Experimental report

23/12/2021

Proposal:	**5-23-760**	**Council:**	10/2020
Title:	Lithium cation distribution and mobility in lithium inserted $Li_{1+x}NbWO_6$ ($0 < x < 3$) as promising host for lithium storage applications		
Research area:	Chemistry		

This proposal is a new proposal

Main proposer:	**Alois KUHN**
Experimental team:	Alois KUHN
Local contacts:	Emmanuelle SUARD

Samples:
LiNbWO6-T
LiNbWO6-R
Li2NbWO6-R
Li2NbWO6-T
Li3NbWO6-T
Li4NbWO6-T

Instrument	Requested days	Allocated days	From	To
D2B	4	4	10/06/2021	14/06/2021

Abstract:

Tetragonal $LiNbWO_6$ with a trirutile structure has recently attracted interest as candidate for energy storage applications, with a high theoretical lithium storage capacity (282.4 mAh g-1) due to multielectron transfer, superior to state-of-the-art $Li_4Ti_5O_{12}$ (175 mAh g-1). In contrast, the rhombohedral form shows limited lithium uptake. Previous in operando XRD study evidences several phase transformations in $LiNbWO_6$-T upon Li insertion. So far, ND experiments on $LiNbWO_6$ have only been carried out at room temperature. Furthermore, the crystallographic sites for lithium in intercalated $Li_{1+x}NbWO_6$ compounds have not been revealed yet. High-resolution neutron diffraction on $Li_{1+x}NbWO_6$ with different Li content and different temperatures enables us to accurately differentiate changes in the Li^+ substructure including Li^+ motion. D2B offers the suitable combination of high-flux and high-resolution for our experiment. We expect a significant improvement of the structure model for both $LiNbWO_6$ and its lithiated derivatives concerning cation distribution (especially Li, O, Nb/W site disorder) and occupancies. This study will be completed by solid state NMR and electric characterization

Experimental report on proposal 5-23-760:
Lithium cation distribution and mobility in lithium inserted $Li_{1+x}NbWO_6$ ($0 < x < 3$) as promising host for lithium storage applications

The dimorphic oxide with formula $LiNbWO_6$ has been recently reported as a promising host for highly efficient lithium storage applications [1]. This proposal had the following objectives: a) re-evaluation of the crystal structures reported for both the low-temperature tetragonal trirutile phase (T) and the high-temperature rhombohedral $LiNbO_3$-related phase (H); b) elucidation of crystal structures of lithium inserted $Li_{1+x}NbWO_6$ compounds; c) thermal evolution of structural parameters.
In particular, pristine samples with x=0 (T, H) were prepared by a solid-state reaction, and the lithiated compounds were obtained by a soft-chemical route (T: x= 1, 2, 3; H: x=1) starting from both pristine compounds. The outstanding versatility that D2B offers for different sample environments to be run simultaneously allowed the study of 6 samples and at different temperatures (T=19, 130, 330 and 500ºC).

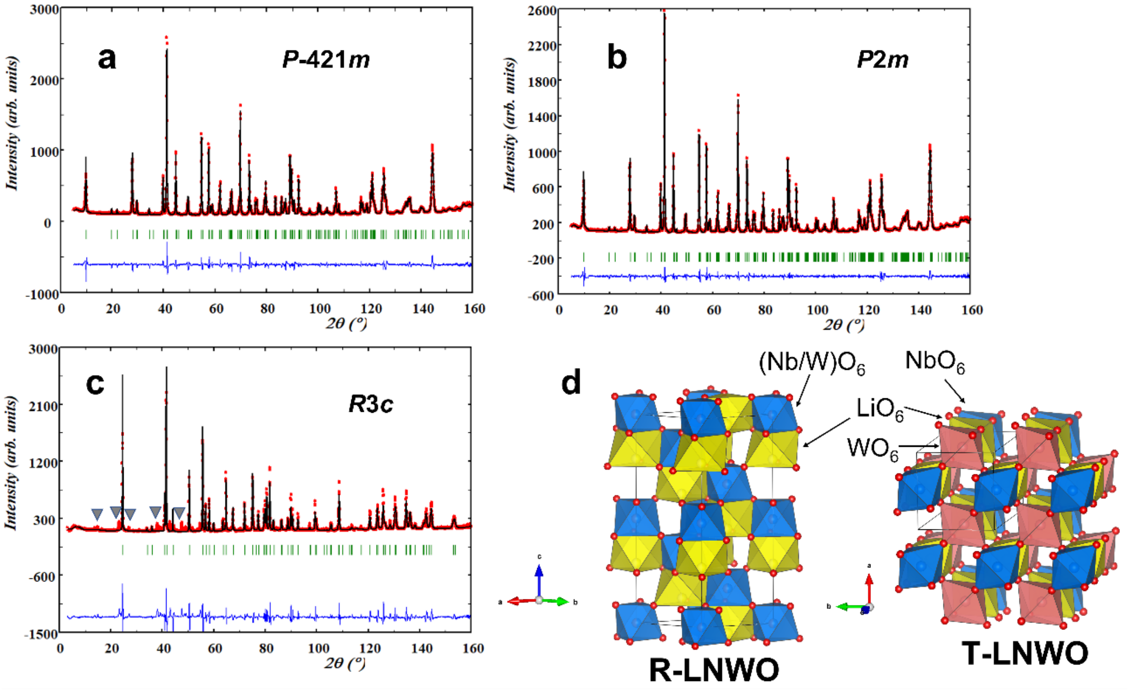

Fig. 1. Graphic result of Rietveld refinements for $LiNbWO_6$ (x=0) samples: trirutile phase in tetragonal SG *P*-421*m* (a) and with a slight monoclinic distortion in SG *P*2*m* (b); rhombohedral phase SG *R*3*c*, hexagonal setting (c). The corresponding structural models are depicted in d).

Graphic results of the Rietveld refinements for the known tetragonal (S.G. *P*-421*m*) and rhombohedral (S.G. *R*3*c*) structures are shown in Fig. 1. Although structural refinements of the trirutile phase yielded acceptable R factors in tetragonal SG *P*-4 21*m* [2] (Fig. 1a,d), better agreement factors were achieved assuming a slight monoclinic distortion with a monoclinic angle of 90.1º in SG *P*2*m* (Fig. 1b). We are now evaluating the correctness of the lower symmetry space group by means of electron diffraction. Refinements of the ND pattern of the rhombohedral phase evidences the presence of a minor secondary phase ($LiNb_3O_8$, labelled with grey triangles in Fig. 1c,d), in agreement with previous reports [2].

Table 1: Unit cell parameters of different $Li_{1+x}NbWO_6$ samples.

T (ºC)	Sample	a (Å)	b (Å)	c (Å)	β (º)	Vol (Å^3)
19	T, x=0, *P*-421*m*	4.6812(2)	4.6812(2)	9.2793(9)	90	203.35(2)
19	T, x=0, *P*2*m*	4.6793(1)	4.6808(1)	9.2772(1)	90.09(1)	203.20(1)
19	T, x=1, *P*-421*m*	4.8156(2)	4.8156(2)	8.9270(5)	90	207.02(1)
19	H, x=0, *R*3*c*	5.15144(9)	5.15144(9)	13.6651(1)	120	314.05(1)

Lithiated trirutile phase and location of inserted lithium

Location of lithium in lithiated $Li_{1+x}NbWO_6$ compounds was performed in the trirutile phase with x=1 (1 inserted lithium). For this, a structure model without inserted lithium is refined. Next, difference Fourier maps (Fig. 2a) provides evidence for residual negative neutron density, corresponding to inserted lithium. The final structural model of lithiated trirutile $LiNbWO_6$ is shown in Fig. 2b and 2c along [001] and [010]. The simultaneous increase of *a* parameter and decrease of *c* parameter upon lithiation (Table 1) results in a small change in unit cell volume (+1.9%). For lithiated trirutile, we could not confirm the monoclinic distortion observed in non-lithiated $LiNbWO_6$. Our preliminary structural analysis of the fully lithiated phase (x=3), which had never been reported before, evidences an irreversible structural transition. The results will appear together with an electrochemical study of the lithium insertion mechanism in $LiNbWO_6$ in an upcoming paper.

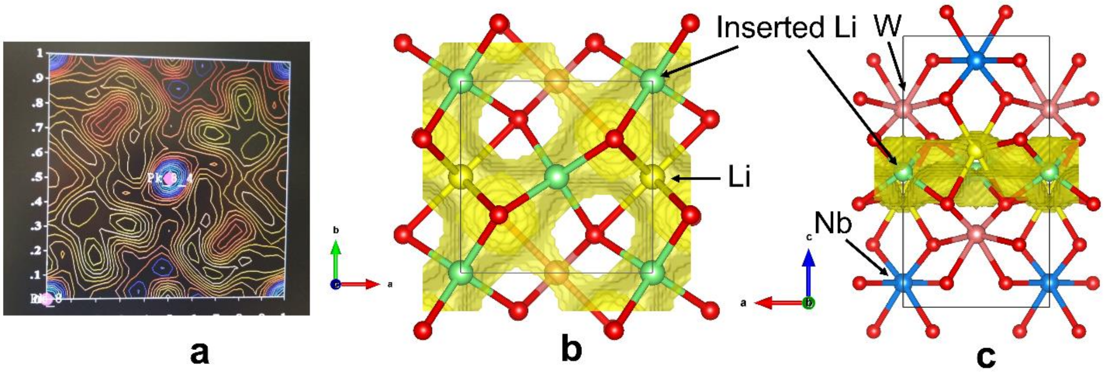

Fig. 2. Location of inserted lithium from difference Fourier map in Li_2NbWO_6-T (a), together with its crystal structure viewed along [001] (b) and [010] (c). BVS isosurfaces for Li^+ are indicated in yellow.

Further pending tasks concern the full structural characterization of the lithiated rhombohedral phase, as well as investigation of the temperature dependence of structural parameters in the $Li_{1+x}NbWO_6$ trirutile phases (cell parameters, isotropic thermal displacement parameters B).

References

[1] X. Cheng, T. Liu, H. Yu, F. Ran, W. Ye, H. Zhu, M. Shui, Y. Xie, J. Shu, Polymorphism-Controlled Electrochemical Energy Storage Performance of $LiNbWO_6$, Chem. Mater. 2020, 32, 3376–3384.

[2] J.L. Fourquet, A. Le Bail, P.A. Gillet, $LiNbWO_6$: Crystal Structure of Its Two Allotropic Forms. Mater. Res. Bull. 1988, 23, 1163–1170.