The lamellar $Na_2CoP_2O_7$ pyrophosphate: Preparation, structural and spectroscopic studies

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Intensive scientific investigations have been devoted to phosphates. These investigations have concerned the synthesis, the structural features or the physical properties (electrical, magnetic, optic, electrochemical….). As layered materials are attractive for the electrochemical applications, we have prepared and studied $Na_2CoP_2O_7$ which could be used as starting material for $Li_2CoP_2O_7$ preparation by Na/Li exchange reaction. $Na_2CoP_2O_7$ was prepared by coprecipitation method and the structure was refined by using the Rietveld method. $Na_2CoP_2O_7$ exhibits a layered structure (S.G. $P4_2/mnm$; a = 7.704 (3) Å, c = 10.293 (5) Å). Within de CoP_2O_7 sheets, each CoO_4 tetrahedron shares corners with P_2O_7 rings. Sodium ions are located in a very large crystallographic site. The prepared phosphate has been characterized by IR spectroscopy which confirms the structural results.

Keywords: pyrophosphate; Positive Electrode; lithium-ion Batteries; Rietveld method; IR Spectroscopy

I. INTRODUCTION

The technological advancement in the area of electronics and the onset of electric vehicles require low cost, environment friendly and high energy density batteries. The lithium-ion batteries have been already accepted in the power sources for various kinds of portable devices such as cellular phones, laptop computers and other consumer electronic tools because these have a high volumetric and gravimetric energy density. The lithium-ion batteries usually consist of lithium intercalation compound as cathode, graphite or carbon as anode and an organic electrolyte. The cathode is a key component in the lithium-ion batteries, and the $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$ are currently used as cathode materials. The use of high cost and toxic or unsafe cathode materials ($LiCoO_2$ and $LiNiO_2$) restricts the development of zero-emission types of cars based on these batteries. Therefore, attention of many research groups has been focused on [1-2].

The literature gives a great number of materials with general formula AMP_2O_7 or $A_2MP_2O_7$ (A=alkali metal, M = transition metal) [3-4-5]. The structure of these phases has generally an open framework which leads to a good mobility of cations making easier the intercalation/deintercalation reactions [6]. The existence of transition metal ions coupled to the high ionic conductivity of this type of materials reveals that these phosphates are a potential candidates to positive electrode material for lithium ion batteries.

With the aim to prepare new positive electrode materials, we have investigated $Na_2CoP_2O_7$ pyrophosphate, which has been used as pristine phase for preparing lithium homologous ones. Indeed, it appears more difficult to prepare $Li_2CoP_2O_7$ material directly at high temperature.

II. EXPERIMENTAL SECTION

II.1. Synthesis

The investigated compound $Na_2CoP_2O_7$ was obtained as poly-crystalline powders form by coprecipitation reactions from $(NH_4)_2HPO_4$, Na_2HPO_4 and $Co(NO_3)_2,6H_2O$ according to the following stoichiometries :

$$Na_2HPO_4 + (NH_4)_2HPO_4 + Co(NO_3)_2 \rightarrow Na_2CoP_2O_{7(s)} + 2NO_3^-{}_{(aq.)} + 2NH_4^+{}_{(aq.)} + H_2O$$

The obtained product was kept at 120°C for 12 hours and heated progressively to 400°C. After decomposition of the nitrate and the phosphate, the mixture was fired at 650°C for 12 hours.

II.2. X-Ray diffraction study

X-ray powder pattern was carried out at room temperature using a phillips Xpert MPD diffractometer in the step scan mode (CuKα radiation, at a step value of 0.02°).

II.3. IR Spectroscopy

The infrared study of Na_2CoP2O_7 was carried out using an FTIR UNICAM spectrometer (4000-400 cm^{-1} range). For the measurements, pellets have been made with the studied compounds diluted (2 wt%) in KBr.

III. RESULTS AND DISCUSSION

III.1. Crystal structure

X-ray analysis of the $Na_2CoP_2O_7$ shows that this phase crystallizes in the tetragonal system (Space Group :$P4_2/mnm$) with the following unit cell parameters : a = 7.704(3) Å ; c = 10.293(5) Å.

Atomic positions have been refined using Rietveld method. The obtained Rietveld coefficients are indication of a good concordance between the observed and calculated diagram profiles.

Figure 1 gives the observed, calculated and difference powder XRD profiles of $Na_2CoP_2O_7$. The Bragg positions are also indicated. Results of the structural refinement of $Na_2CoP_2O_7$ are given in Table I:

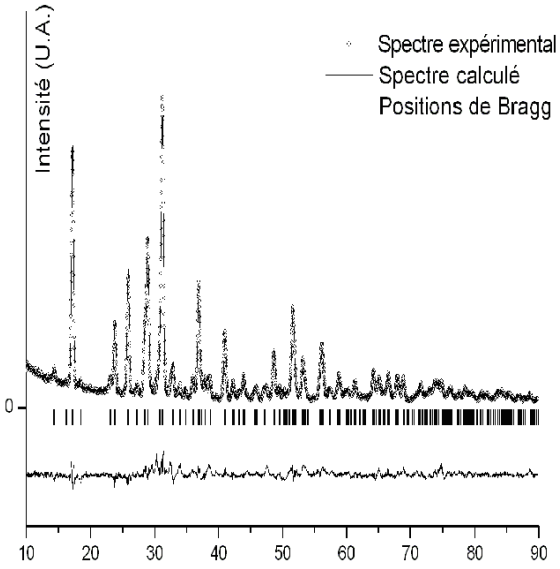

FIGURE 1: Observed, calculated and difference powder XRD profiles of $Na_2CoP_2O_7$.

Table I: Results of the Rietveld refinement of $Na_2CoP_2O_7$ phase.

Space group: $P4_2/mnm$ with a = 7.704(3) Å, c = 10.293(5) Å ; R_p = 8,7% R_{wp} = 12,2% ; R_B = 5,6%					
Atom	Wyckoff positions			occupancy	B(Å^2)
Na1	0.853(3)	0.148(3)	0(0)	1	1.5(9)
Na2	0.8(3)	0.2(3)	0.5(0)	1	3.7(1)
Co	0.5(0)	0(0)	0.25(0)	1	2.2(4)
P	0.636(2)	0.365(2)	0.214(2)	2	2.4(5)
O1	0.633(4)	0.367(4)	0.364(3)	2	3.9(1)
O2	0.582(3)	0.2(4)	0.144(3)	4	3.9 (1)
O3	0.5(0)	0.5(0)	0.152(5)	1	3.9(2)

The structure of this sample could be described as a succession of two types of sheets. The first one contains only sodium ions, the second consists of $[CoP_2O_7]$ group (Figure 2).This bidimensional structure is very convenient for the sodium/lithium exchange reaction and for sodium deintercalation.

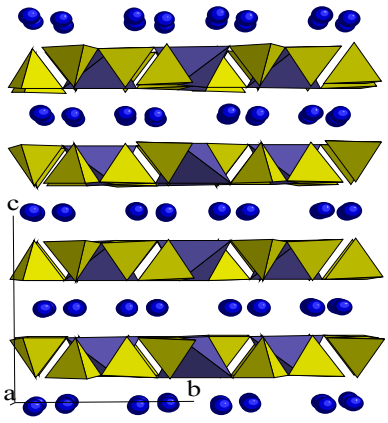

FIGURE 2: Projection of $Na_2CoP_2O_7$ structure along (100) plane

III.2. IR Spectroscopy

The vibrational study by infrared spectroscopy of phosphates allows to have a very fast structural information, in particular the identification of the various basic groupings forming phosphatic material. Indeed, the number and the distribution of the bands frequencies depend on local symmetry nature of the $P_2O_7^{4-}$ anion.

The spectrum of $Na_2CoP_2O_7$ compound (Figure 3) shows the existence of two distinct bands around 917 cm^{-1} and 710 cm^{-1} assigned respectively with asymmetric and symmetric stretching vibration of the P-O-P bridge. These bands are characteristic of pyrophosphate groups ($P_2O_7^{4-}$) In the 975-1300 cm^{-1} domain, frequencies related to the symmetric and antisymmetric vibration modes of terminal $(PO_3)^{2-}$ groups have been evidenced. The bands around 400-700 cm^{-1} were assigned to the deformation and rocking modes of PO_3 groups.

Furthermore, the existence of $\nu_s(PO_3)$ frequencies in the infrared spectrum indicates that $[P_2O_7]$ ring adopts a bent configuration.

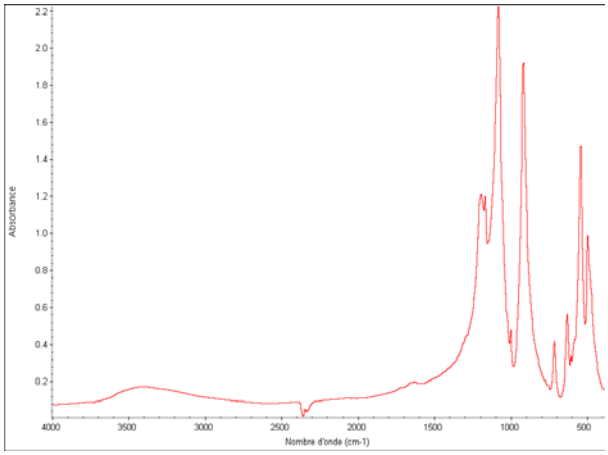

FIGURE 3: IR Spectrum of $Na_2CoP_2O_7$ pyrophosphate

Table II summarizes the band assignments for $Na_2CoP_2O_7$.

Frequency value (cm^{-1})	Assignment
1190 1167 1082 997	$\nu_{as}PO_3$
1012	ν_sPO_3
917	ν_{as}P-O-P
710	ν_sP-O-P
635 551 545 494	δPO_3 & ρPO_3

IV. CONCLUSION

$Na_2CoP_2O_7$ pyrophosphate has been prepared as polycrystalline sample by coprecipitation method, at moderate temperature. The blue color of this prepared phosphate is characteristic of the presence of Co^{2+} ions.

Structural refinement by the Rietveld method shows that this phosphate exhibits a 2D structure. Alternate sheets of sodium ions and $[CoP_2O_7]$ group has been evidenced. IR spectroscopy confirms these structural results.

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