

High-Pressure Investigations of spinel-type $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as a cathode material

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Introduction

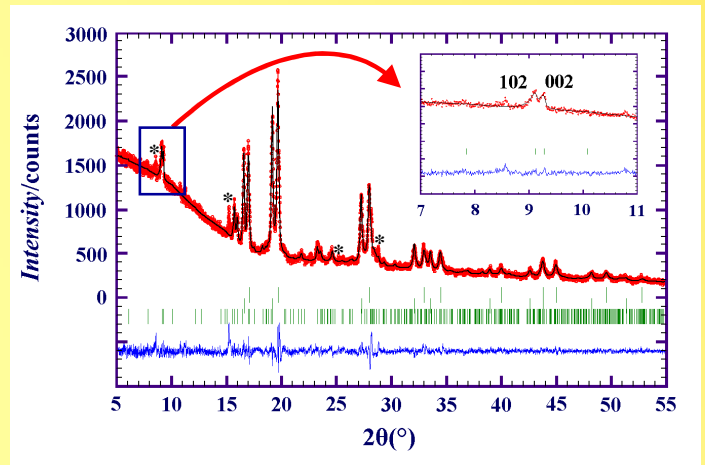
New synthesis strategies are needed to prepare novel electrode materials for lithium-ion batteries. High-pressure / high-temperature routes are widely used within other fields of Solid State Chemistry to induce structural transformations of materials, conducting to novel polymorphs possessing structures not accessible at ambient pressure. The high pressure treatment changes both the crystal structure as well as the electronic characteristics of the material. High pressure driven transformations of several electrode materials have been studied and reported, for example Li_xFePO_4 ,^[1,2] V_2O_5 ,^[3] Li_2MSiO_4 (M = Mn, Co).^[4,5] It is proven that after exposure to high pressure/high temperature conditions, the electrochemical properties varied compared to the ambient pressure materials. For LiMn_2O_4 various studies report structural examinations at high pressure of these spinel phase^[6-10]. But, only little is known about the electrochemical behaviour of these phases, when they are used as intercalation compounds for an electrode in a lithium ion battery.^[10] The high pressure phase of LiMn_2O_4 ^[10] was identified as the CaFe_2O_4 - (Calciumferrite) structure type, which is approximately 6% more dense than the spinel structure type. The partial substitution of Mn in LiMn_2O_4 by transition metal ions, such as e.g. Ni, was shown to result in the electrochemical activity at potentials close to 5 V vs Li/Li+.^[11] In this work we investigate the pressure driven structural and electrochemical modifications of spinel LiTM_2O_4 (TM = transition metal) cathode materials.

Experimental Approach: Multianvil-Press



High-pressure experiments are performed in a 1000 tons Walker-type multianvil press. The figure shows the step by step process of mounting the assembly.

Diffraction pattern of HP treated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$



Phase transition of „ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ “ (CaFe₂O₄-type) after 18 GPa .

Observed (circles) and calculated (line) X-ray powder diffraction pattern together with their difference curve after Rietveld refinement ($\lambda = 0.70926 \text{ \AA}$). The two upper lines of reflection marks corresponds to rocksalt type (Li,Ni)O and (Li,Mn)O and the lower line to HP- $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. * At least 4 weak reflections belong to one unidentified phase.

Comparison of HP- $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and HP- LiMn_2O_4 ^[10]

Crystallographic data of HP- $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$

Spacegroup *Pnma* (No.62)
formula mass 182.56 g · mol⁻¹
lattice parameters
 $a = 8.7669(9) \text{ \AA}$
 $b = 2.8482(3) \text{ \AA}$
 $c = 10.3612(10) \text{ \AA}$
cell volume $V = 258.71 \text{ \AA}^3$
X-ray density 4.63 g · cm⁻³

Wyckoff sites of „HP- $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ “

Atom	Wyck.	x	y	z
Li	4c	0.27800	1/4	0.37000
Mn1/Ni	4c	0.0637(15)	1/4	0.1198(15)
Mn2/Ni	4c	0.0784(15)	1/4	0.6011(12)
O1	4c	0.270(5)	1/4	0.674(4)
O2	4c	0.390(4)	1/4	0.882(5)
O3	4c	0.430(5)	1/4	0.189(3)
O4	4c	0.137(5)	1/4	0.921(4)

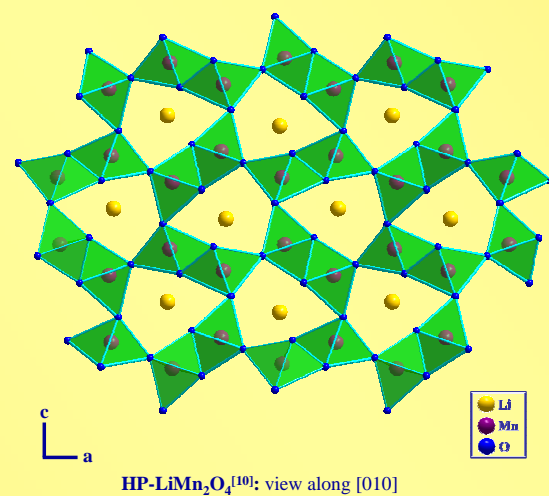
Crystallographic data of HP- LiMn_2O_4

Spacegroup *Pnma* (No.62)
formula mass 180.93 g · mol⁻¹
lattice parameters
 $a = 8.8336(5) \text{ \AA}$
 $b = 2.83387(18) \text{ \AA}$
 $c = 10.6535(7) \text{ \AA}$
cell volume $V = 266.69 \text{ \AA}^3$
X-ray density 4.49 g · cm⁻³

Wyckoff sites of HP- LiMn_2O_4

Atom	Wyck.	x	y	z
Li	4c	0.278(4)	1/4	0.370(4)
Mn1	4c	0.0584(10)	1/4	0.1188(8)
Mn2	4c	0.0828(8)	1/4	0.6082(6)
O1	4c	0.3061(6)	1/4	0.6508(6)
O2	4c	0.3801(9)	1/4	0.9799(6)
O3	4c	0.4764(8)	1/4	0.2072(6)
O4	4c	0.0707(8)	1/4	0.9269(6)

CaFe₂O₄ Structure type



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