the effective contact area of the sample with the electrode respectively. The ionic conductivities of both samples are presented in Table 3. As shown the conductivities in both samples are increasing with an increase in temperature and have the same order of magnitude.

Fig. 9 displays the temperature dependency of the conductivities for $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG samples in the form of an Arrhenius type plot. For both materials, a linear evolution of the conductivity with the temperature is observed. As could be expected from the lattice structure of the materials, the bulk conductivity is strictly the same and follows the same slope with temperature. This further confirms that both materials are the same independent of the synthesis method. The ionic conductivity increases from 1.76×10^{-4} S/cm at 300 °C to 3.59×10^{-2} S/cm at 450 °C. This type of temperature dependence of conductivities indicates that the conduction in the material is a thermally activated process governed by the relation (6):

$$\sigma_T \cdot T = A \exp(-E_a / kT) \quad (6)$$

where A is the pre-exponential factor, E_a is the activation energy, k is the Boltzmann constant and T is the absolute temperature. Such mechanism suggests the hopping of Na^+ ions from site to site. The activation energy is obtained from the slope of the $\log(\sigma T)$ versus $1000/T$ plot, and it is found as -0.70 eV, in both the samples.

The ionic conductivity values remain low in comparison to the best

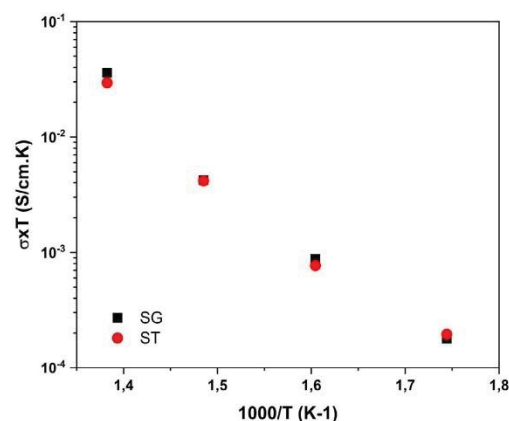


Fig. 9. Arrhenius plot computed for $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG samples.

Table 4
Comparison of the conductivities of the $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$, $\text{Na}_2\text{CoP}_2\text{O}_7$ and $\text{Na}_2\text{Co}_8(\text{PO}_4)_6$ compounds at 573 K.

Samples	$\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST	$\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG	$\text{Na}_2\text{CoP}_2\text{O}_7$ [56]	$\text{Na}_2\text{Co}_8(\text{PO}_4)_6$ [13]
Conductivity (S/cm^{-1}) at 300 °C (573 K)	1.94×10^{-4}	1.76×10^{-4}	2×10^{-5}	10^{-6}

ionic conductors in the range of 10^{-3} S/cm at room temperature with high activation energy [49,50]. The same aspects has been observed with LiFePO_4 , a well documented Li-ion battery material [51]. Nevertheless, considering the presence of Co with potentially different electronic states, proper material processing, i.e. particle size reduction, and carbon coating similar to that used for the production of carbon coated LiFePO_4 [52–55] could lead to a new electrode active material for sodium batteries.

On the other hand, a comparison of the conductivities of the $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$, $\text{Na}_2\text{CoP}_2\text{O}_7$ and $\text{Na}_2\text{Co}_8(\text{PO}_4)_6$ materials at 573 K, presented in Table 4, clearly shows that the $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ compound prepared by sol-gel and solid-state has a higher conductivity than the other two.

4. Conclusion

$\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ was successfully synthesized by solid-state and sol-gel procedures. The XRD studies reveal the monoclinic system with space group $P2_1/n$. SEM indicate a particle size distribution ranging between 8 to 35 μm and 1 to 20 μm , respectively for $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG, having a homogeneous composition in both materials. The oxidation states of sodium, cobalt, phosphorus, and oxygen were obtained by XPS for $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ samples prepared by solid-state and sol-gel methods and showed the following values: Na(I), Co(II/III), P(V) and O(-II). Based on the UV-Vis diffuse reflectance spectra; the optical, the direct and indirect bandgaps of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG are estimated to be 1.79 eV, 1.87 eV, 1.75 eV and 1.78 eV, 1.77 eV and 1.72 eV respectively. The ionic conductivity for both samples is of the order of 10^{-4} S/cm and 10^{-2} S/cm, at 300 °C and 450 °C, respectively. Thus, the variation of ionic conductivity with temperature indicates that the ionic conduction in this material is a thermally activated process. In summary, considering the results from XRD, SEM/EDS, DRS and EIS on $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST and $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG samples, the sol-gel method presents more interesting results than the solid-state one.

CRedit authorship contribution statement

Erman Eloge Nzaba Madila: Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Software, Writing – review & editing, Investigation, Writing – original draft. **Yasmine Benabed:** Writing – review & editing. **Prabhjot Kaur:** Methodology, Writing – review & editing. **Steeve Rousselot:** Software, Writing – review & editing. **Mickaël Dollé:** Writing – review & editing. **Adam Duong:** Visualization, Supervision, Funding acquisition, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jssc.2022.123338>.

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Chapitre 4: Investigation of structural, optical, dielectric and electrical properties of $\text{NaMn}_4(\text{PO}_4)_3$ with fillowite-type structure

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4.1. Introduction

Le quatrième chapitre fait allusion à ‘ *Investigation of structural, optical, dielectric and electrical properties of $\text{NaMn}_4(\text{PO}_4)_3$ with fellovite-type structure*’. Il s’agit, de la synthèse d’un phosphate de manganèse et de sodium, $\text{NaMn}_4(\text{PO}_4)_3$ par la méthode sèche, l’état solide dont la température de traitement est de 900 °C pendant 10 h. L’analyse d’affinement de Rietveld du diagramme de diffraction des rayons X de la poudre a confirmé que l’échantillon cristallin $\text{NaMn}_4(\text{PO}_4)_3$ préparé avait une structure monoclinique et ne présentait aucun signe de pics de phase secondaire. Les spectroscopies Raman et Infrarouge ont confirmé la présence des groupements phosphates. Les images MEB de l’échantillon présentent des grains sphériques agglomérés avec des limites de grain distinctes et des tailles de grain variables. La formation de particules de même forme, mais de tailles différentes, est évidente. Certaines de ces particules sont creuses et sphériques. La taille moyenne des grains est d’environ 5,598 μm et 8,24 μm dans la plupart des cas. La spectroscopie de rayons X à dispersion d’énergie (EDS) a confirmé la présence des éléments sodium (Na), manganèse (Mn), phosphore (P) et oxygène (O) dans l’échantillon. Les cartographies élémentaires indiquent que ces éléments sont répartis de manière homogène dans l’échantillon. Le troisième aspect de ce chapitre, montre à travers la spectrophotométrie en Réflectance Diffuse, qu’en utilisant l’équation de Kubelka-Munk et les tracés de Tauc que ces composés sont des semiconducteurs. La bande interdite optique (E_g) de l’échantillon a été évaluée à environ 1,57 eV. Les valeurs des bandes interdites indirectes et directes trouvées par la méthode du tracé de Tauc sont de 2,89 et 1,96 eV, respectivement. Ces bandes interdites indiquent que le composé $\text{NaMn}_4(\text{PO}_4)_3$ peut être classé comme semi-

conducteur. Les coordonnées de chromaticité CIE de l'échantillon (0,174 ; 0,011) ont été déterminées à partir du tracé CIE en utilisant les données PL. La pureté de la couleur du composé s'est avérée être de 68%. De plus, la température CCT du composé calculé à partir de la CIE 1931 était de 1935 K. L'étude de l'impédance électrochimique sur ces composés, ont aidé d'évaluer le niveau de la conductivité. L'étude des propriétés diélectriques du composé $\text{NaMn}_4(\text{PO}_4)_3$ montre le comportement d'un matériau conducteur ionique. Le tracé de Nyquist conduit à un demi-cercle unique qui mène à trois circuits RC parallèles, mettant en évidence la présence de grains, de joints de grains et de l'interface matériau-électrode où le comportement électrique dominant se produit dans les joints de grains.

4.2. Les points forts de ce travail

- Synthèse à l'état solide de $\text{NaMn}_4(\text{PO}_4)_3$ à 900 °C pendant 10 h.
- Confirmation des phases pures de $\text{NaMn}_4(\text{PO}_4)_3$ par affinement de Rietveld.
- Des études de spectroscopie Raman et infrarouge ont été réalisées.
- Études de la morphologie et de la composition élémentaire.
- Les bandes interdites optiques de $\text{NaMn}_4(\text{PO}_4)_3$ ont été calculées.
- Des propriétés diélectriques et électriques par l'impédance.

4.3 Contribution des auteurs

- ❖ **Erman Eloge Nzaba Madila:** Conceptualisation, méthodologie, analyse formelle, investigation, Recueil de données, Logiciels, traitement des données, rédaction du premier projet, révision et édition.
- ❖ **Amina Lahrichi:** Préparation des échantillons pour les mesures d'impédance, révision et édition.
- ❖ **Youness El Issmaeli:** Préparation des échantillons pour les mesures d'impédance, révision et édition.
- ❖ **Malak Slaoui:** Mesure d'impédance et logiciel.
- ❖ **Love Karan Rana:** Révision et édition.
- ❖ **Taj-dine Lamcharfi:** Rédaction- révision et édition.
- ❖ **Adam Duong:** Visualisation, Supervision, Acquisition de financement, Rédaction-révision et édition.

4.4. Conclusion

En résumé, le composé $\text{NaMn}_4(\text{PO}_4)_3$ a été préparé par synthèse conventionnelle à l'état solide à 900 °C pendant 10 heures. Les données de diffraction des rayons X ont confirmé que l'échantillon était monophasé, sans impuretés détectables, et qu'il cristallisait dans une structure trigonale en utilisant l'axe hexagonal de groupe d'espace R-3. La MEB indique que la taille moyenne des grains est d'environ 7 μm . Les états d'oxydation du sodium, du manganèse, du phosphore et de l'oxygène ont été déterminés par l'analyse XPS, conduisant aux valeurs suivantes: +1, +2, +5 et +2, respectivement. Les bandes interdites directe et indirecte déterminées par la méthode du tracé de Tauc sont

respectivement de 2,89 et 1,96 eV, ce qui indique que le matériau $\text{NaMn}_4(\text{PO}_4)_3$ peut être classé comme semi-conducteur. Les coordonnées de chromaticité CIE pour le composé $\text{NaMn}_4(\text{PO}_4)_3$ ont été calculées comme étant (0,174, 0,011). Les coordonnées chromatiques du $\text{NaMn}_4(\text{PO}_4)_3$ indiquent que ce composé peut être un candidat pour un matériau émetteur bleu-violet. La spectroscopie ultraviolet-visible (UV-vis) à l'état solide à partir de la réflectance diffuse en utilisant la fonction de Kubelka-Munk et la relation de Tauc et les études de photoluminescence indiquent que le $\text{NaMn}_4(\text{PO}_4)_3$ présente des propriétés intéressantes. L'étude des propriétés diélectriques du composé $\text{NaMn}_4(\text{PO}_4)_3$ montre le comportement d'un matériau conducteur ionique. Le tracé de Nyquist conduit à un demi-cercle unique qui mène à trois circuits RC parallèles, mettant en évidence la présence de grains, de joints de grains et de l'interface matériau-électrode où le comportement électrique dominant se produit dans les joints de grains.

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Investigation of structural, optical, dielectric, and electrical properties of $\text{NaMn}_4(\text{PO}_4)_3$ with fillowite-type structure

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**Materials Science and Engineering B: Solid-State Materials
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Abstract

$\text{NaMn}_4(\text{PO}_4)_3$ was prepared by a solid-state procedure. The obtained phase was characterized by PXRD. Rietveld analysis refinements confirmed that the prepared crystalline sample was pure and belong to the trigonal system with $R\bar{3}$ space group. The morphology analyzed by SEM give an average grain size of $\sim 7 \mu\text{m}$. The EDS confirms the homogeneity of the sample. Raman and FTIR spectroscopies show characteristic bands of P-O bonds of the $(\text{PO}_4)^{3-}$ functional group. The optical bandgap energy of 1.57 eV was determined by the diffuse reflectance using the Kubelka-Munk function and the Tauc's relation. Its dielectric properties exhibit the behavior of an ionic conducting material. The Nyquist plot displays a single semicircle which leads to three parallel RC circuits, highlighting the presence of grains, grain boundaries and the material-electrode interface where the dominant electrical behavior occurs in the grain boundaries.

KEYWORDS: $\text{NaMn}_4(\text{PO}_4)_3$, Phosphates, solid-state reaction, X-ray diffraction, Rietveld analysis, Kubelka–Munk function, Tauc's relation, luminescence properties, dielectric properties.

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1. Introduction

Phosphates composed of alkali metals (A) and transition metals (M) with a general formula $AMPO_4$ have been widely studied in the past years[1] because of their interesting electrochemical properties in batteries,[2–11] supercapacitors[12] as well as their ferroelectric[13,14] and magnetic[15–19] properties. Another phosphate group, combining alkali metals (A) and transition metals (M) with a general formula $A_xM_y(PO_4)_z$ [20–28] ($x=1, 2, \dots$, $y=1, 2, \dots$, $z=6$) has similarly been extensively studied while it presents in some cases the same properties as $AMPO_4$. The $A_xM_y(PO_4)_z$ group, can be found with fillowite structure which shows various properties depending on the chemical composition[29–34][35]. Agreeing to the first description by Brush and Dana (1878)[36], fillowites can be defined as sodium phosphates of manganese and iron, in the Branchville pegmatite (Connecticut). There are five minerals belonging to the fillowite group, including fillowite, chladniite, galileiite, johnsomervilleite and stornesite-(Y). These minerals emanate mainly in granitic pegmatites (Araki and Moore, 1981; Franolet *et al.*, 1998), as well as in metamorphic context (Livingstone, 1980; Grew *et al.*, 2006), but also in meteorites (McCoy *et al.*, 1994; Olsen and Steele, 1997; Floss, 1999)[37]. Up to date only few studies have been made on $A_xM_y(PO_4)_z$ with fillowite structure, especially on the synthesis and characterization. As an example, Rondeux *et al.* synthesized $NaMn_4(PO_4)_3$ by solid-state and hydrothermal route and confirmed the phase purity of the materials by XRD. However, the team had not looked at the application side for these compounds. In order to study the properties of some phosphate compounds, we first synthesized the $NaMn_4(PO_4)_3$ compound, proving that it crystallizes in a hexagonal fillowite structure, as obtained by Rondeux[37].

In this work, we were paying attention in a sodium manganese phosphate phase, $NaMn_4(PO_4)_3$, which was synthesized for the first time by Rondeux[37] but not yet reported. We successfully prepared the $NaMn_4(PO_4)_3$, with a fillowite structure, by solid-state method and their physicochemical properties were investigated using the powder X-ray diffraction (PXRD), thermogravimetric analysis(TGA/DTA), Raman spectroscopy, Fourier-transform infra-red spectroscopy (FTIR), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), ultraviolet-visible spectroscopy, X-ray photoelectron spectroscopy (XPS), photoluminescence analysis and impedance spectroscopy.

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2. Experimental and data processing

NaMn₄(PO₄)₃ powders were prepared by the solid-state reaction method. Stoichiometric ratios of Na₂CO₃ (Alfa Aesar, 98%), MnO (Alfa Aesar, 99.99%) and NH₄H₂PO₄ (Alfa Aesar, 98%) were mixed and ground in an agate mortar for 30 min to form a homogeneous mixture. Then, the mixture was put in alumina crucible and heated at 500 °C for 5 h, the resulting material was reground, and the final NaMn₄(PO₄)₃ products were obtained by heating at 900 °C for 10 h in a Vulcan Model A-550 furnace. The temperature accuracy of the furnace is ± 25°C.



The X-ray diffraction (PXRD) data of NaMn₄(PO₄)₃ was collected on a D8 Bruker diffractometer (Cu-K α radiation, θ -2 θ geometry, back monochromator) with a step-wise scanning mode over the 2 θ range of 14–60°, using CuK α radiation (1.5406 Å) under the operating electric voltage and current of 40 kV and 100 mA, respectively and for a total measurement time of 2 h using a step size of ~0.006° and a fixed divergence slit of 0.3°. The presence of a nearly single-phase material was identified by a database match. To further verify this, the data were analyzed by using the Rietveld method as implemented in TOPAS V6[38].

The thermogravimetric analysis (TGA) was carried out by a Diamond Pyris 6000 TGA/DTA apparatus from Perkin-Elmer in the temperature range between 100 °C and 850 °C using aluminum crucibles under N₂ flow at a heating rate of 20 °C/min. The temperature accuracy of the device is ± 0.5 °C.

The Fourier transform infrared (FTIR) absorption and Raman spectrum were recorded with a Nicolet iS 10 Smart FT-IR Spectrometer in the range of 1500 to 400 cm⁻¹ and ThermoScientist Raman DXR3 spectrometer with a green laser source of excitation wavelength of 532 nm, respectively.

The morphology characteristics (sintered pellets at 1000 °C for 10 h) was observed by scanning electron microscopy (SEM) analysis using the secondary electron detector of a Hitachi model SU1510 scanning electron microscope operating at 30 keV. The EDS measurements were made to determine the elementary topographic composition of NaMn₄(PO₄)₃ sample. The measurements

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were carried out using the column EDS, OXFORD instrument, X-max 20 mm² microscope from Hitachi. The mean particle diameter was determined using ImageJ software [39].

To evaluate the optical absorption properties of NaMn₄(PO₄)₃, the solid-state ultraviolet-visible (UV-vis) spectroscopy was performed on the pellets at room temperature in diffuse reflectance mode using a UV/Visible Agilent Cary 60 spectrophotometer. The reflectance versus wavelength data was recorded over a wavelength range of 800 nm to 200 nm. Pure BaSO₄ powder was used as a reference for 100% reflectance. The bandgaps of these compounds were further calculated by converting reflectance to absorption data according to the Kubelka–Munk equation (2)[40]. The bandgaps were estimated by using the Tauc Plot using the equation (3)[1,41].

$\frac{\alpha}{S} = \frac{(1-R)^2}{2R}$ (2) here R, α , and S are the reflectance, the absorption, and scattering coefficients, respectively. $(\alpha h\nu)^n = A(h\nu - E_g)$ (3) where α , h, and ν are absorption coefficient, Planck's constant, and frequency of light. A is a proportionality constant, and E_g is the bandgap. The value of constant n determines the nature of bandgap: n=2 and n=1/2 value suggest direct and indirect bandgap, respectively.

The X-ray photoelectron spectroscopy (XPS) was carried out to evaluate the valence states of the metals/ions in solids because that method is extensively applied in the characterization of cathode materials. The XPS was performed in a VG Escalab 220i-XL equipped with hemispherical analyzer, applying a Twin Anode X-Ray Source. The binding energies were calibrated using containment carbon (C 1s = 284.4 eV).

Room temperature photoluminescence emission (PL) spectra for NaMn₄(PO₄)₃ sample were measured using a Cary Eclipse fluorescence spectrophotometer by using an excitation wavelength of 285 nm from a UV laser.

Using an Ag/NaMn₄(PO₄)₃/Ag parallel plate capacitor geometry, the dielectric and electrical properties were studied. Impedance spectroscopy measurements were performed using an HP 4284A impedance meter running in the frequency range of 100 Hz to 2 MHz and at a temperature varying from room temperature to 500 °C. Knowing that the permittivity was measured by placing the sample between the two planar electrodes of the dielectric test device, after processing, the output data are the impedance (Z' , Z''), capacitance (C_p) and resistance (R_p). Complex permittivity (ϵ' , ϵ'') and conductivity can be calculated by the formulas:

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$\epsilon' = \frac{eC_p}{A\epsilon_0}$ (4) and $\epsilon'' = \frac{e}{\omega AR_p \epsilon_0}$ (5) while $\sigma = \frac{e}{SR_p}$ (6), by replacing the expression of e obtained from formula (6) in the formula (5), we can write the new expression of ϵ'' as: $\epsilon'' = \frac{\sigma}{\omega \epsilon_0}$ (7), which gives the following expression of the conductivity $\sigma = \omega \epsilon'' \epsilon_0$ (8). It is from formula (8) that the conductivity in this compound was calculated.[42] With e is the thickness of the sample, A is the surface area of the electrode, ϵ_0 is the absolute permittivity of free space ($8.85 \cdot 10^{-12}$ F/m) and $\omega = 2\pi f$, with f, the electric field frequency.

3. Results and discussion

3.1 Simultaneous thermal analysis

Quantitative thermal analysis of reactions is often complemented by several changes, such as evaporation, gas adsorption, and decomposition by dehydration of the reactive starting materials. Fig. 1 displays the TGA/DTA profiles of $\text{NaMn}_4(\text{PO}_4)_3$ precursor mixture in the stoichiometric ratio at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ from $100 \text{ }^\circ\text{C}$ to $800 \text{ }^\circ\text{C}$.

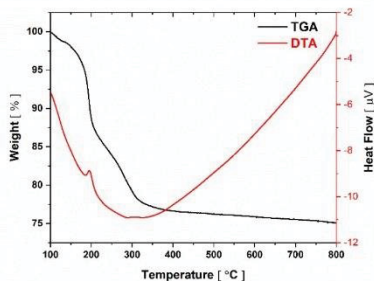


Fig. 1. TG/DTA curves of the precursor mix of $\text{NaMn}_4(\text{PO}_4)_3$

The TG curve evidence that there are two main weight losses in the measured region. The small weight loss of $\sim 1.34 \%$ between $100 \text{ }^\circ\text{C}$ and $135 \text{ }^\circ\text{C}$ is assigned to water evaporation. The larger weight loss of $\sim 23.24\%$ in the range $135 - 500 \text{ }^\circ\text{C}$ accompanied by an exothermic peak at $196.8 \text{ }^\circ\text{C}$ can be attributed to the decomposition of phosphates and carbonates,[43] indicating that a large

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amount of CO₂ and NH₃ are generated. Above 500 °C, negligible weight loss is detected indicating the complete decomposition of organic species and the formation of pure NaMn₄(PO₄)₃[2,44,45].

3.2 X-Ray Diffraction

NaMn₄(PO₄)₃ has a trigonal using hexagonal axis packing of three types of rods parallel to the *c*-axis (space group *R*-3), structure with an open three-dimensional framework of MnO₆ octahedra sharing all corners with PO₄ tetrahedra and vice versa, like described by Rondeux 2006[37]. An approximately single-phase material, Na_{14.11}Mn_{45.31}(PO₄)₃₆[46] was identified using ICSD database match. To further validate, the data were analyzed by using the Rietveld method as implemented in TOPAS V6[38]. The Rietveld analysis of the sample is displayed in Fig. 2a. For that, the structure of Na_{14.11}Mn_{45.31}(PO₄)₃₆[46] was carried as the starting model for the main phase and was used for Rietveld refinement of NaMn₄(PO₄)₃. We confirmed the presence of a nearly single-phase material crystallizing in the trigonal crystal system space group *R*-3 with the unit cell parameters of *a* = *b* = 15.248(6) Å, *c* = 43.344(2) Å, close to those described by Rondeux[37].

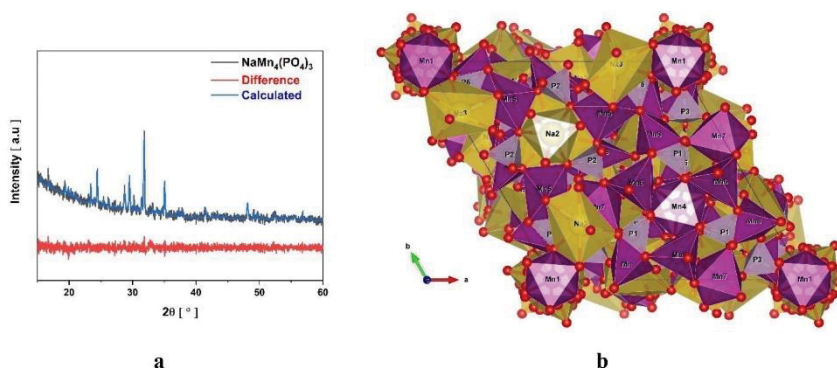


Fig. 2. (a) Rietveld analysis and (b) Crystal structure of NaMn₄(PO₄)₃.

The crystallographic data confirm the formation of NaMn₄(PO₄)₃ phase, and no additional peaks were observed in the sample. The refinement was stable and finished with relatively low R-factors (Table 1). Fig. 2b represents the refined crystal structures by VESTA[47]. The final structural parameters and the details of the refinement are listed in Table 1.

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Other Rietveld-refinement parameters were background parameters, scale parameters, profile parameters, microstructure parameters, zero error, and so on. The main results of the Rietveld structural refinement are presented in Table 1 and the atomic parameters of $\text{NaMn}_4(\text{PO}_4)_3$ are listed in Table 2. The Rietveld refinement is in good agreement with the one obtained by Rondeux, 2006[37].

Table 1 Crystallographic data, experimental details of X-ray powder diffraction, and Rietveld refinement data for $\text{NaMn}_4(\text{PO}_4)_3$.

Chemical formula	$\text{NaMn}_4(\text{PO}_4)_3$
Crystal system	Hexagonal
Space group	$R\bar{3}$
Cell parameters	$a=15.248(6) \text{ \AA}$, $c=43.344(2) \text{ \AA}$
Cell volume	$V=8720(7) \text{ \AA}^3$
Number of formula per unit cell	$Z=18$
Calculated density	$D_c=3.557(3) \text{ g/cm}^3$
R-factors	$R_p=2.89$, $R_{wp}=3.71$, $R_{exp}=3.25$, $GOF=1.14$
Diffraction	Bruker D8 Advance (Bragg-Brentano geometry)
Radiation type	$\text{CuK}\alpha$
Scan range	14 to 60 (deg. 2θ)
Step width	0.006 (deg. 2θ)

The asymmetric part of the unit cell of $\text{NaMn}_4(\text{PO}_4)_3$ is composed of 45 crystallographic independent sites (2 Mn/Na, 6 P, 3 Na, 10 Mn and 24 O sites). The Mn2/Na1 and Mn12/Na5 atoms are randomly disordered in the structure at 3b and 18f crystallographic sites with site symmetries of $\bar{3}$ and 1, respectively. All phosphorous and oxygens atoms lodge to the 18f crystallographic site (site symmetry: 1). Thus, each P atom form a distorted tetrahedral PO_4 units through bonding with oxygen atoms. The disordered Mn and Na atoms at the same crystallographic site could be bonded to six oxygen atoms that forming a distorted octahedral geometry. The details of Rietveld refinement and structural parameters of $\text{NaMn}_4(\text{PO}_4)_3$ are presented in Table S1.

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3.3 Fourier-Transform Infrared and Raman Spectroscopies

Raman and infrared spectra were recorded, and the observed bands were assigned as shown in Fig. 3. The IR spectrum displays absorption bands between 1143-600 cm^{-1} that can be associated with the stretching vibrations of the P-O bonds of the PO_4 tetrahedra. The two bands in the region of 630-547 cm^{-1} are assigned to the O-P-O bending vibrations[48]. In order to confirm the homogeneity of the sample and the presence of $(\text{PO}_4)^{3-}$ groups, Raman spectrum was collected in different areas of the $\text{NaMn}_4(\text{PO}_4)_3$ sample. As can be seen in Fig. S1, all Raman spectra are similar indicating that the composition of the polycrystalline phase is homogeneous. The Raman spectrum shows a strong band at 958 cm^{-1} which can be attributed to the symmetric stretching mode of the P-O bonds in the $(\text{PO}_4)^{3-}$ units. The bands at 1040 and 1100 cm^{-1} can be attributed to the asymmetric stretching modes of P-O bonds in $(\text{PO}_4)^{3-}$ units[49,50]. Raman and IR analyses confirm the presence of PO_4 in the $\text{NaMn}_4(\text{PO}_4)_3$ sample powder.

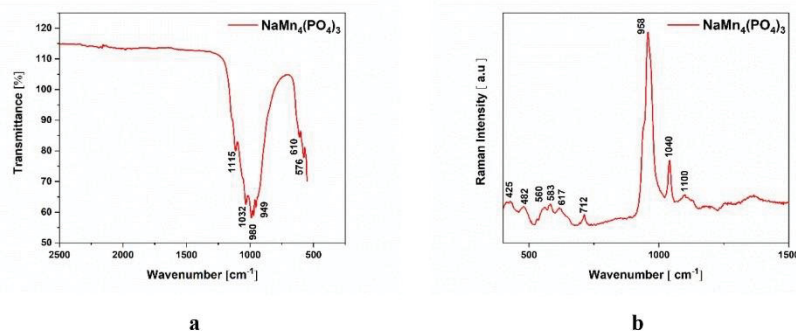


Fig. 3. (a) Infrared and (b) Raman spectra of $\text{NaMn}_4(\text{PO}_4)_3$ sample.

3.4 Scanning Electron Microscopy

To determine the morphology and particles size of $\text{NaMn}_4(\text{PO}_4)_3$, scanning electron microscopy (SEM) was carried out on pellets. In Fig. 4, SEM images of $\text{NaMn}_4(\text{PO}_4)_3$ show uniform particle distributions in the sample (Fig. 4b and 4d). The micrographs show agglomerative spherical grains with distinctive grain boundaries and varying grain sizes. The formation of particles with same shapes but different sizes are evidenced. Some of these particles are hollow and spherical as shown

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in Fig. 4a. The average grain sizes are of $\sim 5.598 \mu\text{m}$ as determined in Fig. 4a and $\sim 8.24 \mu\text{m}$ in Fig. 4c.

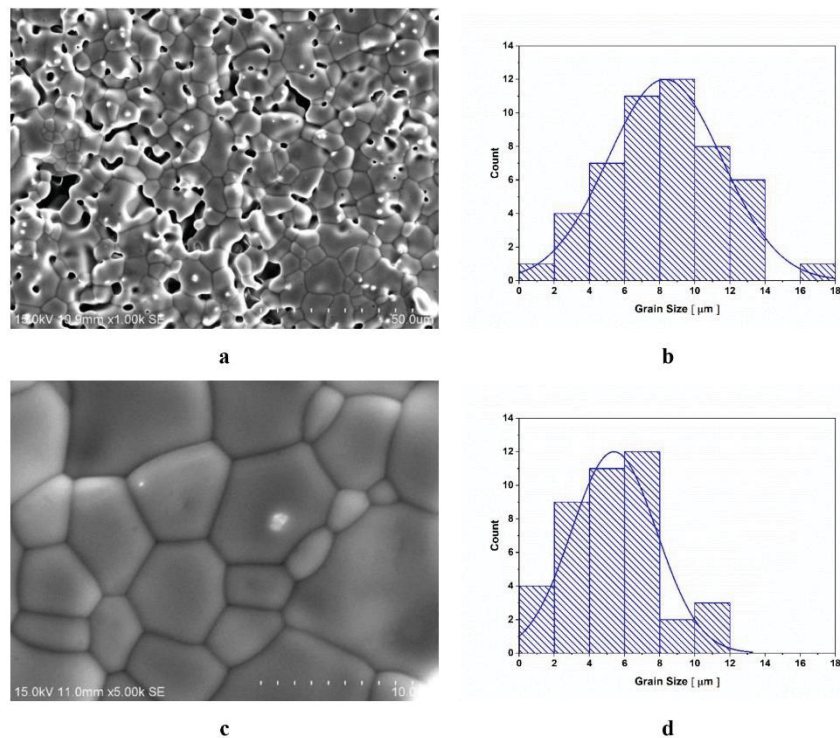


Fig. 4. SEM micrographs showing the morphology and particle size of $\text{NaMn}_4(\text{PO}_4)_3$ pellet at (a) 1k and (c) 5k magnifications. Grain size distribution of $\text{NaMn}_4(\text{PO}_4)_3$ pellet at (b) 1k and (d) 5k magnifications.

These results are in agreement with Figs. 4b and 4d, which were obtained by statistical analysis of these SEM images. In view of the above, the average grain size is $\sim 7 \mu\text{m}$ for the $\text{NaMn}_4(\text{PO}_4)_3$ sample. In addition, direct grain-to-grain contacts exist at the grain boundaries in most cases (Fig. 4c). No other phases are found between the two adjacent grains, confirming that the $\text{NaMn}_4(\text{PO}_4)_3$ phase is pure. However, when the grain size of the powders becomes large enough, greater than 55

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nm, grain growth can be dominated by the intrinsic mobility of the grain boundaries. Grain boundary migration is mainly caused by the interfacial energy of the grains[51].

3.5 Energy-Dispersive X-Ray Spectroscopy

Elemental analysis of the $\text{NaMn}_4(\text{PO}_4)_3$ powder was performed using energy dispersive X-ray spectroscopy (EDS). It confirms the presence of sodium (Na), manganese (Mn), phosphorus (P) and oxygen (O) elements in the sample (Figs. 5a and 5b). The elemental ratios of Na, Mn, P and O were found to be approximately 1:4:3:12. Figs. 5a and 5b show typical EDS plots for $\text{NaMn}_4(\text{PO}_4)_3$ selected at two different positions. The compositions found at the two positions are $\text{Na}_{1.0}\text{Mn}_{4.0}\text{P}_{3.3}\text{O}_{12.3}$ (Fig. 5a) and $\text{Na}_{1.0}\text{Mn}_{3.9}\text{P}_{3.0}\text{O}_{11.2}$ (Fig. 5b). Thus, the ratio Na:Mn:P:O calculated using the EDS matches well with the chemical formula. The elemental mappings indicated that these elements are homogeneously distributed in the materials (Fig. 5c).

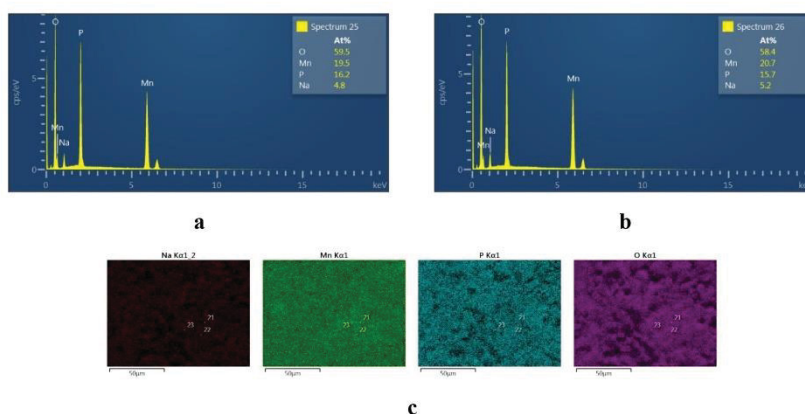


Fig. 5. EDS (a)-(b) Point at two different positions and (c) Mapping of $\text{NaMn}_4(\text{PO}_4)_3$ particles.

3.6 X-Ray Photoelectron Spectroscopy (XPS)

The XPS study was carried out to observe the changes of oxidation state of the elements and to confirm the presence of all elements in the $\text{NaMn}_4(\text{PO}_4)_3$ sample. Fig. 6 shows the complete

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XPS spectrum of $\text{NaMn}_4(\text{PO}_4)_3$ and narrow spectra of sodium (Na), manganese (Mn), carbon (C), phosphorus (P) and oxygen (O) elements.

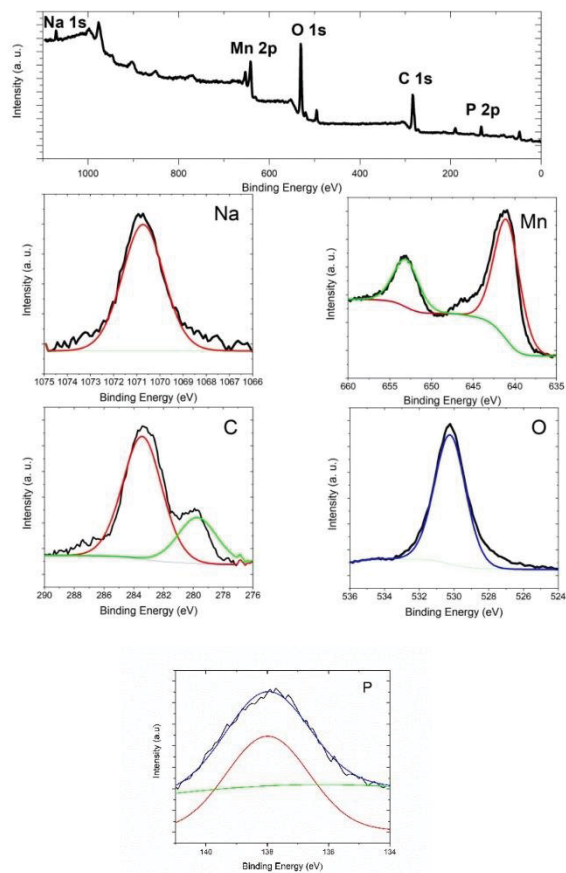


Fig. 6. Wide survey XPS spectrum of $\text{NaMn}_4(\text{PO}_4)_3$ and narrow spectra of Na (1s), Mn (2p), C (1s) and O (1s).

The binding energy of the central Na 1s level emission peak for the compound $\text{NaMn}_4(\text{PO}_4)_3$ is located at 1070.84 eV. This value is close to that of NaCl[52],[53]. The Mn 2p region shows two

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peaks Mn2p3/2 and Mn2p1/2, respectively at 641 eV and 653.22 eV. According to the literature, the peaks at 641 (Mn2p3/2) and 653.22 eV (Mn2p1/2) are ascribed to Mn²⁺ ions[54],[55]. The binding energy for P(2p) spectrum is located in the range of 130-138 eV. These energies can be assigned to the (PO₄)³⁻ group of NaMn₄(PO₄)₃. The O(1s) appear at 531 eV. The peak at 531 eV can be attributed to the O²⁻ ions of the (PO₄)³⁻ group.[28,56] According to the XPS results of the NaMn₄(PO₄)₃ sample, the oxidation states of sodium, manganese, phosphorus and oxygen are +1, +2, +5 and -2, respectively. Like for the EDS, the XPS study of NaMn₄(PO₄)₃ confirms the presence of Na, Mn, P and O in the sample.

3.7 UV-Vis diffuse reflectance spectra and bandgap determination

The bandgap of NaMn₄(PO₄)₃ was evaluated by the optical absorption properties. The measurement of the diffuse reflectance was performed on a pellet. The UV-Vis reflectance and absorbance spectra of NaMn₄(PO₄)₃ are shown in Fig. 7. Tauc's plot based on the Kubelka-Munk function (eq (2)) is used to estimate the bandgaps[57],[40],[1],[41].

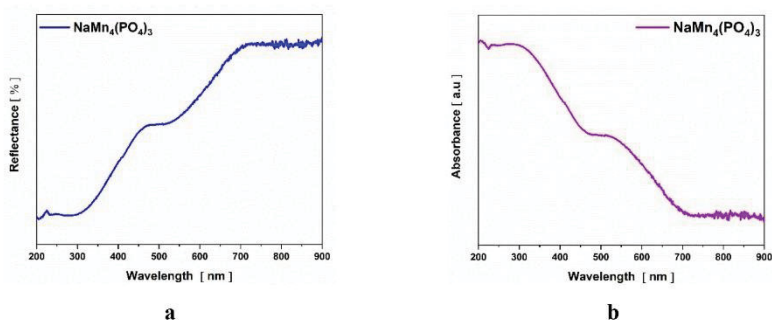


Fig. 7. UV-Vis of (a) diffuse reflectance and (b) absorbance spectra of NaMn₄(PO₄)₃.

Using equation (3), the curve $(h\nu\alpha)^{1/n}$ as a function of $E = h\nu$ was plotted. The bandgap (E_g) was obtained by the tangent line at the inflection point. Since there is no knowledge of the nature of the transition in the compound NaMn₄(PO₄)₃, the two values $n= 1/2$ and 2 were examined to estimate the direct and indirect bandgap. The bands with maximum absorption were used to estimate the bandgaps. The optical bandgap (E_g) of NaMn₄(PO₄)₃ was evaluated to be about 1.57 eV (Fig. 8a).

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The values of indirect and direct bandgaps found from the Tauc's plot method are 2.89 eV and 1.96 eV, respectively (Fig. 8b). These indicate that the material can be classified as a semiconductor.

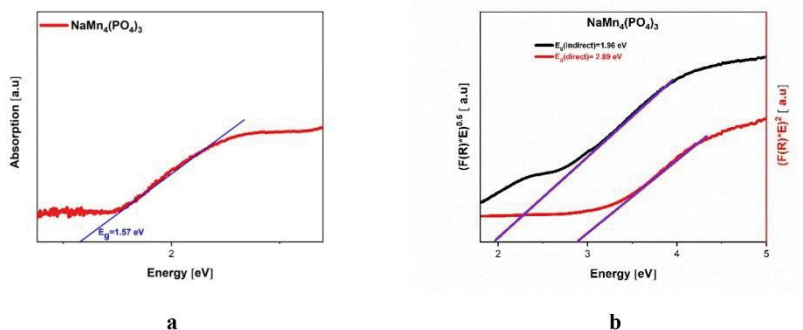


Fig. 8. (a) Optical absorption spectra and (b) Tauc's plots for $\text{NaMn}_4(\text{PO}_4)_3$.

3.8 Photoluminescence spectra analysis

The room temperature emission spectrum of $\text{NaMn}_4(\text{PO}_4)_3$ after excitation at 285 nm (λ_{ex}) show a small band at 313 nm and two broad and intense bands at 358 nm and 371 nm. The weak blue emission with $\lambda_{\text{emission}}$ at 371 nm can be assigned to radiative ${}^4\text{T}_{1g}(\text{G}) \rightarrow {}^6\text{A}_{1g}(\text{S})$ transition. Rational of observed emission can be given based on strong crystal field effect of phosphate ions around octahedral Mn^{2+} ions, which leads to a large energy gap between ground and first excited state of the material resulting in emission at lower wavelength. The CIE chromaticity coordinates of the $\text{NaMn}_4(\text{PO}_4)_3$ (0.174, 0.011) were determined from CIE plot (Fig. 9b) using photoluminescence data. The dominant wavelength and the corresponding color purity of the compound relative to the 1931 CIE standard source C illuminant ($x_i, y_i = 0.3101$ and 0.3162) were also determined using the emission spectrum.

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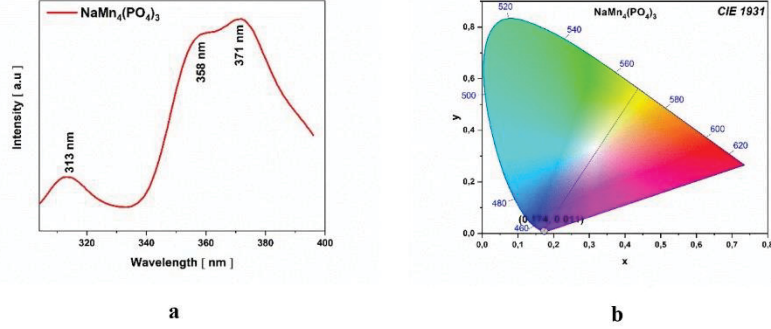


Fig. 9. (a) The emission spectrum of NaMn₄(PO₄)₃ compound and (b) CIE chromaticity coordinates of NaMn₄(PO₄)₃ under 285 nm excitation.

The dominant wavelength also called single monochromatic wavelength of the spectrum was obtained by extending the straight line between sample point (x_s, y_s) and the illuminant point (x_i, y_i) to the other side of plot. The color purity of the compound was calculated using the formula.[58]

$$\text{Color purity} = \frac{\sqrt{(x_s - x_i)^2 + (y_s - y_i)^2}}{\sqrt{(x_d - x_i)^2 + (y_d - y_i)^2}} \times 100\% \quad (9)$$

Where, (x_d, y_d) is the color coordinate of the dominant wavelength. The color purity of the compound was found to be 68%. Furthermore, the calculate color temperature (CCT) of the compound calculated from CIE 1931 was 1935 K.

4. Complex impedance spectroscopy

The dielectric and conductive behavior of the NaMn₄(PO₄)₃ was performed over a wide range of frequencies (from 100 Hz to 2 MHz) and temperatures (from room temperature to 500 °C). With the complex impedance spectroscopy technique, it is possible to separate the real and imaginary components of the dielectric parameters and provide informations of the material properties. The Dielectric constant expressed in the complex formalism can be written:

$$\epsilon^* = \epsilon' - j\epsilon'' = \frac{1}{j\omega C_0 Z^*} = \frac{1}{j\omega C_0 (Z' - jZ'')} \quad (10) \text{ and } \tan\delta = \frac{\epsilon''}{\epsilon'} \quad (11)$$

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ϵ' represents the real part of the complex permittivity or dielectric constant, ϵ'' the imaginary part of the dielectric permittivity, ϵ^* the complex permittivity, Z^* is the complex impedance, $C_o = \frac{\epsilon_o A}{e}$ the empty cell capacitance and ω ($\omega = 2\pi f$ where f is the frequency) is the angular frequency and $j^2 = -1$. A is the sample area, e is the sample thickness, and ϵ_o is the permittivity of free space, $\epsilon_o = 8.854 \cdot 10^{-12} \text{ F/m}$.

To study the dielectric properties in the polycrystalline compound of $\text{NaMn}_4(\text{PO}_4)_3$, the variation of the relative dielectric constant with the change of frequency and temperature was investigated. Fig. 10a shows the frequency dependence of the real parts ϵ' of the dielectric constant at different temperatures. It can be seen that there is no relaxation peak in the frequency range used. As the temperature increases, ϵ' shows a dispersive behavior at low frequencies. In addition, the increase in the value of ϵ' with the increase in temperature can be attributed to the increase in the polarization process of the space charge.[59–61] At high frequencies, a constant limit value $\epsilon'_\infty(\omega)$ is almost reached. This can be interpreted as the result of a rapid polarization process without the contribution of the ionic movement, because the frequency is too high and the ions can only oscillate without achieving the interface of the sample electrode. Another aspect of this study is that the response of $\text{NaMn}_4(\text{PO}_4)_3$ to the dielectric constant is mainly attributed to the influence of polarization which include electronic, ionic, dipolar, and interfacial polarizations. However, ionic and interfacial polarization seem to have the largest contribution in the total polarization mechanism while the others give only a small influence. The decrease in ϵ' with increasing frequency proves that the contribution of charge carriers (ions) decrease at higher frequencies[62]. At low frequencies, one can observe that with decreasing frequency, we have an increase in the dielectric constant ϵ' . This can also be explained by the accumulation of charges at the sample-electrode interface. When the temperature is increasing from room temperature to 500°C and in the low frequency range, the dielectric constant increases. This is attributed to the low energy of the charge carriers at low temperatures. Ions do not have the energy to follow the direction of the applied field at very low temperatures. Hence, the contribution of the polarization mechanism is weakened. Dielectric loss is the amount of electrical power dissipated within the sample under the influence of the applied electric field. The thermal energy generated by the loss of energy due to the displacement of charge carriers in the presence of an electric field is called the dielectric loss ($\tan\delta$). Fig. 10b shows the plots of $\tan\delta$ of the compound $\text{NaMn}_4(\text{PO}_4)_3$ as a function of frequency (ω) at different measurement temperatures. The plots of dielectric constant $\epsilon'(\omega)$ and dielectric loss ($\tan\delta$) for

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NaMn₄(PO₄)₃ show similar trends. The dielectric losses decrease with increasing frequency and also increase with increasing measurement temperature from room temperature to 500 °C. The compound NaMn₄(PO₄)₃ exhibits the behavior of an ionic conducting material, indicating the effects of frequency and temperature on the dielectric losses associated with the formation of charge carriers at the sample-electrode interface that leads to interfacial polarization. It is clearly observed that the dielectric losses increase with decreasing frequency in the low frequency region. The increase in dielectric loss in the low frequency region is attributed to the migration of charge carriers. However, at higher frequencies, charge carrier migration is weakened, resulting in a decrease in dielectric loss. The increase in $\tan\delta$, as the measurement temperature increases, is associated with the increase in energy loss by charge carriers at high drift rates. The frequency dependence of AC conductivity at different temperatures for the NaMn₄(PO₄)₃ sample is shown in Fig. 10c. The AC conductivity also increases with higher measurement temperatures, as observed in Fig. 10c. The plots in this temperature range are revealing like the presence of a conductivity plateau at low frequency, followed by a dispersion of conductivity at high frequency. In the low-frequency region, the conductivity was independent of frequency and identical to the DC conductivity. The phenomenon of conductivity dispersion is usually analyzed using Jonscher's law[63–67]: $\sigma(f) = \sigma_{DC} + Bf^n$ (12) where σ_{DC} is the direct current conductivity of the sample, B is a constant for a particular temperature, and n is the power exponent, it represents the degree of interaction between mobile ions and the environments surrounding them. The power law has been applied to many materials such glasses, phosphate and amorphous semiconductors[63–67].

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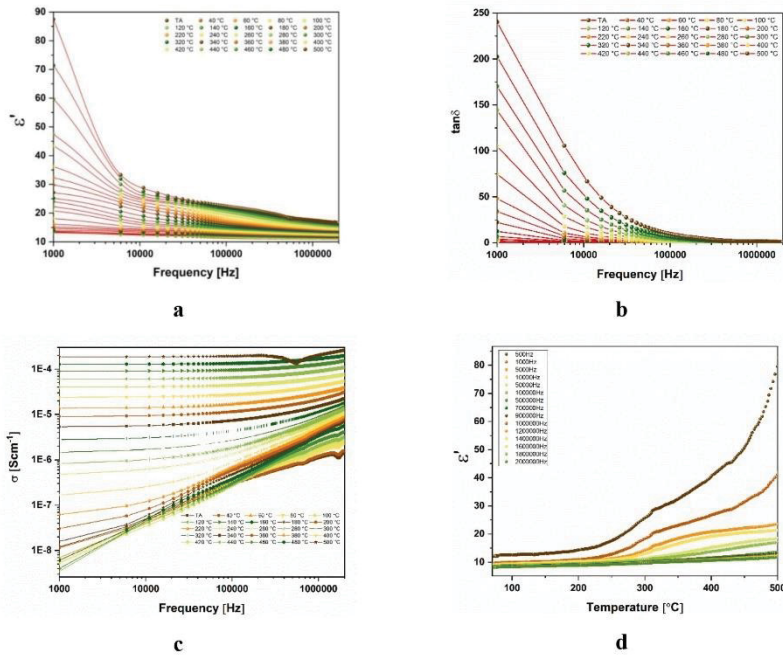


Fig. 10. (a) Dielectric constant at different temperatures vs. ω . (b) Dielectric loss at different temperatures vs. ω . (c) Conductivity at different temperatures vs. ω (d) Dielectric constant at different ω vs. temperature.

Thus, the evolution of the conductivity can be divided into three ranges: from room temperature to 180 °C, the conductivity increases with temperature and then takes lower values at 200 °C and increases again with temperature up to 320 °C and from 340 °C, the same phenomenon occurs. This behavior can be attributed to the gain of thermal energy by the charge carriers as the temperature increases. Another remark is that the conductivity of the compound increases with the increase of the frequency due to the jump of the charge carriers between the different localized sites. Possibly, as the frequency increases (beyond 2 MHz), the conductivity of the compound could converge to almost the same value (Fig. 10c).

Fig. 10d shows the behavior of ϵ' as a function of temperature at specific frequencies. Looking at this figure, their values increase as the temperature increases. The evolution of ϵ' as a function of

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temperature under different specific frequencies is similar except for the frequencies 500 and 1000 Hz where the evolution of ϵ' becomes relatively fast beyond the temperature of about 400°C. This behavior is a confirmation of the contribution of different polarization mechanisms in this compound, as observed in the variation of the real part of the dielectric permittivity at different temperatures as a function of frequency (Fig. 10a).

Complex impedance spectroscopy provides separation of grain, grain boundary and electrode properties. It also provides insight into the electrical mechanisms taking place in the system and their correlation with the sample, when modelled in terms of an equivalent circuit. Several types of samples have been studied by impedance spectroscopy[21,35,68].

Fig. 11 shows the Nyquist plot of the compound $\text{NaMn}_4(\text{PO}_4)_3$ measured at 340 °C. The Nyquist plot shows a semicircle centered on the real axis. In an ideal Nyquist plot, the half circle at lower frequencies is attributed to the material-electrode interface resistance, the middle is related to grain boundaries, and the half circle at higher frequencies is attributed to the grains. The three contributions to the electrical behavior are represented with an ideal circuit model in the associated frequency range: the grains, the grain boundaries and the material-electrode interface, each represented as a parallel RC circuit. However, the Nyquist plot in the Fig. 11 appears as a single semicircle, which corresponds to the case where the dominant electrical behavior occurs in the grain boundaries of the material rather than in the grains and electrode[69].

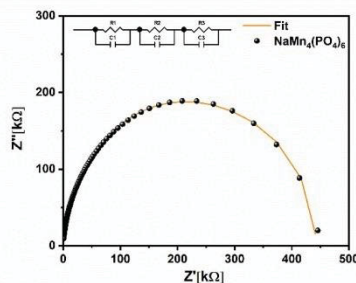


Fig. 11. Nyquist plot of $\text{NaMn}_4(\text{PO}_4)_3$ at 340 °C

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5. Conclusions

In summary, $\text{NaMn}_4(\text{PO}_4)_3$ was prepared by conventional solid-state synthesis at 1000 °C for 10 hours. X-ray diffraction data confirmed that the sample was single phase with no detectable impurities and crystallized in the Trigonal using hexagonal axis space group $R\bar{3}$. SEM indicates the average grain size of about 7 μm . The oxidation states of sodium, manganese, phosphorus, and oxygen were determined by the XPS analysis, leading to the following values: +1, +2, +5 and +2, respectively. Direct and indirect bandgaps found from the Tauc's plot method are 2.89 and 1.96 eV, respectively, indicating that $\text{NaMn}_4(\text{PO}_4)_3$ material can be classified as semiconductor. The CIE chromaticity coordinates for $\text{NaMn}_4(\text{PO}_4)_3$ compound was calculated to be (0.174, 0.011). The chromatic coordinates of the $\text{NaMn}_4(\text{PO}_4)_3$ indicate that this compound can be a candidate for blue-purple emitting material. Solid-state ultraviolet-visible spectroscopy (UV-vis) from the diffuse reflectance by using the Kubelka–Munk function and Tauc's relation and photoluminescence studies indicate that $\text{NaMn}_4(\text{PO}_4)_3$ display interesting properties. The study of the dielectric properties on $\text{NaMn}_4(\text{PO}_4)_3$ compound exhibits the behavior of an ionic conducting material. The Nyquist plot leads to a single semicircle which leads to three parallels RC circuits, highlighting the presence of grains, grain boundaries and the material-electrode interface where the dominant electrical behavior occurs in the grain boundaries.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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Chapitre 5: Conclusions et perspectives

5.1. Conclusions

Cette thèse s'inscrit dans le cadre de la recherche de nouveaux phosphates de métaux de transition $\text{Na}_{2+2x}\text{Co}_{8-y}\text{M}_z(\text{PO}_4)_6$ pouvant être utilisés comme matériaux pour les batteries ion sodium rechargeables. Les composés à structure polyanionique, plus particulièrement les phosphates ont montré un fort engouement depuis la découverte du potentiel du phosphate de fer olivine LiFePO_4 . Dorénavant, la faible conductivité électronique des phosphates n'est plus un obstacle à leur utilisation, contrairement à ce qui était généralement admis, grâce au développement de la mise en forme des batteries.

Notre choix d'étude était porté par le système $\text{Na}_{2+2x}\text{Co}_{8-y}\text{M}_z(\text{PO}_4)_6$ qui nous a conduit aux phases : $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ et $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$, $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ et $\text{NaMn}_4(\text{PO}_4)_3$, de structure présentant des tunnels contenant les alcalins. Les travaux effectués dans cette thèse de doctorat, avaient deux primordiaux objectifs. D'une part, de synthétiser sous forme de poudre fine et de les caractériser. D'autre part, de caractériser par différentes techniques les poudres obtenues après synthèse pour mieux comprendre leur structure.

Les phases $\text{Na}_2\text{Co}_6\text{M}_2(\text{PO}_4)_6$ ($\text{M} = \text{Mn}, \text{Ni}$) ont été préparées par la méthode à l'état solide à 800 °C et 850 °C respectivement. Les données de diffraction des rayons X ont confirmé que les échantillons étaient des phases pures sans impuretés détectables et cristallisaient dans la structure monoclinique. Le MEB indique des distributions de taille de particules allant de 1 à 10 μm , ayant une composition homogène dans les deux matériaux. Les valeurs de la bande interdite optique sont de 1,78 eV et 1,86 eV pour les matériaux dopés au Mn- et au Ni respectivement. Ces valeurs des bandes interdites optiques sont en bon

accord avec les couleurs des échantillons. La conductivité totale pour chaque composé suggère un mécanisme de conduction ionique. Les valeurs sont de 2.29×10^{-5} – 1.21×10^{-3} S/cm et 2.29×10^{-5} – 6.58×10^{-4} S/cm de 674 à 874 K pour $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ et $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ respectivement. La spectroscopie ultraviolet-visible (UV-vis) à l'état solide à partir de la réflectance diffuse en utilisant la fonction de Kubelka-Munk et la relation de Tauc et les études d'impédance indiquent que les deux matériaux présentent des propriétés intéressantes en tant que semi-conducteurs.

La phase $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ a été préparée avec succès par deux techniques de synthèse: l'état solide et sol-gel. Les études DRX révèlent que la phase est monoclinique (groupe d'espace $P2_1/c$). La MEB indique une distribution de la taille des particules comprise entre 8 à 35 μm et 1 à 20 μm , respectivement pour $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST et $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG. Ces phases ont une composition homogène dans les deux matériaux selon les résultats de la Spectroscopie de rayons X à dispersion d'énergie. Les états d'oxydation du sodium, du cobalt, du phosphore et de l'oxygène ont été obtenus par les résultats XPS pour les échantillons de $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ préparés par les deux méthodes et ont montré les valeurs suivantes: Na(I), Co(II/III), P(V) et O(-II). D'après les spectres de réflectance diffuse UV-Vis, les bandes interdites optique, directe et indirecte du $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST et du $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -SG sont estimées à 1,79 eV, 1,87 eV, 1,75 eV et 1,78 eV, 1,77 eV et 1,72 eV respectivement. La conductivité ionique pour les deux échantillons est de l'ordre de 10^{-4} S/cm et 10^{-2} S/cm, à 300 °C et 450 °C, respectivement. Ainsi, la variation de la conductivité ionique avec la température indique que la conduction ionique dans les matériaux est un processus thermiquement activé. Par conséquent, en considérant les résultats de XRD, SEM/EDS, DRS et EIS sur les échantillons $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ -ST et

$\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-SG}$, il est clair que la méthode sol-gel présente des résultats plus intéressants que la méthode à l'état solide.

Pour la phase $\text{NaMn}_4(\text{PO}_4)_3$, préparée par synthèse conventionnelle à l'état solide à 900 °C pendant 10 heures, les données de diffraction des rayons X ont confirmé que l'échantillon était monophasé, sans impuretés détectables, et qu'il cristallisait dans le trigone en utilisant l'axe hexagonal (groupe d'espace R-3). Le MEB indique que la taille moyenne des grains est d'environ 7 μm . Les états d'oxydation du sodium, du manganèse, du phosphore et de l'oxygène ont été déterminés par l'analyse XPS, conduisant aux valeurs suivantes : +1, +2, +5 et +2, respectivement. Les bandes interdites directe et indirecte déterminées par la méthode de Tauc sont respectivement de 2,89 et 1,96 eV, ce qui indique que le matériau $\text{NaMn}_4(\text{PO}_4)_3$ peut être classé comme semi-conducteur. Les coordonnées de chromaticité CIE pour le composé $\text{NaMn}_4(\text{PO}_4)_3$ ont été calculées comme étant (0,174, 0,011). Les coordonnées chromatiques du $\text{NaMn}_4(\text{PO}_4)_3$ indiquent que ce composé peut être un candidat pour un matériau émetteur bleu-violet. La spectroscopie ultraviolet-visible (UV-vis) à l'état solide à partir de la réflectance diffuse en utilisant la fonction de Kubelka-Munk et la relation de Tauc et les études de photoluminescence indiquent que le $\text{NaMn}_4(\text{PO}_4)_3$ présente des propriétés intéressantes. L'étude des propriétés diélectriques du composé $\text{NaMn}_4(\text{PO}_4)_3$ montre le comportement d'un matériau conducteur ionique. Le tracé de Nyquist conduit à un demi-cercle unique qui mène à trois circuits RC parallèles, mettant en évidence la présence de grains, de joints de grains et de l'interface matériau-électrode où le comportement électrique dominant se produit dans les joints de grains.

5.2. Perspectives

La série de phosphates de métaux de transition suivante $\text{Na}_{2+2x}\text{Co}_{8-y}\text{M}_z(\text{PO}_4)_6$ est encore très libre en ce sens qu'il y a moins des composés qui ont été synthétisés pouvant être utilisés comme matériaux pour les batteries ion sodium. Dans le futur, nous allons aborder les points suivants:

- ❖ Préparation de pastilles et de composites d'électrodes pour les tests électrochimiques.
- ❖ Assemblage de batteries pour des échantillons sélectionnés et caractérisation des caractéristiques de charge / décharge et cyclovoltammétrie.
- ❖ Calculs DFT pour aider à comprendre l'état de la conductivité, qui est susceptible d'être de nature électronique.
- ❖ Nous allons aussi investiguer les poudres de composition $\text{Na}_{2+2x}\text{Co}_{8-y}\text{M}_z(\text{PO}_4)_6$ par la méthode de l'état solide et la méthode sol-gel.

**Annexe 1: Informations complémentaires de l'article 1
(Comparative studies of synthesis, structure, optical and
conductivity of the monoclinic phases $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ and
 $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$)**

**Comparative studies of Synthesis, Structure, Optical
Properties and Conductivity of the Monoclinic Phases
 $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$**

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Table S1: Atomic occupancy and coordinates for Na₂Co₈(PO₄)₆ [23]

Atom	Wyckoff position	x	y	z	U _{iso}	BVS
Co(1)	4e	0.99215(8)	0.24835(8)	0.44261(4)	0.01153(13)	1.9(1)
Co(2)	4e	0.49062(8)	0.24311(8)	0.45366(4)	0.01243(14)	1.8(1)
Co(3)	4e	0.26265(10)	0.43210(7)	0.12710(4)	0.00971(15)	2.0(1)
Co(4)	4e	0.24408(19)	0.54597(16)	0.37429(10)	0.0235(3)	1.9(1)
P(1)	4e	0.74769(18)	0.52918(12)	0.43598(8)	0.0071(3)	4.9(1)
P(2)	4e	0.25312(18)	0.04375(12)	0.55795(8)	0.0078(3)	4.9(1)
P(3)	4e	0.25146(17)	0.20334(12)	0.27410(7)	0.0092(3)	(3) 4.9(1)
Na(1)	4e	-20.2602(4)	0.2455(3)	0.21831(18)	0.0338(7)	0.8(1)
Na(2)	4e	0.259(4)	0.411(3)	0.75710(17)	0.0338(7)	0.7(2)
O(1)	4e	0.7464(5)	0.3793(4)	0.46830(2)	0.0135(9)	1.9(1)
O(2)	4e	0.7563(5)	0.6171(4)	0.52190(2)	0.0122(8)	2.1(1)
O(3)	4e	0.5521(5)	0.5631(4)	0.38440(2)	0.0174(10)	1.9(1)
O(4)	4e	0.9364(5)	0.5585(4)	0.38090(2)	0.0167(10)	1.9(1)
O(5)	4e	0.2268(6)	0.1006(4)	0.46310(2)	0.0166(9)	2.0(1)
O(6)	4e	0.2528(5)	-0.1118(4)	0.55040(2)	0.0186(10)	2.0(1)
O(7)	4e	0.0733(5)	0.09570(4)	0.61200(3)	0.0221(11)	1.9(1)
O(8)	4e	0.4589(5)	0.10110(5)	0.59160(3)	0.0304(14)	1.9(1)
O(9)	4e	0.0473(4)	0.25330(4)	0.31524(19)	0.0161(8)	1.9(1)
O(10)	4e	0.2597(4)	0.24590(4)	0.17826(17)	0.0103(6)	2.2(1)
O(11)	4e	0.4469(4)	0.25340(4)	0.32400(2)	0.0175(8)	1.9(1)
O(12)	4e	0.2526(5)	0.04740(3)	0.26710(2)	0.0123(8)	1.9(1)

Table S2: Atomic occupancy and coordinates for Na₂Co₆Mn₂(PO₄)₆

Atom	Wyckoff position	x	y	z	Occupancy
Co(1)	4e	-0.016(6)	0.260(6)	0.4474(19)	1.00
Co(2)	4e	-0.518(6)	0.231(6)	0.460(2)	1.00
Co(3)	4e	-0.753(8)	-0.071(4)	0.375(3)	1.00
Co(4)	4e	-0.773(8)	0.534(4)	0.361(4)	1.00
P(1)	4e	-0.25230	0.52918	0.43598	1.00
P(2)	4e	-0.74690	0.04375	0.55795	1.00
P(3)	4e	0.25146	0.20334	0.27410	1.000
Na(1)	4e	-0.26020	0.24550	0.21831	0.89340
Na(2)	4e	0.25900	0.41100	0.75710	0.1066
O(1)	4e	-0.25360	0.37930	0.46830	1.00
O(2)	4e	-0.24370	0.61710	0.52190	1.00
O(3)	4e	-0.44790	0.56310	0.38440	1.00
O(4)	4e	-0.06360	0.55850	0.38090	1.00
O(5)	4e	-0.77320	0.10060	0.46310	1.00
O(6)	4e	-0.74720	0.11180	0.55040	1.00
O(7)	4e	-0.92670	0.09570	0.61200	1.00
O(8)	4e	-0.54110	0.10110	0.59160	1.00
O(9)	4e	0.04730	0.25330	0.31524	1.00
O(10)	4e	0.25970	0.24590	0.17826	1.00
O(11)	4e	0.44690	0.25340	0.32400	1.00
O(12)	4e	0.25260	0.04740	0.26710	1.00

Table S3: Atomic occupancy and coordinates for Na₂Co₆Ni₂(PO₄)₆

Atom	Wyckoff position	x	y	z	Occ.
Co(1)	4e	0.006(5)	0.239(6)	0.4429(17)	1.00
Co(2)	4e	-0.518(5)	0.255(6)	0.4524(17)	1.00
Co(3)	4e	-0.778(6)	-0.071(4)	0.375(3)	1.00
Co(4)	4e	-0.731(6)	0.546(4)	0.370(3)	1.00
P(1)	4e	-0.25230	0.52918	0.43598	1.00
P(2)	4e	-0.74690	0.04375	0.55795	1.00
P(3)	4e	0.25146	0.20334	0.27410	1.000
Na(1)	4e	-0.26020	0.24550	0.21831	0.89340
Na(2)	4e	0.25900	0.41100	0.75710	0.1066
O(1)	4e	-0.25360	0.37930	0.46830	1.00
O(2)	4e	-0.24370	0.61710	0.52190	1.00
O(3)	4e	-0.44790	0.56310	0.38440	1.00
O(4)	4e	-0.06360	0.55850	0.38090	1.00
O(5)	4e	-0.77320	0.10060	0.46310	1.00
O(6)	4e	-0.74720	0.11180	0.55040	1.00
O(7)	4e	-0.92670	0.09570	0.61200	1.00
O(8)	4e	-0.54110	0.10110	0.59160	1.00
O(9)	4e	0.04730	0.25330	0.31524	1.00
O(10)	4e	0.25970	0.24590	0.17826	1.00
O(11)	4e	0.44690	0.25340	0.32400	1.00
O(12)	4e	0.25260	0.04740	0.26710	1.00

Table S4: Selected distances for Na₂Co₈(PO₄)₆ [23]

Bond type	Bond length(Å)	Bond type	Bond length(Å)	Bond type	Bond length(Å)
Co(1)-O(1)	2.067(4)	Co(2)-O(1)	2.115(4)	Co(3)-O(5)	2.162(4)
Co(1)-O(2)	2.137(4)	Co(2)-O(2)	2.124(4)	Co(3)-O(6)	2.750(5)
Co(1)-O(5)	2.02(4)	Co(2)-O(5)	2.192(4)	Co(3)-O(7)	2.008(3)
Co(1)-O(6)	2.060(4)	Co(2)-O(6)	2.081(4)	Co(3)-O(8)	2.016(4)
Co(1)-O(9)	1.987(3)	Co(2)-O(8)	2.544(5)	Co(3)-O(10)	1.997(4)
		Co(2)-O(11)	2.001(3)	Co(3)-O(12)	1.983(3)
Co(4)-O(1)	2.518(4)	P(1)-O(1)	1.559(4)	P(2)-O(8)	1.562(4)
Co(4)-O(2)	2.261(4)	P(1)-O(2)	1.575(4)	P(2)-O(6)	1.540(4)
Co(4)-O(3)	1.963(4)	P(1)-O(3)	1.496(4)	P(2)-O(7)	1.510(4)
Co(4)-O(4)	1.959(4)	P(1)-O(4)	1.504(4)	P(2)-O(5)	1.504(4)
Co(4)-O(10)	2.130(4)				
Co(4)-O(11)	2.164(4)				
P(3)-O(9)	1.531(3)	Na(1)-O(3)	2.742(5)	Na(2)-O(3)	2.51(3)
P(3)-O(10)	1.527(3)	Na(1)-O(4)	2.626(5)	Na(2)-O(4)	2.45(3)
P(3)-O(11)	1.526(3)	Na(1)-O(7)	2.481(5)	Na(2)-O(9)	2.59(3)
P(3)-O(12)	1.542(3)	Na(1)-O(9)	2.429(4)	Na(2)-O(11)	2.77(3)
		Na(1)-O(11)	2.486(4)	Na(2)-O(2)	2.66(3)

Table S5: Selected distances for Na₂Co₆Mn₂(PO₄)₆

Bond type	Bond length(Å)	Bond type	Bond length(Å)	Bond type	Bond length(Å)
Co(1)-O(1)	1.95(5)	Co(2)-O(6)	2.06(4)	Co(3)-O(8)	1.95(5)
Co(1)-O(2)	2.09(4)	Co(2)-O(5)	2.07(5)	Co(3)-O(10)	1.98(4)
Co(1)-O(5)	2.20(5)	Co(2)-O(11)	2.13(3)	Co(3)-O(12)	2.04(5)
Co(1)-O(6)	2.09(5)	Co(2)-O(2)	2.15(5)	Co(3)-O(7)	2.07(5)
Co(1)-O(9)	2.11(3)	Co(2)-O(1)	2.22(4)	Co(3)-O(5)	2.17(5)
Co(1)-O(7)	3.06(4)	Co(2)-O(8)	2.42(4)	Co(3)-O(6)	2.76(5)
Co(1)-O(4)	3.11(6)	Co(2)-O(3)	2.16(4)		
Co(4)-O(4)	1.90(5)	P(1)-O(3)	1.49	P(2)-O(8)	1.50
Co(4)-O(12)	2.01(6)	P(1)-O(4)	1.52	P(2)-O(6)	1.52
Co(4)-O(3)	2.11(5)	P(1)-O(1)	1.55	P(2)-O(7)	1.53
Co(4)-O(10)	2.17(4)	P(1)-O(2)	1.58	P(2)-O(5)	1.58
Co(4)-O(2)	2.34(6)				
Co(4)-O(1)	2.78(6)				
Co(4)-O(9)	3.05(4)				
Co(4)-O(11)	3.15(5)				
				Na(2)-Na(1)	1.64
				Na(2)-O(4)	2.46
P(3)-O(11)	1.52	Na(1)-O(9)	2.42	Na(2)-O(3)	2.55
P(3)-O(12)	1.53	Na(1)-O(7)	2.48	Na(2)-O(9)	2.57
P(3)-O(9)	1.54	Na(1)-O(11)	2.52	Na(2)-O(11)	2.78
P(3)-O(10)	1.55	Na(1)-O(4)	2.62	Na(2)-O(7)	2.89
P(3)-O(5)	3.11	Na(1)-O(3)	2.76	Na(2)-O(6)	3.00
		Na(1)-O(8)	2.87	Na(2)-O(12)	3.16

Table S6: Selected distances for Na₂Co₆Ni₂(PO₄)₆

Bond type	Bond length(Å)	Bond type	Bond length(Å)	Bond type	Bond length(Å)
Co(1)-O(5)	1.97(4)	Co(2)-O(11)	1.98(3)	Co(3)-O(7)	1.93(4)
Co(1)-O(9)	1.99(3)	Co(2)-O(2)	2.03(5)	Co(3)-O(10)	1.99(4)
Co(1)-O(6)	2.04(4)	Co(2)-O(1)	2.08(4)	Co(3)-O(12)	2.04(5)
Co(1)-O(2)	2.14(4)	Co(2)-O(6)	2.15(5)	Co(3)-O(8)	2.06(4)
Co(1)-O(1)	2.17(4)	Co(2)-O(5)	2.22(5)	Co(3)-O(5)	2.13(4)
Co(1)-O(7)	2.96(4)	Co(2)-O(8)	2.60(4)	Co(3)-O(6)	2.70(5)
		Co(2)-O(3)	3.09(4)		
Co(4)-O(3)	1.84(4)	P(1)-O(3)	1.49	P(2)-O(8)	1.50
Co(4)-O(4)	2.08(4)	P(1)-O(4)	1.49	P(2)-O(7)	1.50
Co(4)-O(12)	2.10(5)	P(1)-O(1)	1.54	P(2)-O(6)	1.52
Co(4)-O(10)	2.11(4)	P(1)-O(2)	1.57	P(2)-O(5)	1.56
Co(4)-O(2)	2.30(5)				
Co(4)-O(1)	2.58(5)				
Co(4)-O(11)	3.17(4)			Na(2)-Na(1)	1.64
		Na(1)-O(9)	2.43	Na(2)-O(4)	2.45
		Na(1)-O(11)	2.47	Na(2)-O(3)	2.49
P(3)-O(9)	1.52	Na(1)-O(7)	2.47	Na(2)-O(9)	2.58
P(3)-O(11)	1.52	Na(1)-O(4)	2.61	Na(2)-O(11)	2.75
P(3)-O(10)	1.52	Na(1)-O(3)	2.72	Na(2)-O(7)	2.89
P(3)-O(12)	1.53	Na(1)-O(8)	2.82	Na(2)-O(6)	2.95
P(3)-O(5)	3.06	Na(1)-O(10)	3.08	Na(2)-O(12)	3.14

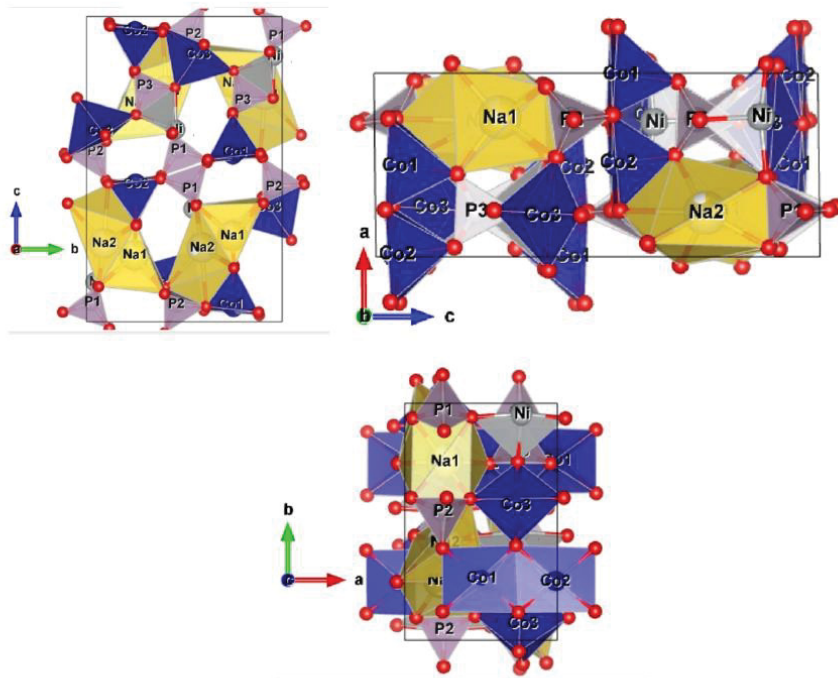


Fig. S1. Crystal structure of $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_3$

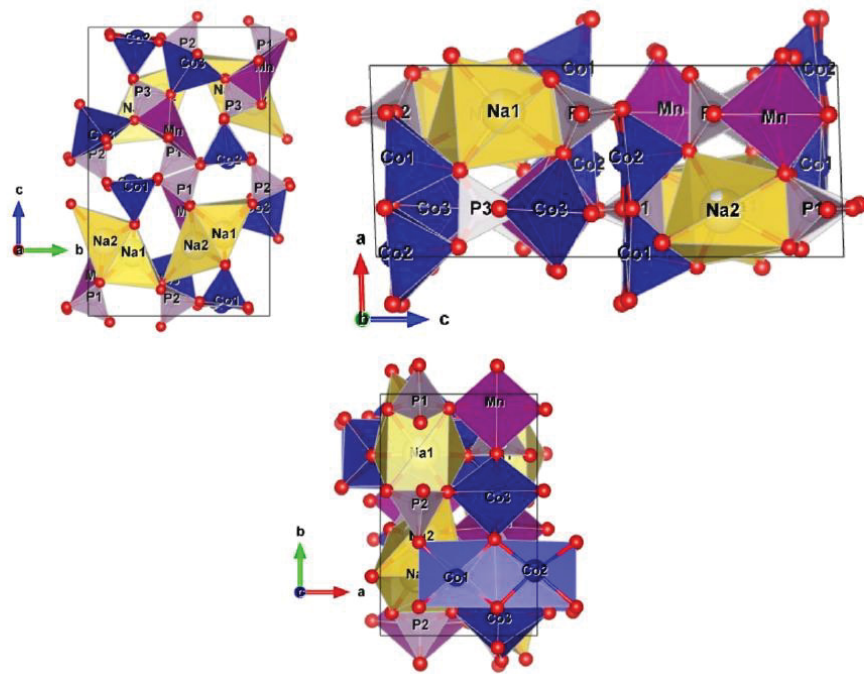


Fig. S2. Crystal structure of $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_3$

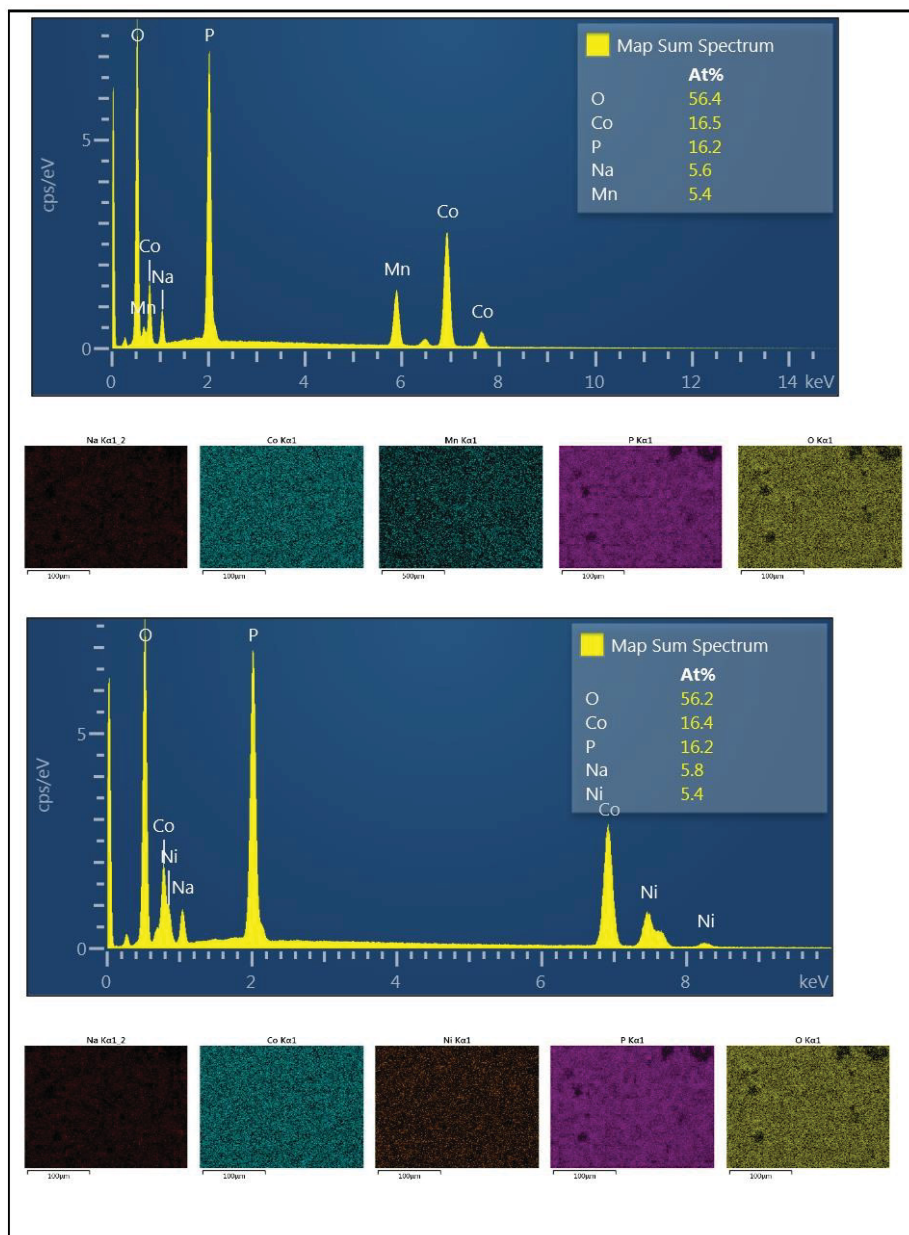


Fig.S3. EDS result of the $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ samples

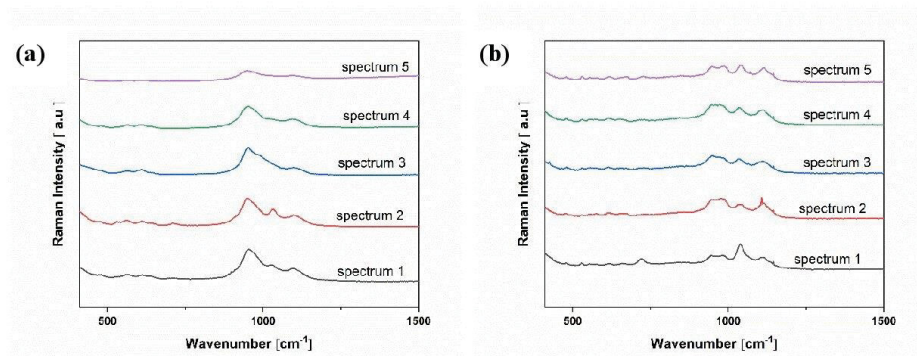


Fig. S4. Raman spectra of all (a) $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and (b) $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$ experiments.

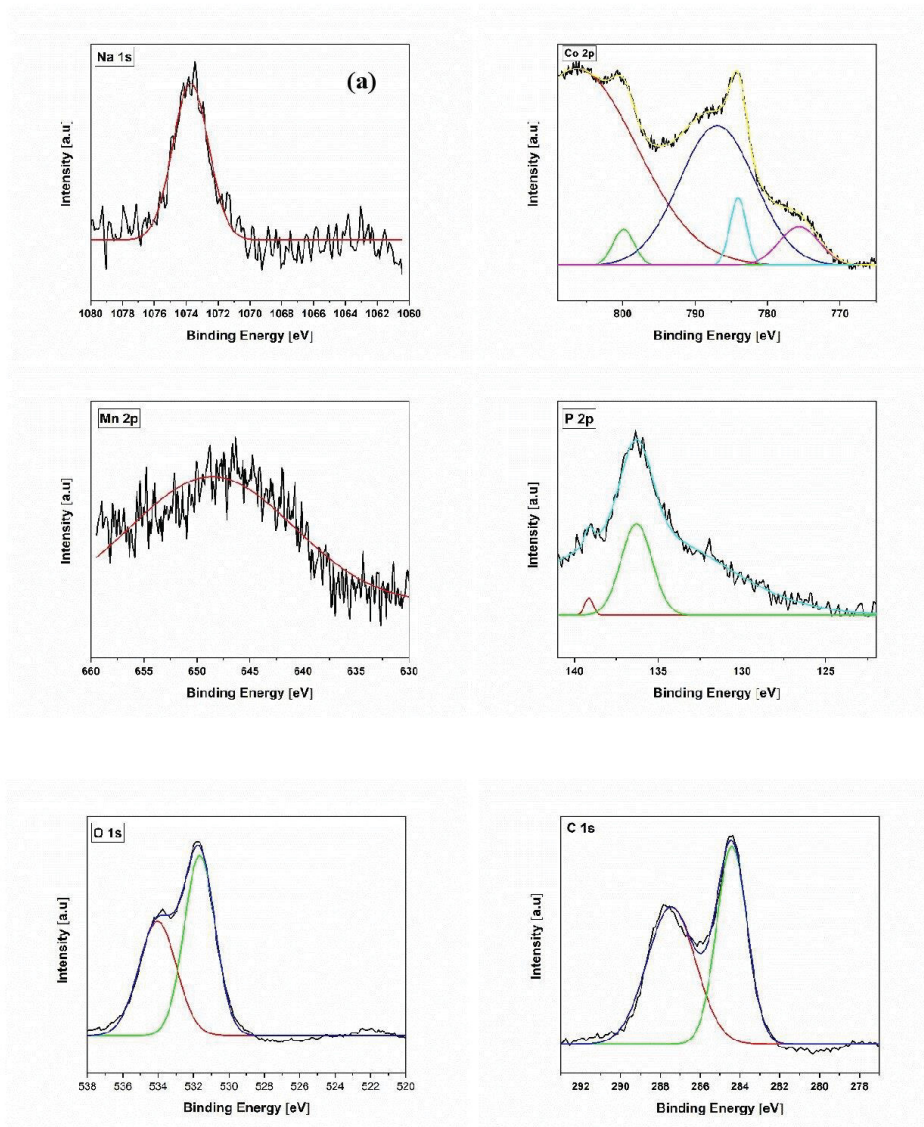


Fig.S5. XPS patterns of $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$: (a–f) the narrow spectra of Na 1s, Co 2p, Mn 2p, P 2p, O 1s, and C 1s, respectively

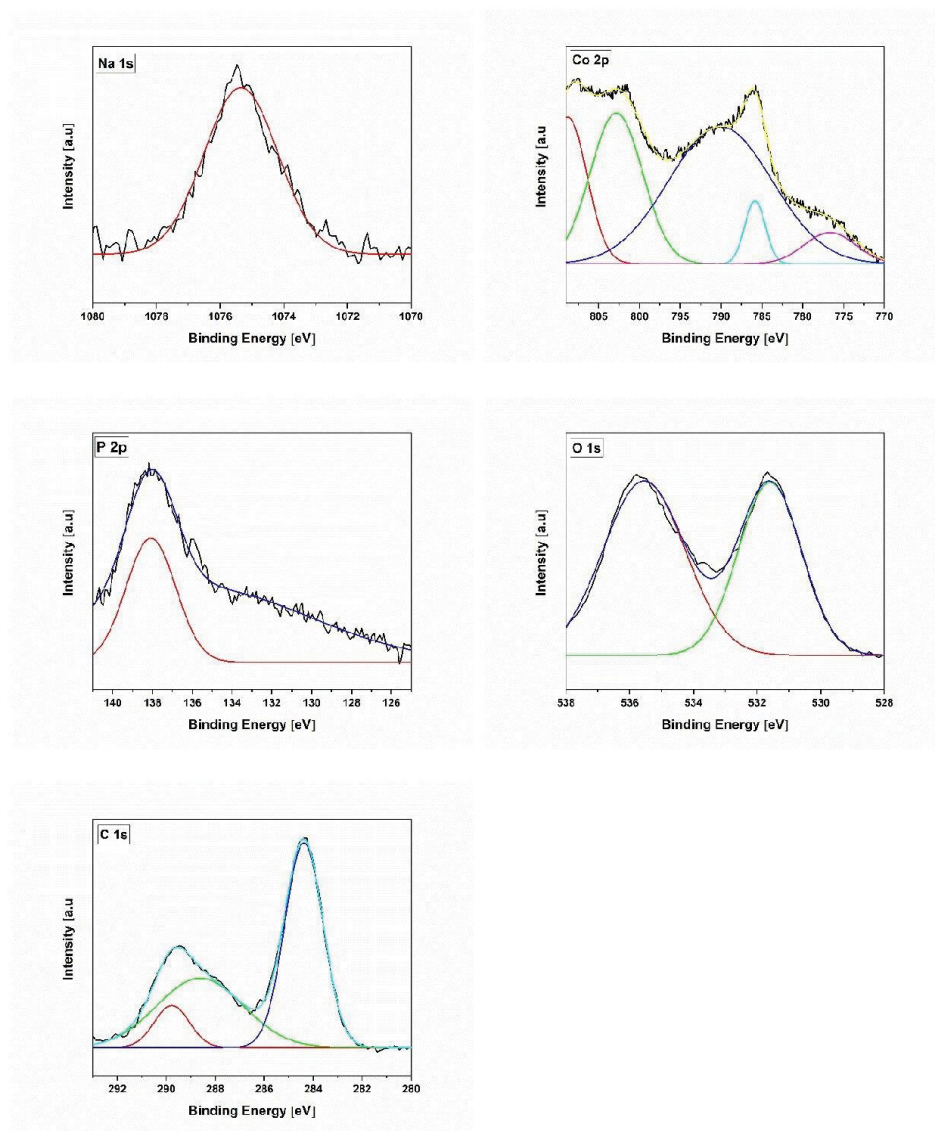


Fig.S6. XPS patterns of $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$: (a–e) the narrow spectra of Na 1s, Co 2p, P 2p, O 1s, and C 1s, respectively

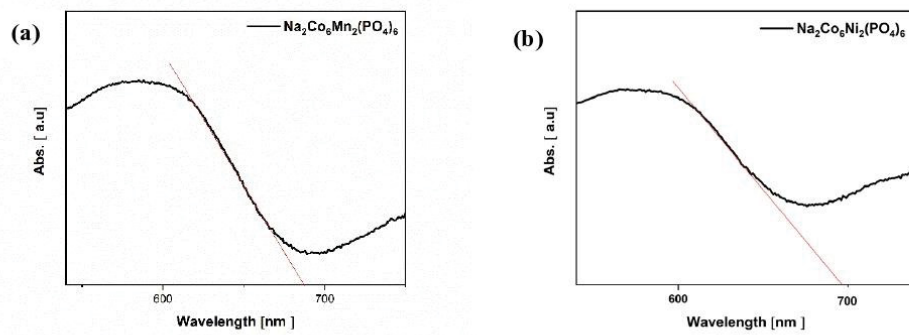


Fig.S7. UV-vis diffuse reflectance spectroscopy of $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$

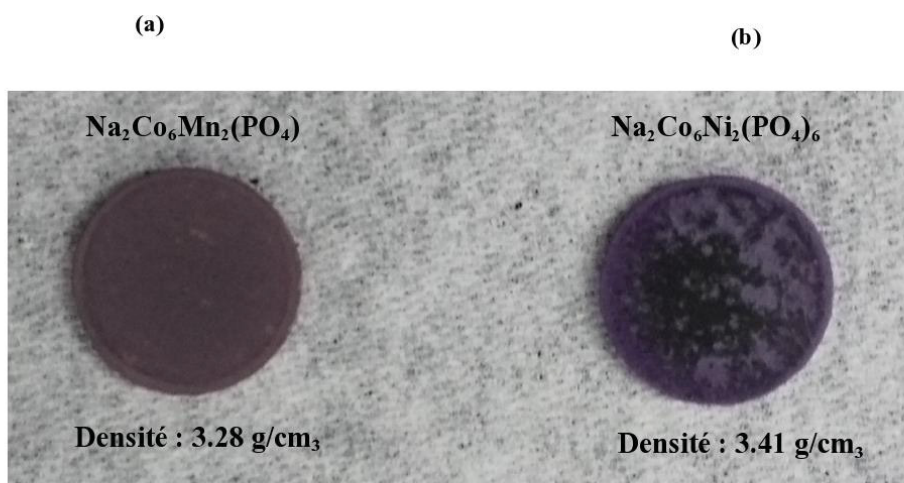


Fig.S8. Sintered pellets of (a) $\text{Na}_2\text{Co}_6\text{Mn}_2(\text{PO}_4)_6$ and (b) $\text{Na}_2\text{Co}_6\text{Ni}_2(\text{PO}_4)_6$

**Annexe 2: Informations complémentaires de l'article 2
(Synthesis of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ via sol-gel and solid-state methods)**

Synthesis of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$ via sol-gel and solid-state methods

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Table S1 Atomic occupancy and coordinates for Na₃Co₇(PO₄)₆-ST

Atom	Wyckoff position	x	y	z	Occupancy
Co(1)	4e	0.015(5)	0.274(4)	0.4437(19)	1.00
Co(2)	4e	-0.484(5)	0.255(6)	0.4555(19)	1.00
Co(3)	4e	-0.771(10)	-0.063(4)	0.378(3)	1.00
Co(4)	4e	-0.755(11)	0.560(4)	0.377(3)	1.00
P(1)	4e	-0.25230	0.52918	0.43598	1.00
P(2)	4e	-0.74690	0.04375	0.55795	1.00
P(3)	4e	0.25146	0.20334	0.27410	1.000
Na(1)	4e	-0.26020	0.24550	0.21831	0.89340
Na(2)	4e	0.25900	0.41100	0.75710	0.1066
O(1)	4e	-0.25360	0.37930	0.46830	1.00
O(2)	4e	-0.24370	0.61710	0.52190	1.00
O(3)	4e	-0.44790	0.56310	0.38440	1.00
O(4)	4e	-0.06360	0.55850	0.38090	1.00
O(5)	4e	-0.77320	0.10060	0.46310	1.00
O(6)	4e	-0.74720	0.11180	0.55040	1.00
O(7)	4e	-0.92670	0.09570	0.61200	1.00
O(8)	4e	-0.54110	0.10110	0.59160	1.00
O(9)	4e	0.04730	0.25330	0.31524	1.00
O(10)	4e	0.25970	0.24590	0.17826	1.00
O(11)	4e	0.44690	0.25340	0.32400	1.00
O(12)	4e	0.25260	0.04740	0.26710	1.00

Table S2 Atomic occupancy and coordinates for Na₃Co₇(PO₄)₆-SG

Atom	Wyckoff position	x	y	z	Occ.
Co(1)	4e	-0.006(5)	0.244(8)	0.448(2)	1.00
Co(2)	4e	-0.499(5)	0.250(8)	0.448(2)	1.00
Co(3)	4e	-0.753(15)	-0.071(3)	0.373(3)	1.00
Co(4)	4e	-0.748(15)	0.545(3)	0.372(3)	1.00
P(1)	4e	-0.25230	0.52918	0.43598	1.00
P(2)	4e	-0.74690	0.04375	0.55795	1.00
P(3)	4e	0.25146	0.20334	0.27410	1.000
Na(1)	4e	-0.26020	0.24550	0.21831	0.89340
Na(2)	4e	0.25900	0.41100	0.75710	0.1066
O(1)	4e	-0.25360	0.37930	0.46830	1.00
O(2)	4e	-0.24370	0.61710	0.52190	1.00
O(3)	4e	-0.44790	0.56310	0.38440	1.00
O(4)	4e	-0.06360	0.55850	0.38090	1.00
O(5)	4e	-0.77320	0.10060	0.46310	1.00
O(6)	4e	-0.74720	0.11180	0.55040	1.00
O(7)	4e	-0.92670	0.09570	0.61200	1.00
O(8)	4e	-0.54110	0.10110	0.59160	1.00
O(9)	4e	0.04730	0.25330	0.31524	1.00
O(10)	4e	0.25970	0.24590	0.17826	1.00
O(11)	4e	0.44690	0.25340	0.32400	1.00
O(12)	4e	0.25260	0.04740	0.26710	1.00

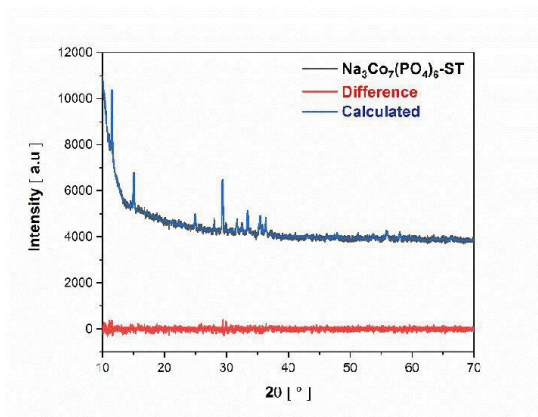


Fig. S1. Rietveld refinement of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-ST}$

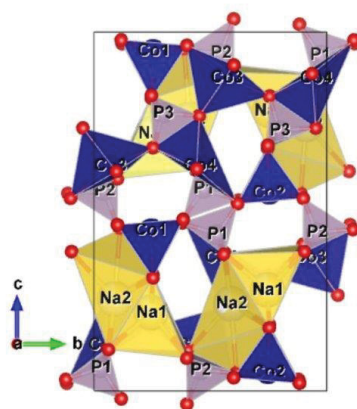


Fig. S2. Schematic crystal structure illustrations of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6$

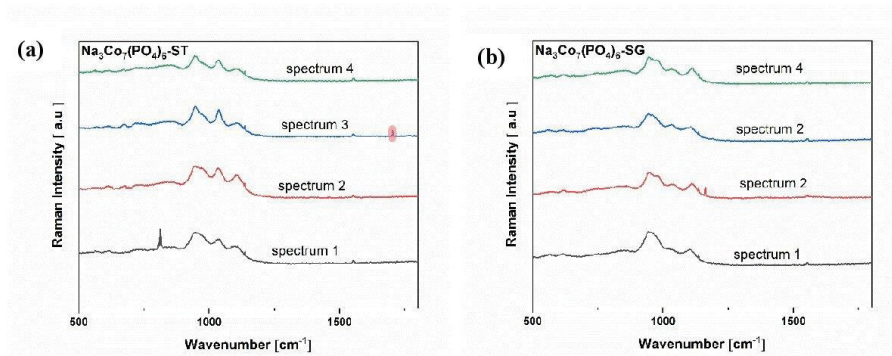


Fig. S3. Raman spectra of all (a) $\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-ST}$ and (b) $\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-SG}$ experiments.

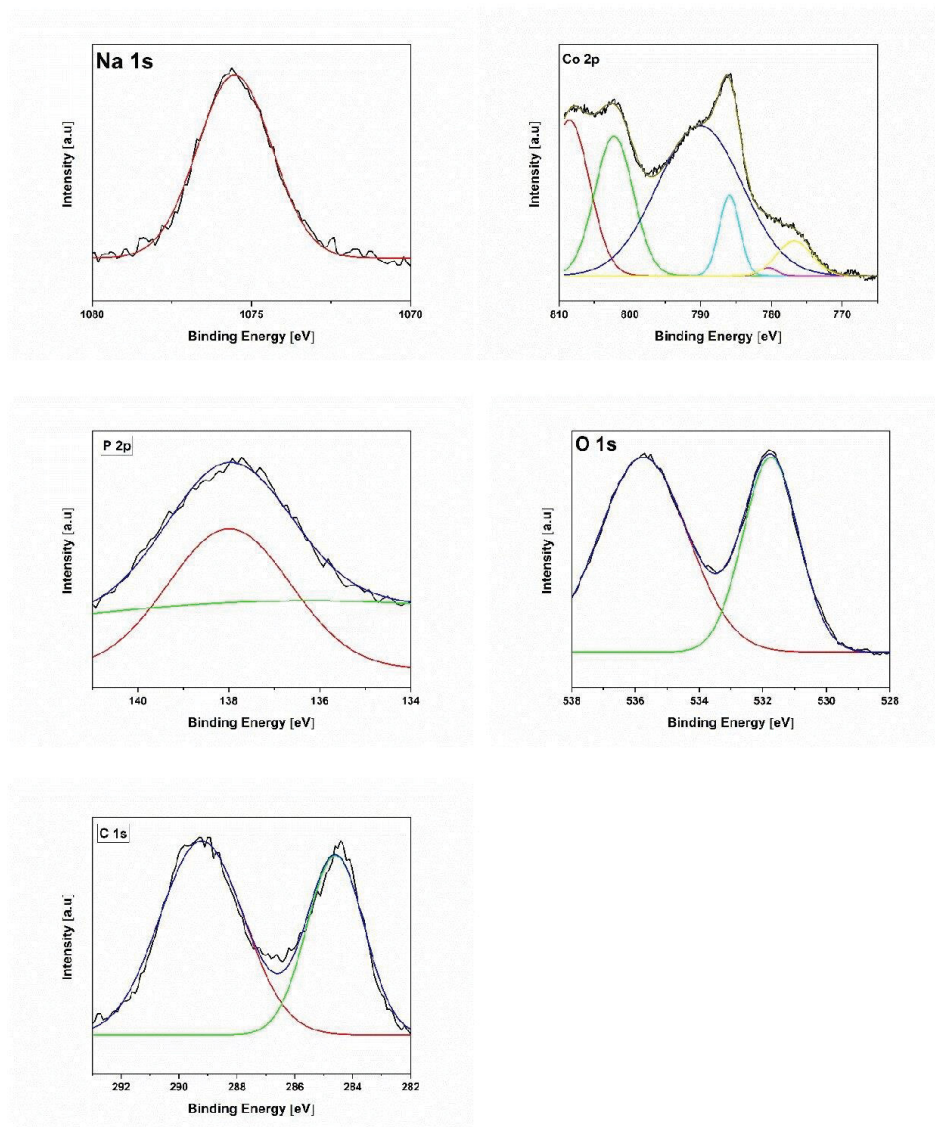


Fig. S4. XPS patterns of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-ST}$: the narrow spectra of Na 1s, Co 2p, P 2p, O 1s, and C 1s.

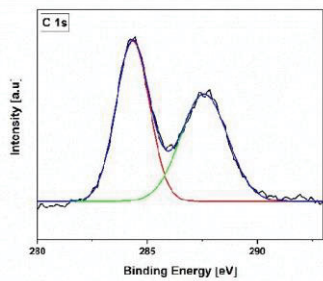
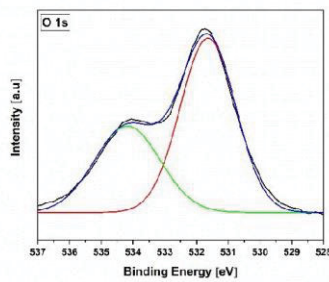
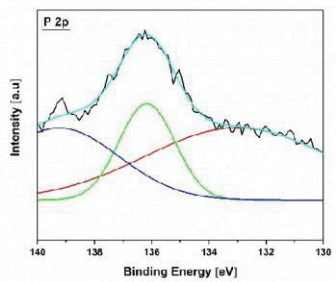
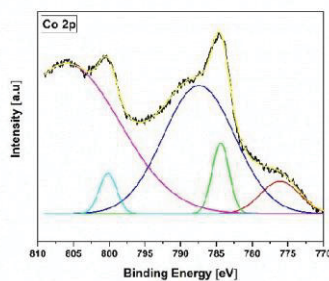
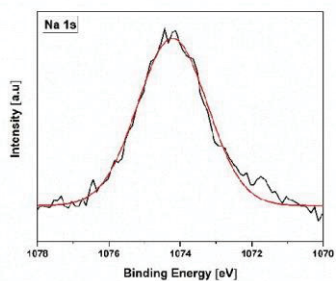


Fig. S5. XPS patterns of $\text{Na}_3\text{Co}_7(\text{PO}_4)_6\text{-SG}$: the narrow spectra of Na 1s, Co 2p, P 2p, O 1s, and C 1s.

Annexe 3: Informations complémentaires de l'article 3 (Investigation of structural, optical, dielectric and electrical properties of $\text{NaMn}_4(\text{PO}_4)_3$ with Fallowite-type Structure)

Investigation of structural, optical, dielectric and electrical properties of $\text{NaMn}_4(\text{PO}_4)_3$ with fillowite-type structure

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Table S1 Atomic occupancy and coordinates for $\text{NaMn}_4(\text{PO}_4)_3$

Atom	Wyckoff position	x	y	z	Occupancy
Mn1	3	0.00000	0.00000	0.00000	1
Mn2	3	0.00000	0.00000	0.50000	0.666
Na1	3	0.00000	0.00000	0.50000	0.33
Mn3	6	0.00000	0.00000	0.10168	0.894
Na2	6	0.00000	0.00000	0.32551	0.977
Mn4	6	0.00000	0.00000	0.39924	1
Mn5	18	0.41464	0.24021	0.04200	0.985
Mn6	18	0.11118	0.55297	0.03256	1
Mn7	18	0.01293	0.34372	0.08470	0.988
Mn8	18	0.26644	0.33550	0.08094	1
Mn9	18	0.58341	0.09693	0.11487	1
Mn10	18	0.22225	0.12632	0.12888	1
Na3	18	0.23963	0.25453	-0.00158	0.982
Mn11	6	0.00000	0.00000	0.17518	0.982
Na4	6	0.00000	0.00000	0.25154	1
Na5	18	0.04168	0.40027	0.16758	0.654
Mn12	18	0.04168	0.40027	0.16758	0.343
P1	18	0.21534	0.42413	0.03298	1
P2	18	0.54439	0.11516	0.04296	1
P3	18	0.57651	0.10079	0.19429	1
P4	18	0.21817	0.13357	0.20528	1
P5	18	0.21507	0.46676	0.22111	1
P6	18	0.46069	0.22580	0.27765	1
O1	18	0.15670	0.37187	0.06266	1
O2	18	0.24058	0.53569	0.03131	1
O3	18	0.31566	0.42224	0.03514	1
O4	18	0.15690	0.36389	0.00474	1
O5	18	0.53090	0.20750	0.04025	1
O6	18	0.44463	0.01620	0.05071	1
O7	18	0.62536	0.13630	0.06798	1
O8	18	0.58810	0.09870	0.01343	1
O9	18	0.55137	0.04753	0.16284	1
O10	18	0.63070	0.21737	0.19194	1
O11	18	0.47581	0.06480	0.21135	1
O12	18	0.65120	0.07680	0.21043	1
O13	18	0.24220	0.17950	0.17271	1
O14	18	0.11774	0.03031	0.20529	1
O15	18	0.20571	0.20733	0.22631	1
O16	18	0.29861	0.11000	0.21733	1
O17	18	0.21490	0.52740	0.19344	1
O18	18	0.10094	0.37984	0.22550	1
O19	18	0.27810	0.41570	0.21565	1
O20	18	0.24530	0.52460	0.25158	1
O21	18	0.51961	0.25361	0.24695	1
O22	18	0.40176	0.10755	0.28036	1
O23	18	0.37551	0.25310	0.27714	1
O24	18	0.52760	0.27230	0.30529	1

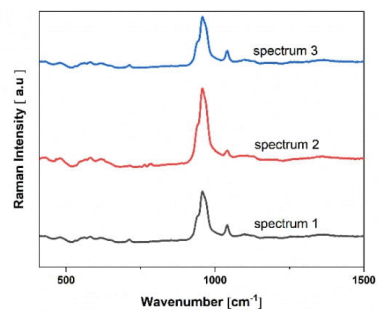


Fig. S1 All Raman spectra of $\text{NaMn}_4(\text{PO}_4)_3$ experiments.