Experimental report

14/03/2024

Proposal: **5-22-806**

Council: 10/2022

Title: Localizing lithium cations in new alkali-ordered honeycomb layered compounds

Research area: Chemistry

This proposal is a new proposal

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Samples: $Li_2Ni_2TeO_6$
$Li_2Ni_2TeO_6$ (O3)
$LiKNi_2TeO_6$
$LiNa_{0.5}K_{0.5}Ni_2TeO_6$
$LiNaNi_2TeO_6$

Instrument	Requested days	Allocated days	From	To
D20	1	1	13/04/2023	14/04/2023
D2B	2	1	06/03/2023	07/03/2023

Abstract:

EXPERIMENTAL REPORT FOR PROPOSAL 5-22-806

Title: Localizing lithium cations in new alkali-ordered honeycomb layered compounds

Context and Objectives: In the search for new alkali-mixed layered oxides, we investigated the ternary system between the 3 honeycomb-ordered layered oxides $Li_2Ni_2TeO_6$, $Na_2Ni_2TeO_6$ and $K_2Ni_2TeO_6$. In a previous study, we confirmed the existence of $NaKNi_2TeO_6$, a particular composition with alternated layers of Na and K.[1] During the run at ILL, we analyzed other new compositions with Li as one of the alkali cations: $LiKNi_2TeO_6$, $LiNaNi_2TeO_6$ and $LiNa_{0.5}K_{0.5}Ni_2TeO_6$. These compositions have been obtained directly by solid-state reaction, or by a 2-step solid-state process involving reaction between two single-alkali layered precursors $A_2Ni_2TeO_6$. It is important to note that this proposal is part of a greater research project with other large-scale facility like ANSTO (Australia) for neutron diffraction as well, and ALBA (Spain) for synchrotron X-ray diffraction. The results shown below are now published in Chem. Mater.[2] As requested, the DOI of the ILL proposal is mentioned in the article.

Results: We first investigate the single-alkali layered compounds $Na_2Ni_2TeO_6$ and $K_2Ni_2TeO_6$ prepared directly by solid-state synthesis, and $Li_2Ni_2TeO_6$ layered polymorph obtained through ionic exchange, by SXRPD and ND (data collected at ANSTO). Rietveld refinement were performed considering the crystallographic structure given in the literature for these three compositions.[3–5] We then analyzed the intermediate composition $Li_{1-x}Na_xNi_2TeO_6$ and $Li_{1-x}K_xNi_2TeO_6$ and revealed two monophasic compositions for roughly half of each alkali cation. A superstructure peak at low angle calls for an alternation of distinct alkali layers. NPD data for $LiKNi_2TeO_6$ has been collected at ANSTO (Fig. 1a), NPD data for $LiNaNi_2TeO_6$ has been collected at ILL (Fig. 2). The patterns were very similar for the two compositions, but we focused on the first one to propose a common crystallographic structure, because of the presence of residue of $Na_2Ni_2TeO_6$ in the second pattern. The alternation of lithium and potassium layers was assumed from the beginning thanks to the presence of a superstructure peak at low angle. We initially stated with the structural model of OP4-$Li_xNa_yCoO_2$, exhibiting a similar alkali layer alternation.[6] We then expand the hexagonal (*a*,*b*) plane to consider the Ni/Te honeycomb ordering, and finally we propose a helical arrangement of the Te along three layers to match with the tripling of the c_{hex} cell parameter (Fig. 2).

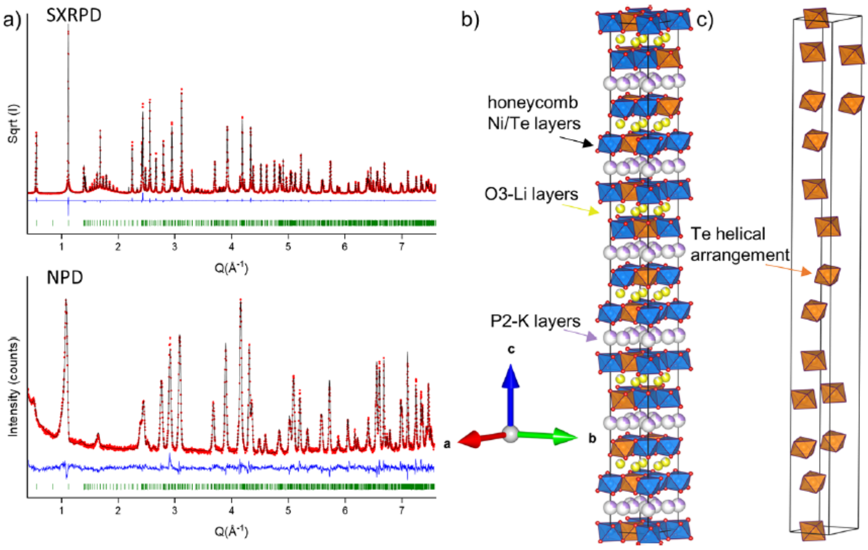

Figure 2: SXRPD and NPD patterns of $LiKNi_2TeO_6$ with corresponding Rietveld refinement and the proposed structural model with the particular helical Te arrangement (NPD data collected at ANSTO).

Then, we investigated alkali-mixed compositions containing lithium, sodium and potassium cations, either through 1-pot solid-state synthesis or by heating mixture of $A_2Ni_2TeO_6$ with A'A"Ni_2TeO_6 (A, A' and A" being either Li, Na or K). We revealed the existence of a single-phase composition $LiNa_{0.5}K_{0.5}Ni_2TeO_6$. Considering that sodium and potassium do not occupy the same layer in $NaKNi_2TeO_6$,[1] we firstly assumed three distinct alkali layers for this new composition. However, the experimental c_{hex} cell parameter did not match with a theoretical one determined assuming a stacking with distinct layers of lithium, sodium and potassium cations. In fact, the experimental value was very close to the one of $LiKNi_2TeO_6$. In addition to powder diffraction, we also performed ^{23}Na NMR spectroscopy and showed an important disordering on the Na layer, compared to $Na_2Ni_2TeO_6$ and even $NaKNi_2TeO_6$. Given the very strong similarities of the SXRPD and NPD patterns of $LiNa_{0.5}K_{0.5}Ni_2TeO_6$ with $LiKNi_2TeO_6$ and $LiNaNi_2TeO_6$, with finally hypothesized a crystal structure with an alternation of layers of only lithium and layers containing both sodium and potassium cations.

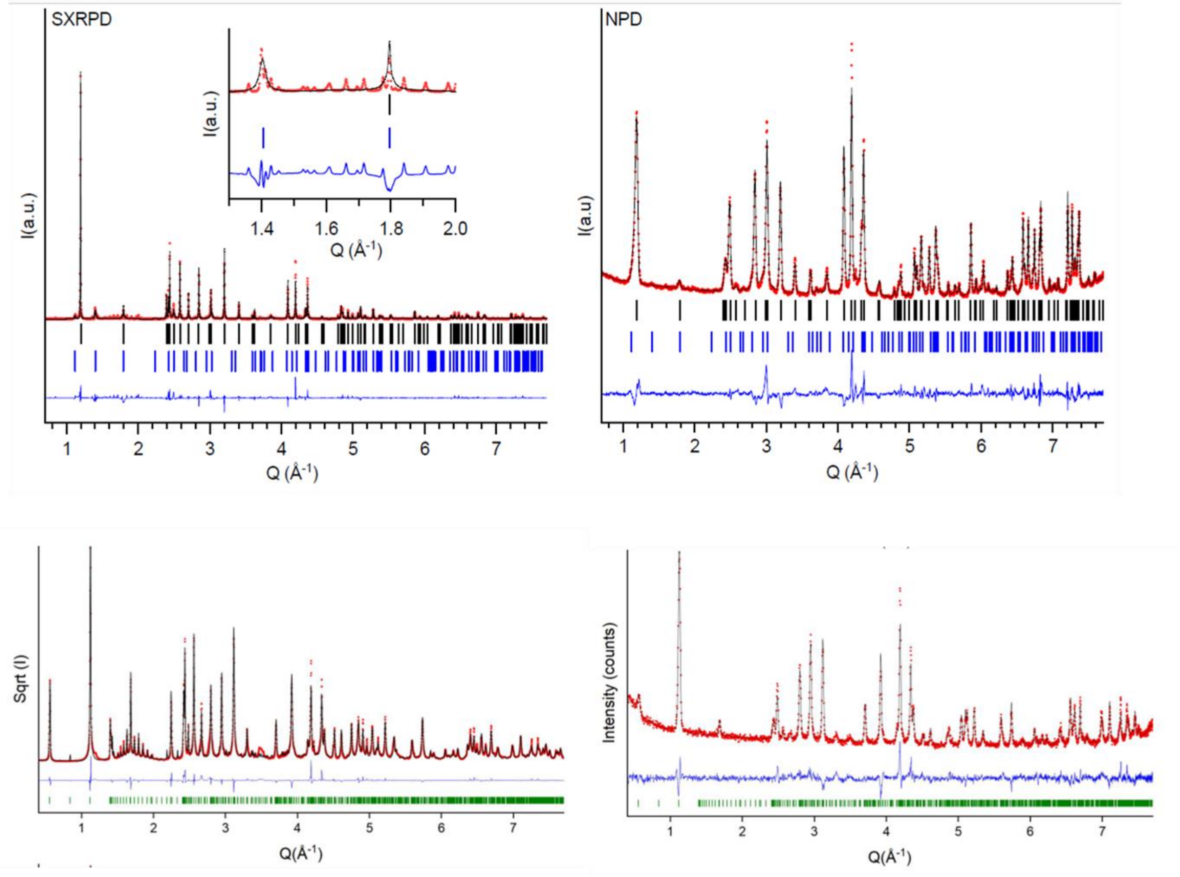

Figure 2 SXRPD and NPD patterns of $LiNaNi_2TeO_6$ (top) and $LiKNa_{0.5}K_{0.5}Ni_2TeO_6$ (bottom), with corresponding Rietveld refinement. NPD data collected at ILL

In parallel to understanding the crystal structure, we were also interesting in determining how these alkali-ordered layered compositions are obtained, especially when a 2-step synthesis is followed, through heating a mixture of single-alkali layered precursors. Indeed, considering the high mobility of alkali cations in these layered structure, a topochemical ionic exchange has been hypothesized. To confirm or not this mechanism we followed the formation of $LiKNi_2TeO_6$ from the mixture of $Li_2Ni_2TeO_6$ and $K_2Ni_2TeO_6$ (data collected at ILL on D20). As shown in Figure 3, around the region 1 Q (Å-1), the main diffraction peaks of the two precursors progressively decreases in intensity, while a new peak appears in-between and is the signature of the alkali-ordered composition. This observation is in line with similar SXRPD experiment performed at ALBA. As there is not regular shift of the main peak of the precursors, the thickness of their alkali layers do not evolve significantly, which does not go in the direction of a topochemical ionic exchange.

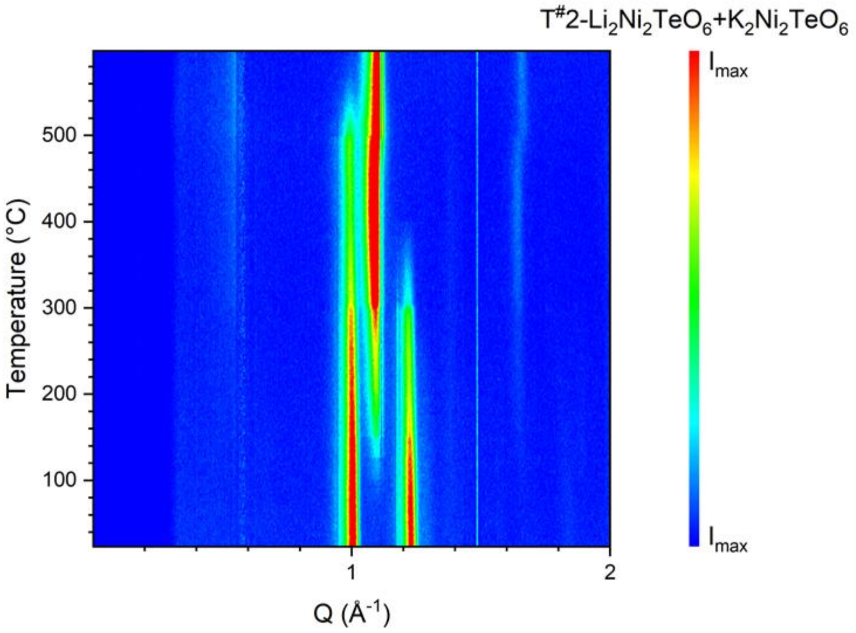

Figure 3: NPD temperature follow-up of the synthesis of $LiKNi_2TeO_6$.

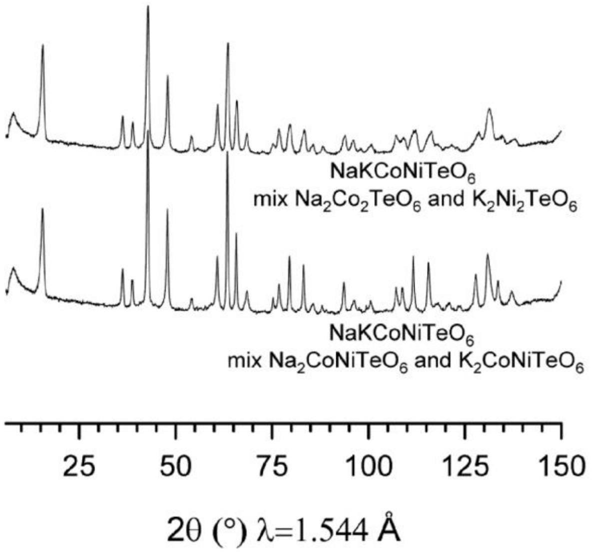

Figure 4: Experimental NPD patterns of $NaKNiCoTeO_6$ prepared in two different synthesis pathway. Data collected at ILL.

To continue, we took advantage of the chemical versatility of these honeycomb-ordered layered phase by considering cobalt to partially or totally substitute nickel, as it is known to be possible.[7] Our idea was to obtain the alkali-ordered composition $NaKCoNiTeO_6$ by two ways: from a mixture of $Na_2Co_2TeO_6$ and $K_2Ni_2TeO_6$, or from a mixture of $Na_2NiCoTeO_6$ and $K_2NiCoTeO_6$. With a topochemical ionic exchange, in the first case distinct Co/Te and Ni/Te honeycomb layers must be seen in the end-product, whereas in the second case the mixed occupancy of Ni and Co in the same honeycomb layers characterizing the layered precursors must remain in the end-product. Given the very close scattering factors of Ni and Co in X-ray diffraction, these two crystal structures would give very similar patterns. However this is not the case for neutron diffraction, as shown with simulated patterns (not shown here), for which significant changes of intensity are observed for lot of diffraction peaks. As shown in Figure 4, the patterns of $NaKCoNiTeO_6$ appear very similar at a first glance. It is first interesting to notice slightly narrower peaks in the case of $NaKCoNiTeO_6$ obtained from $Na_2NiCoTeO_6$ and $K_2NiCoTeO_6$. This could be explained by a better random distribution of the transition metals (Co, Ni) in the honeycomb lattice. Indeed, following this pathway the transition metals are mixed and heated together twice, whereas in the other pathway the first heating is separate ($Na_2Co_2TeO_6$ and $K_2Ni_2TeO_6$). There are however minor differences in terms of peaks' intensity, which could be related to different stacking sequence of Te, as it has shown for $NaKNi_2TeO_6$ to influence the powder diffraction pattern.[1]

To conclude on this report, the first series of analysis performed at room temperature enables us to improve our understanding on the crystal structure of these new alkali-ordered layered compositions, whereas the analysis carried out on temperature, coupled with analyses on $NaKCoNiTeO_6$, allow us to claim that the formation of such phases follows a classical nucleation/growth process. Most of these NPD analyses are included in a published article and will be also included in the PhD thesis document of Eunice Mumba (defence expected late 2024).

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