

Experimental report

14/09/2022

Proposal: EASY-1029

Council: 4/2021

Title: Structural characterization of LNMO spinel oxides

Research area: Materials

This proposal is a new proposal

Main proposer: Ilia TERTOV

Experimental team:

Local contacts: Emmanuelle SUARD

Samples: LiNi_{0.5}Mn_{1.5}O₄

Instrument	Requested days	Allocated days	From	To
D2B	8	8	19/09/2021	20/09/2021

Abstract:

The main purpose of the experiments is to perform structural investigation of ordered and disordered samples of LNMO spinel oxides (disordering of Li, Ni and Mn cations) by means of Neutron diffraction.

Report on the D2B's EASY-1029 proposal

In the frame of the proposal we wanted to perform structural investigation of two industrial samples (T4249 and T4250) of perspective cathode materials $\text{LiNi}_{0.5-x}\text{Mn}_{1.5+x}\text{O}_4$ (LNMO) for Li-ion batteries by means of neutron powder diffraction in order to examine the extent of Ni/Mn ordering which is distinctive for such materials.

For Rietveld refinement the structural model of disordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel phase (S.G. $Fd-3m$) was used for both samples. Atomic displacement parameters (ADP) were fixed for all atoms in order to refine occupancies of atoms in 16d position – Mn and Ni. Occupancies of other atoms were fixed. It should be noted that reflections of rock salt phase (S.G. $Fm-3m$) are observed for both samples. Rietveld plots with refined compositions, lattice constants and information of refinement are given in Figure 1.

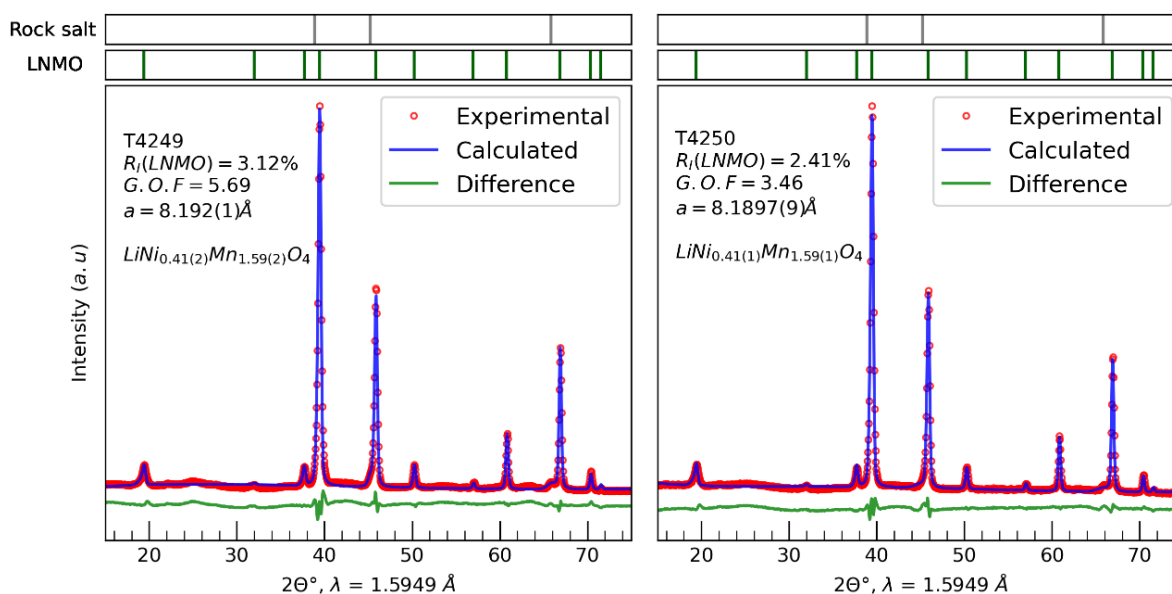


Figure 1. Experimental, calculated and difference patterns after the Rietveld refinement ($\lambda = 1.5949 \text{ \AA}$) of T4249 (left) and T4250 (right).

Both samples possess same Ni:Mn composition of 21:79 %, which is lower than expected (23:77 %). This fact could be related to the presence of rock salt impurity, which is nickel-rich. Also, it can be seen (Fig. 1) that there are additional peaks at $\approx 25^\circ 2\theta$ for the samples, which do not refer to the disordered LNMO and rock salt phases. These small peaks together with others can be indexed in primitive cubic cell. So, these

reflections can be associated with “superstructural” reflections of ordered LNMO phase (Fig. 2) with $P4_332$ space group. In the case of T4250 the intensity of these superstructural reflections is lower. This is in good agreement with lower values of goodness of fit (G.O.F) and errors for T4250 sample. It could be concluded that T4250 is more “disordered”.

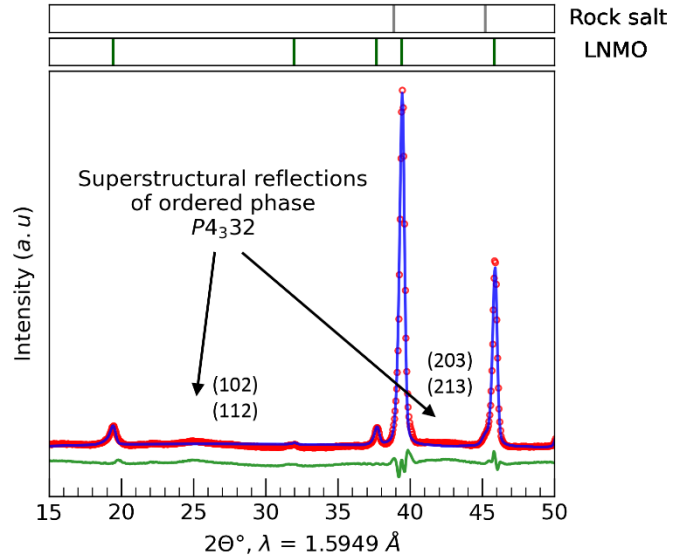


Figure 2. The Rietveld pattern of T4249 in range of 15-50° 2θ.