

Experimental report

13/06/2024

Proposal: 5-23-775

Council: 10/2022

Title: Crystallographic structure of disordered rock-salt materials

Research area: Materials

This proposal is a new proposal

Main proposer: Matteo BIANCHINI

Experimental team: Sylvia KUNZ
Matteo BIANCHINI
Agnese REITANO

Local contacts: Emmanuelle SUARD

Samples: Li_{2y}Ni_yTi_{2-3y}O₂

Instrument	Requested days	Allocated days	From	To
D20	2	0		
D2B	3	2	06/06/2023	08/06/2023

Abstract:

Li-ion batteries are a key technology to reduce CO₂ emissions. The current generation of batteries rely on cathode materials either rich in Co or in Ni and with a layered structure. However these elements are limited and expensive, motivating the search for alternative cathodes with reduced Ni content and no Co, but retaining high specific capacity. One possible alternative are disordered rock salt materials, and in particular we are investigating Ni and Ti based disordered rock salt oxides. After verifying the unit cell size by XRD in our lab (as well as the materials' electrochemical behaviour) we now seek to investigate the cationic distribution of the different elements (Li, Ni, Ti) for samples prepared under different conditions. These elements are well suited to be investigated by neutrons diffraction, and in combination with XRD and ICP-OES we aim at fully describing the cationic distribution in the materials. Moreover, we aim at investigating by operando neutron diffraction the crystallographic changes occurring in such materials during Li deinsertion (volume change, phase transitions, etc).

Crystallographic structure of disordered rock-salt materials

Experimental Report for proposal 5-23-775_Matteo Bianchini

In our work a series of samples with a target composition $\text{Li}_{2y}\text{Ti}_y\text{Ni}_{2-3y}\text{O}_2$ ($y=0.50, 0.55, 0.60, 0.67$) has been synthesised by solid-state reaction using 3 different annealing temperature (700°C, 800°C, 900°C). X-ray diffraction (XRD) has been exploited to investigate the crystal structures of all the materials. The samples annealed at 900°C and 800°C revealed a pure rock salt phase, while for the samples at 700°C a secondary phase was found associated to a Li_2TiO_3 -like phase, clearly growing with the increasing of the Li content, as shown in Fig.1. For this reason, we exploited the use of neutrons and in particular their sensitivity to light elements (Li, O) and to Debye-Waller factors to determine the cations distribution in the rock salt-type phase.

Neutron diffraction (ND) was carried out on the D2B neutron diffractometer at the Institut Laue-Langevin (ILL) (DOI:10.5291/ILL-DATA.5-23-775). Powder samples were put into cylindrical vanadium cans and measured in transmission geometry. Firstly, λ has been opportunely refined ($\lambda = 1.59485(3)$) starting from the fixed cell parameters values obtained by x-ray diffraction, then we carried out a combined XRD and ND analysis for the samples with $y=0.50, 0.55$ and 0.60 at 700°C. An exemplary refined has been reported in Fig.2.

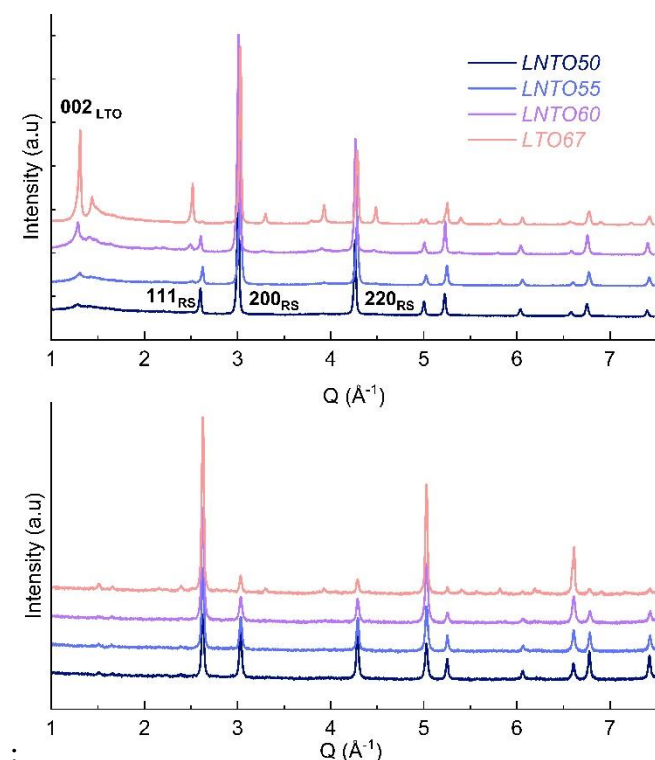


Figure 1. X-ray diffraction (top) and neutron diffraction (bottom) patterns of the samples annealed at 700 °C

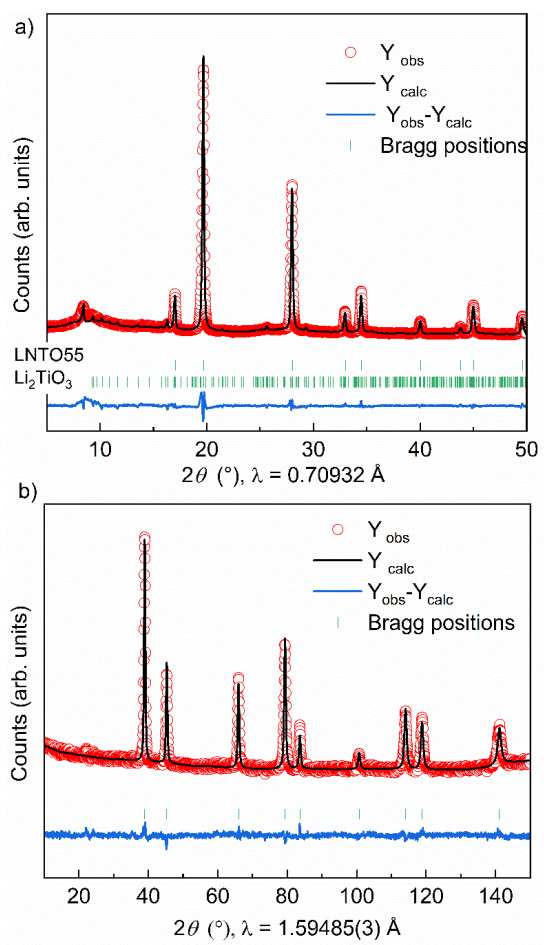


Figure 2 Combined Rietveld refinement of XRD a) and NPD b) patterns for the sample LNT055 synthesized at 700 °C.

Publications

The data of this proposal will be published in the Journal of Material Chemistry A.