# Experimental report

08/06/2020

**Proposal:** 5-21-1121 **Council:** 10/2018

**Title:** Discriminate the crystallographic sites of lithium and sodium in honeycomb-ordered layered (Li1-xNax)3Ni2SbO6

**Research area:** Chemistry

**This proposal is a new proposal**


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**Experimental team:** Romain BERTHELOT

**Local contacts:** Emmanuelle SUARD


**Samples:** Li3Ni2SbO6
Na3Ni2SbO6
Li1.5Na1.5Ni2SbO6
Li2.25Na0.75Ni2SbO6
Li0.75Na2.25Ni2SbO6
Li2NaNi2SbO6
LiNa2Ni2SbO6

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D2B | 2 | 1 | 08/07/2019 | 09/07/2019 |


**Abstract:**

This proposal aims in determining the crystallographic structure of a new honeycomb-ordered layered phase obtained by the high-temperature combination of Li3Ni2SbO6 and Na3Ni2SbO6. Neutron powder diffraction would help in choosing between three possible crystallographic structures according to the location of lithium and sodium ions: in-plane mixed occupancy, in-plane ordering, or out-of-plane ordering.
In all cases, the structure would be unusual, bringing significant input for understanding the structure alkali transition metal layered oxides and for searching new compositions with unusual cationic ordering. The use of neutrons is required as the contrast it offers complementary with X-Ray will enable the precise localisation of Li, Na, Ni and Sb atoms within the octahedral sites of the structure.

EXPERIMENTAL REPORT FOR PROPOSAL 5-21-121

Discriminate the crystallographic sites of lithium and sodium in honeycomb-ordered layered $(Li_{1-x}Na_x)_3Ni_2SbO_6$

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This run enabled to analyze various compositions along the complete solid-solution $Li_{3-x}Na_xNi_2SbO_6$. It comes after a preliminary analysis performed during the EASY access run 352 that specifically focused on the intermediate compositions $Li_{1.5}Na_{1.5}Ni_2SbO_6$.

The interest of using neutron diffraction was to discriminate the position of both lithium and sodium ions if a possible alkali ions ordering appears for any of the investigated compositions. The conclusions of the EASY run are the following ones:

- In the transition metal layer, the in-plane honeycomb-like ordering between nickel and antimony cations is confirmed, with however a significant nickel/antimony intermixing that could result from the final quenching step which is mandatory to get a single-phase end-product
- In the alkali layer, lithium and sodium cations are randomly distributed without any supplementary ordering.

With the additional compositions analyzed through the run 5-21-121, the linear evolutions of the cell parameters confirm the complete solid-state behavior, and similar conclusions have been drawn regarding the random distribution of both lithium and sodium ions. The results are gathered in a published article (Vallée et al. Inorg. Chem. DOI: 10.1021/acs.inorgchem.9b01385).

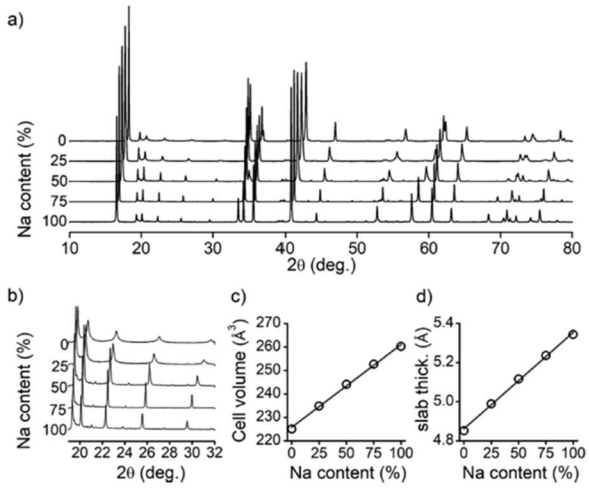


Figure 1. (a) XRD patterns of $Li_{3-x}Na_xNi_2SbO_6$ compositions obtained after a final quench, (b) restricted $2\theta$ window to highlight the honeycomb superstructure peaks, and evolution of (c) the monoclinic cell volume and (d) the slab thickness (calculated by $c \times \sin(\beta)$).

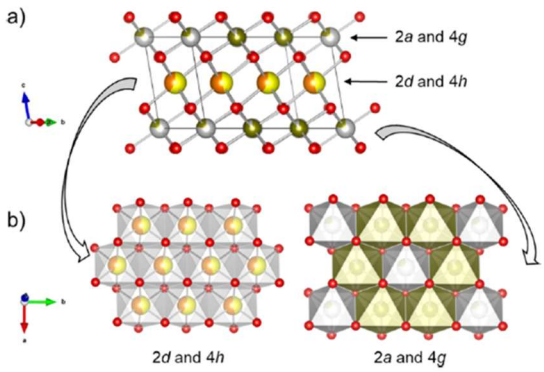


Figure 5. (a) Structural model for $Li_{1.5}Na_{1.5}Ni_2SbO_6$ resulting from the combined X-ray/neutron Rietveld refinement and (b) in-plane views showing the Ni/Sb and Li/Na intermixing.

In a wider scope, this preliminary run will be hopefully followed by other investigations on new layered dual alkali transition metal layered oxides with possible interesting physical features. For example another run was planned during spring 2020 to investigated mixed compositions in the layered systems $Li_2SnO_3$-$Na_2SnO_3$. Due to Covid crisis, it has been postponed however.