Karlsruher Institut für Technologie

2nd International Conference on Materials for Energy - Karlsruhe

Improved wide operation voltage capability of Fe-, Ti- and F-doped $LiNi_{0.5}Mn_{1.5}O_4$ spinel cathodes for lithium ion batteries

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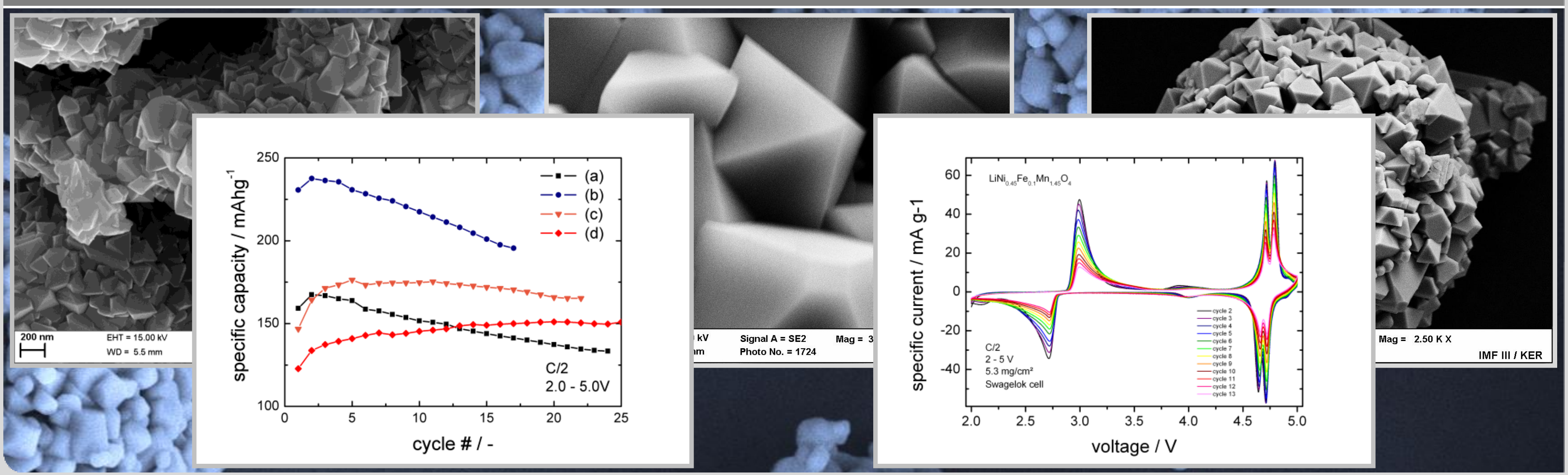
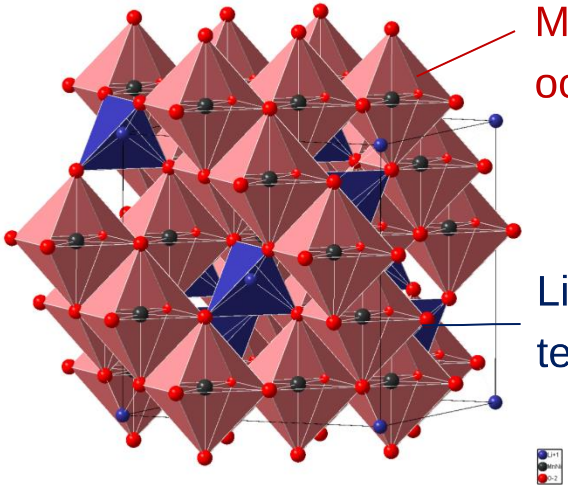
INSTITUTE FOR APPLIED MATERIALS



Outline

- Motivation
- Fe- and F- doped $LiNi_{0.5}Mn_{1.5}O_4$
  - Synthesis
  - Structural characterization
  - Electrochemical results
- Understanding
  - *Insitu* XRD
- Fe-, Ti- and F- doped $LiNi_{0.5}Mn_{1.5}O_4$
  - Synthesis
  - Structural characterization
  - Electrochemical results
- Summary and future prospects



$Fd\bar{3}m$ (227) - spinel

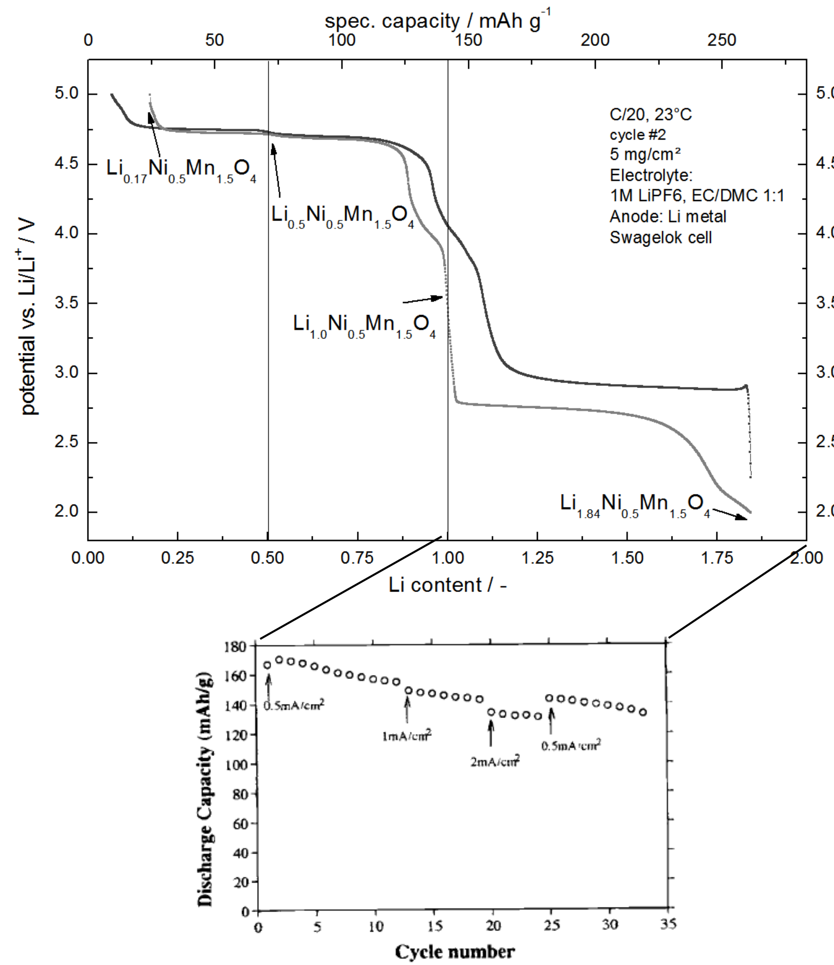
Motivation

- **$LiNi_{0.5}Mn_{1.5}O_4$** spinel
  - power density: 3D intercalation
  - energy: 5V material (vs. 4V $LiMn_2O_4$)
  - life time: less Mn^{3+} (vs. $LiMn_2O_4$)
  - costs: absense of Co

- Known shortcomings
  - Electrolyte unstable above 4.5 V
  - impurity phase $Li_xNi_{1-x}O$
  - Spinel unstable below 3.5V due to Mn^{3+} formation

- Objective
  - Using more than 1 Li per formula
  - F-doping: less Mn dissolution
  - Fe, Ti-doping : improved cycleablitiy

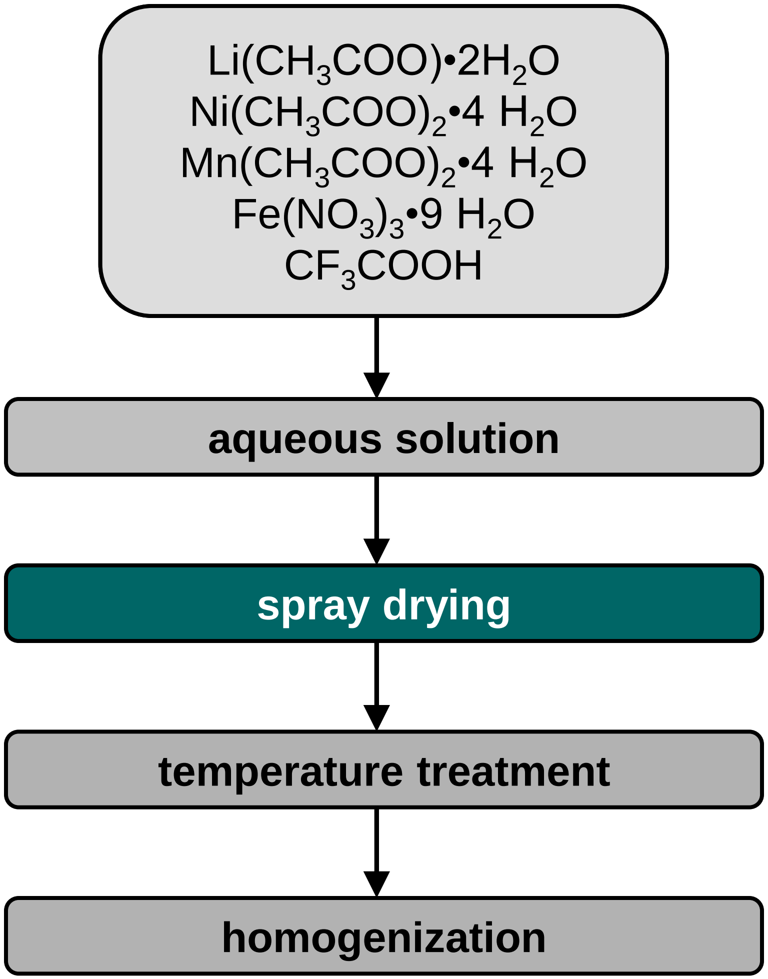
5.0 V $\xrightarrow{146.7\ mAh/g}$ 3.5 V $\xrightarrow{146.7\ mAh/g}$ 2.0 V



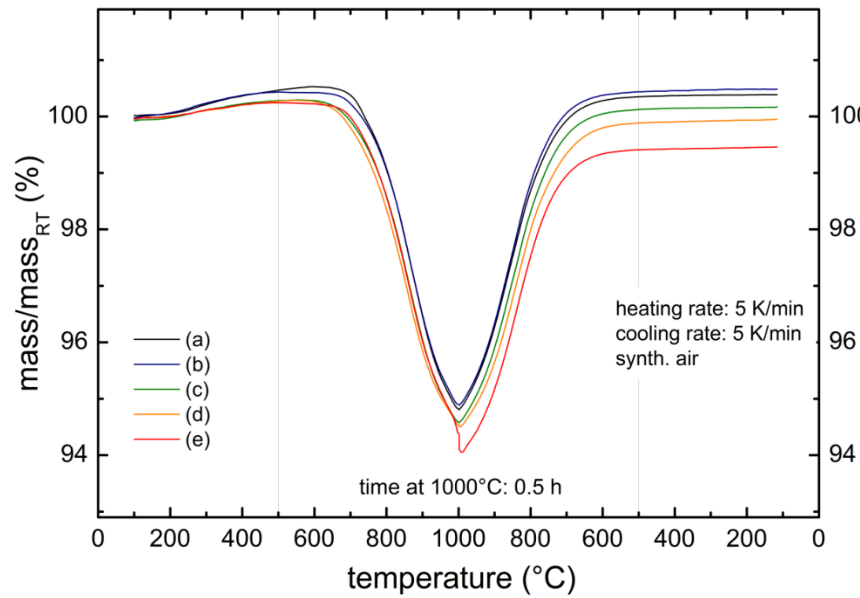
K. Amine. et al. J. El. Soc., ***Vol. 143*** *(1996) 167.*

Synthesis of Fe/F-doped $LiNi_{0.5}Mn_{1.5}O_4$

- Sol-gel-process



- Thermogravimetry



D. Linder

- Chem. analysis

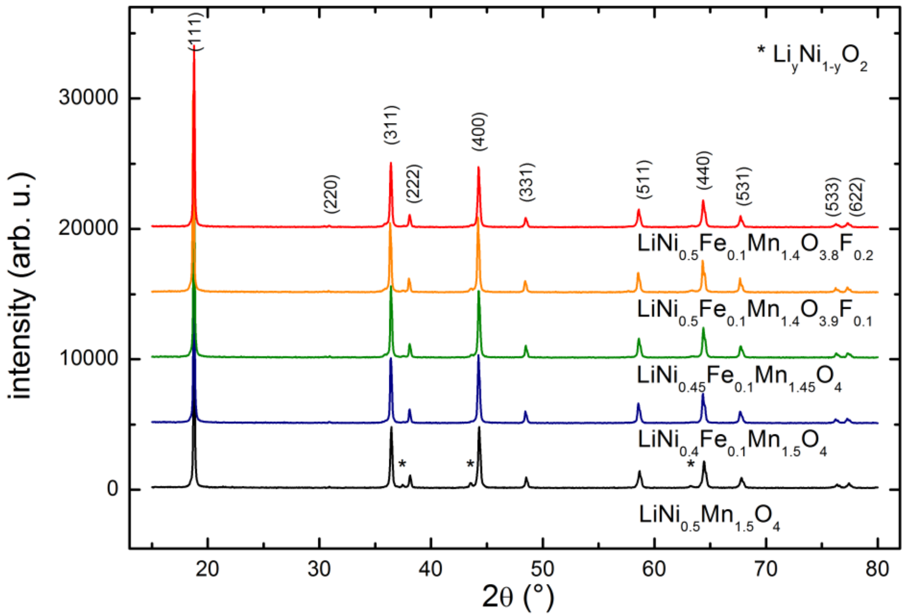
a	$Li_{0.98}Ni_{0.49}Mn_{1.53}O_4$
b	$Li_{0.96}Ni_{0.40}\mathbf{Fe_{0.08}}Mn_{1.56}O_4$
c	$Li_{0.96}Ni_{0.45}\mathbf{Fe_{0.08}}Mn_{1.51}O_4$
d	$Li_{0.95}Ni_{0.50}\mathbf{Fe_{0.08}}Mn_{1.46}O_{3.98}\mathbf{F_{0.02}}$
e	$Li_{0.95}Ni_{0.50}\mathbf{Fe_{0.07}}Mn_{1.47}O_{3.91}\mathbf{F_{0.09}}$

C. Adelhelm
T. Bergfeldt

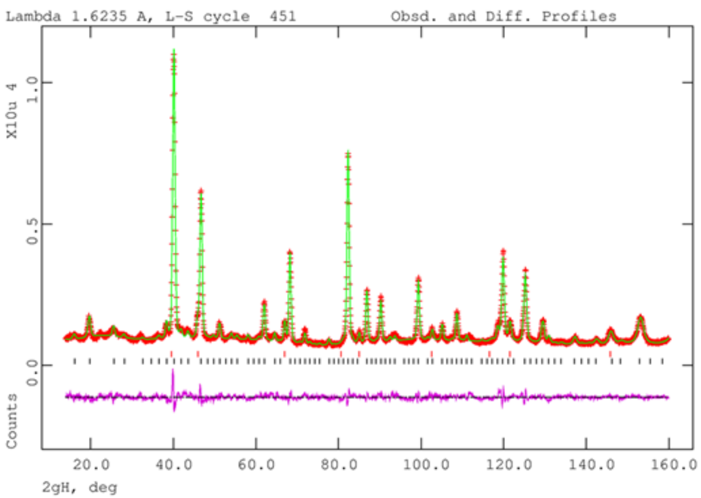
Structure of $LiNi_{0.5-x}Fe_{0.1}Mn_{1.5-y}O_{4-z}F_z$

- x-ray diffraction: Rietveld analysis

	phase ratio			lattice constant	
	spinel 1	spinel 2	$Li_xNi_{1-x}O$	spinel 1	spinel 2
	%	%	%	nm	nm
(a)	93.37	2.59	4.04	8.1729	8.298
(b)	97.63	1.55	0.82	8.1846	8.3045
(c)	95.78	2.42	1.8	8.1792	8.298
(d)	94.18	3.12	2.71	8.1772	8.298
(e)	94.21	4.44	1.35	8.1816	8.298



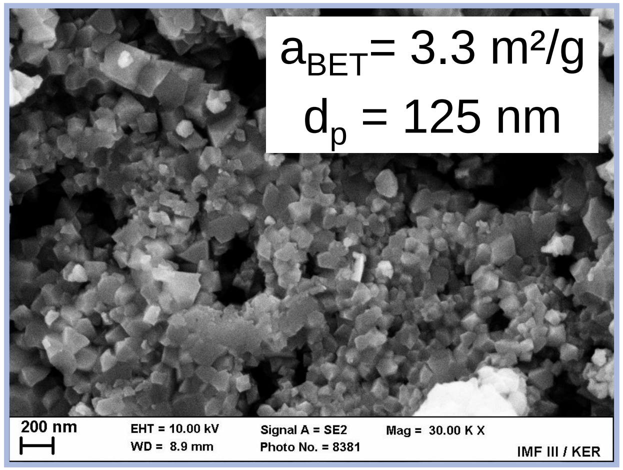
- neutron diffraction



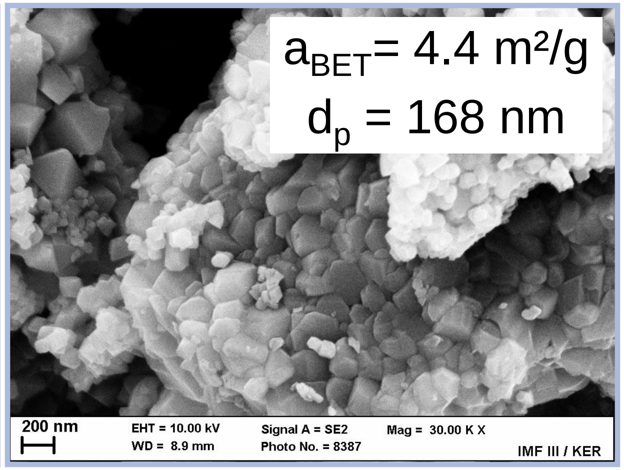
- Results
  - impurity phase $Li_xNi_{1-x}O$ reduced by Fe-doping
  - second spinel phase
  - doped spinels: unordered $Fd\bar{3}m$ (227)
  - undoped spinel: partially ordered $Fd\bar{3}m$ (227) +$P4_332$ (212)

Morphology of $LiNi_{0.5-x}Fe_{0.1}Mn_{1.5-y}O_{4-z}F_z$

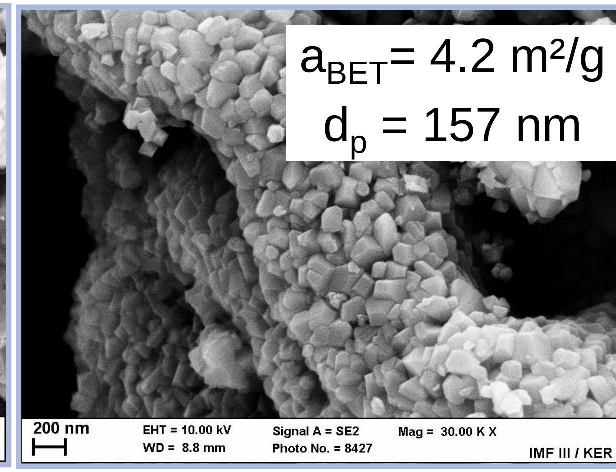
$Li_{0.98}Ni_{0.49}Mn_{1.53}O_4$



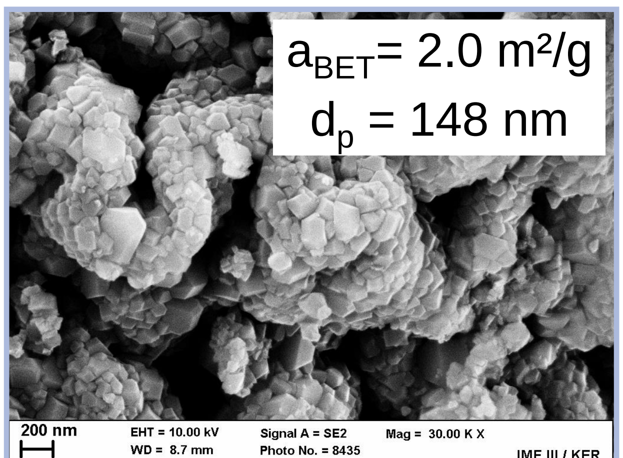
$Li_{0.96}Ni_{0.40}Fe_{0.08}Mn_{1.56}O_4$



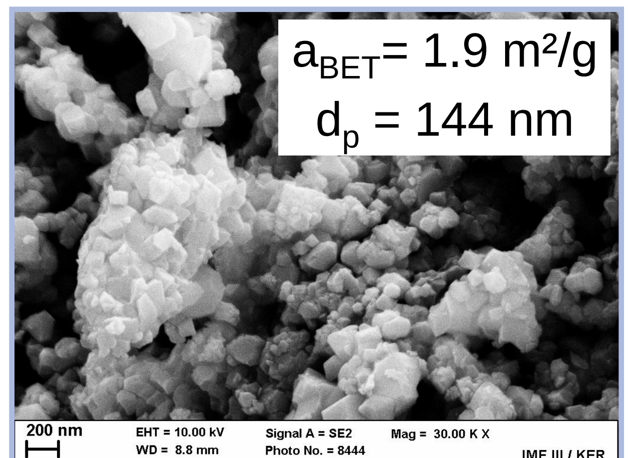
$Li_{0.96}Ni_{0.45}Fe_{0.08}Mn_{1.51}O_4$



$Li_{0.95}Ni_{0.50}Fe_{0.08}Mn_{1.46}O_{3.98}F_{0.02}$



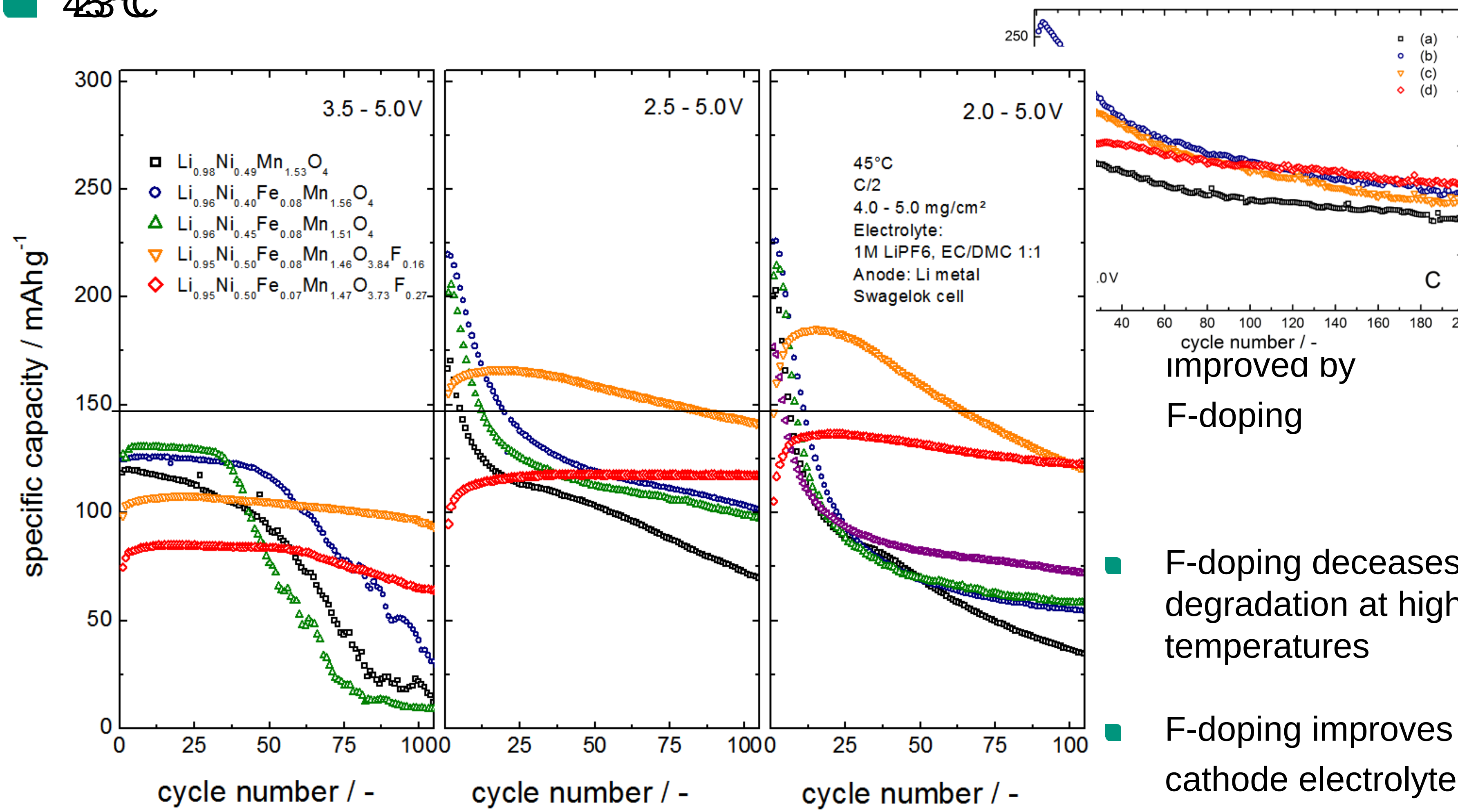
$Li_{0.95}Ni_{0.50}Fe_{0.07}Mn_{1.47}O_{3.91}F_{0.09}$



M. Offermann,
U. Maciejewski

Cycleability of $LiNi_{0.5-x}Fe_{0.1}Mn_{1.5-y}O_{4-z}F_z$

- 425°C



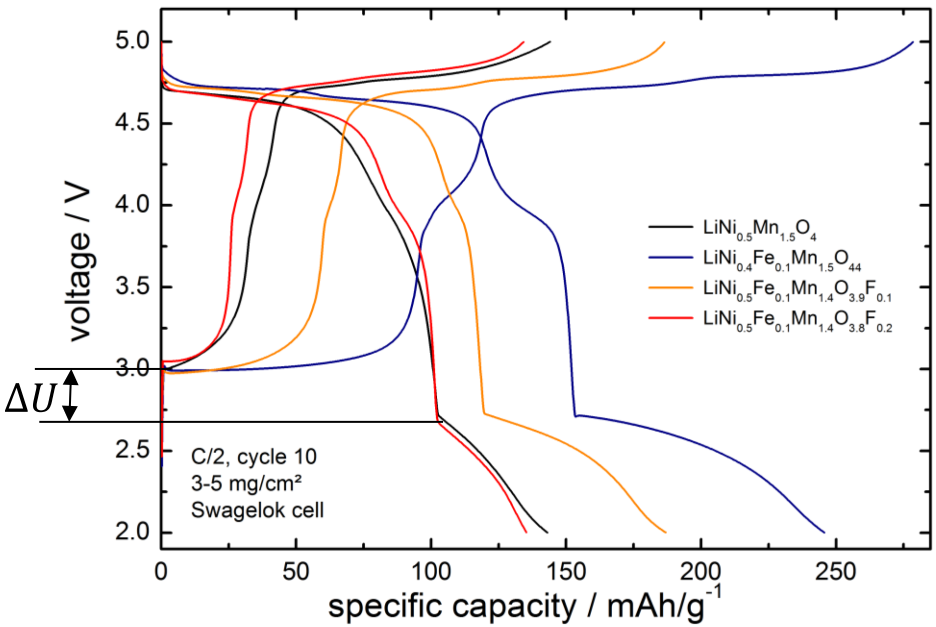
improved by F-doping

- F-doping deceases degradation at higher temperatures
- F-doping improves cathode electrolyte interface:

Cycleability of $LiNi_{0.5-x}Fe_{0.1}Mn_{1.5-y}O_{4-z}F_z$

- Voltage profiles

C/2, cycle 10



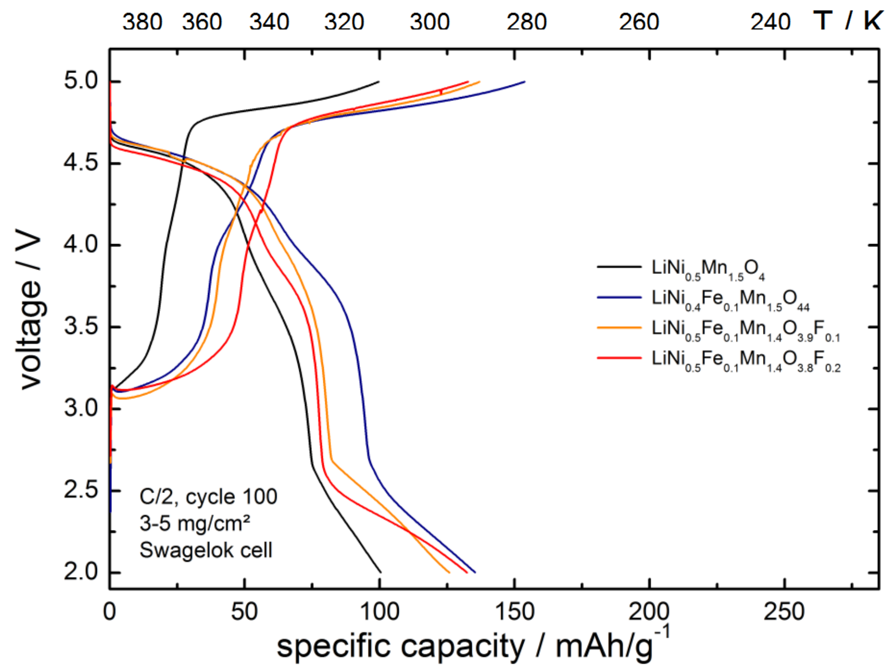
- Voltage hysteresis due to phase transition

$Fd\bar{3}m$ (227) - cubic

$\rightarrow I4_1/a\,m\,\mathrm{d}$ (141) - tetragonal

- Electronic conductivity

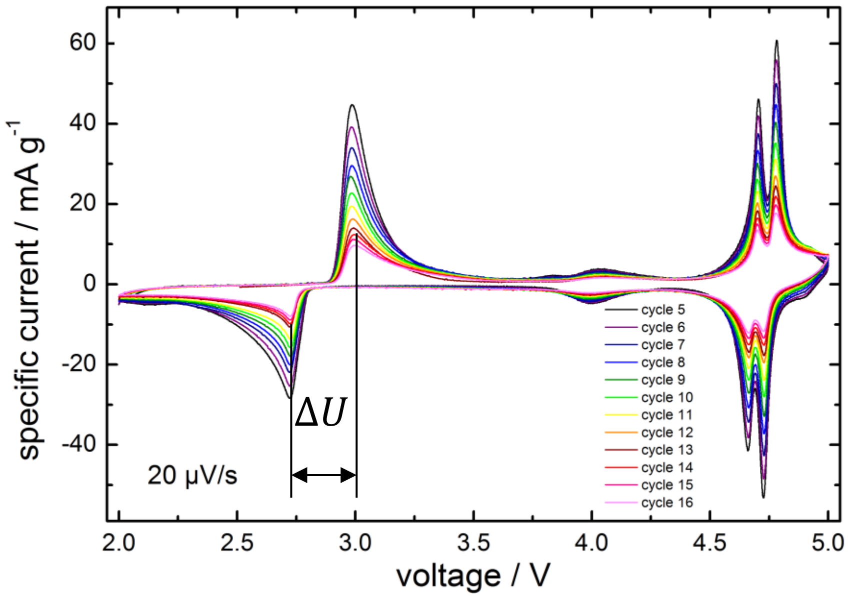
C/2, cycle 100



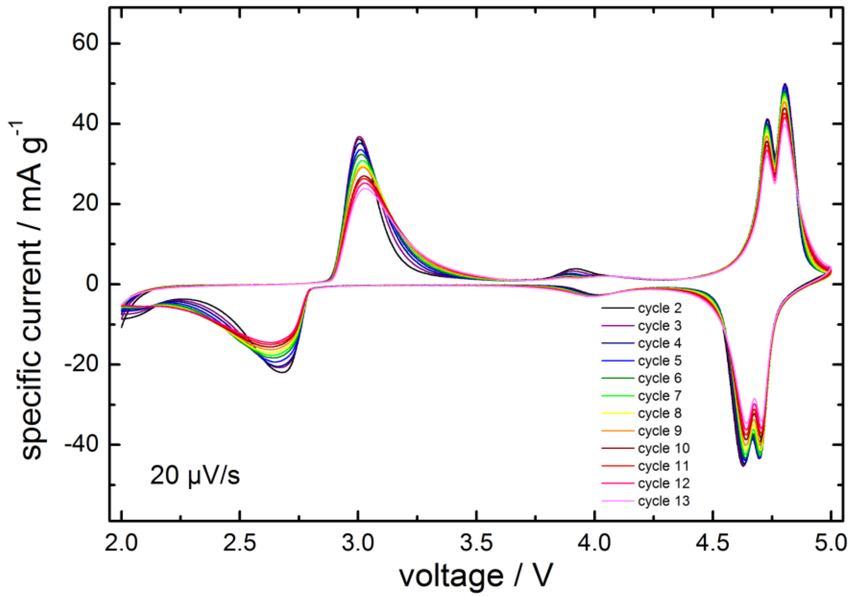
- F-doping does not prevent phase transition
- El. conductivity increases with Mn3+ and Fe content

Cyclo voltammetry

$Li_{0.96}Ni_{0.40}Fe_{0.08}Mn_{1.56}O_4$



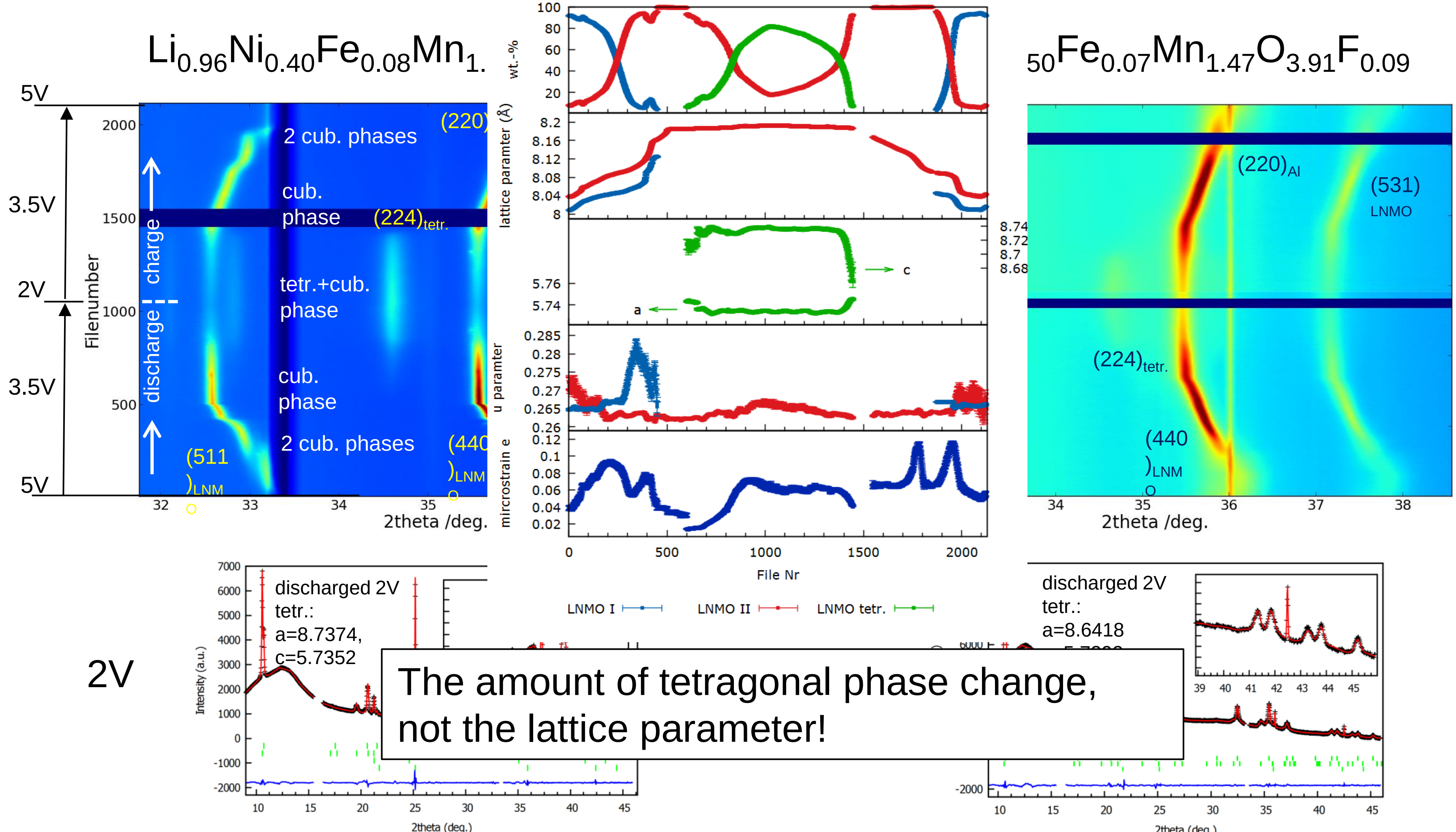
$Li_{0.95}Ni_{0.50}Fe_{0.07}Mn_{1.47}O_{3.91}F_{0.09}$



- Without F-doping:
  Loss of active material

- With F-doping:
- Change of the peak shapes,
  but no loss of active material

Insitu XRD @ Anka: PDIFF beamline

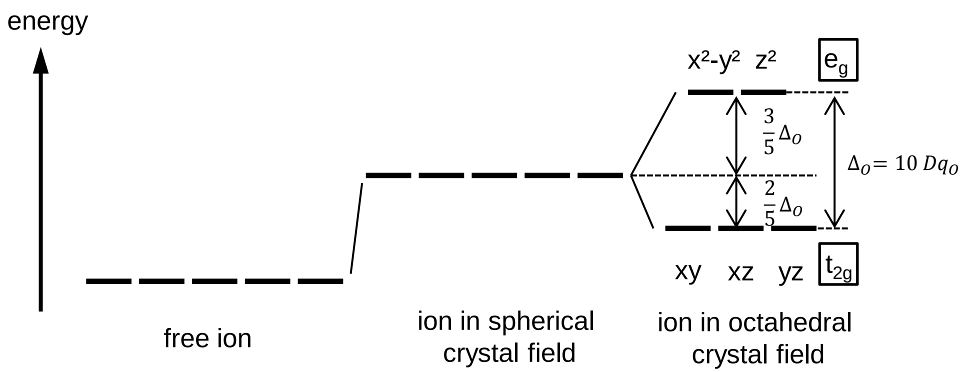


The amount of tetragonal phase change, not the lattice parameter!

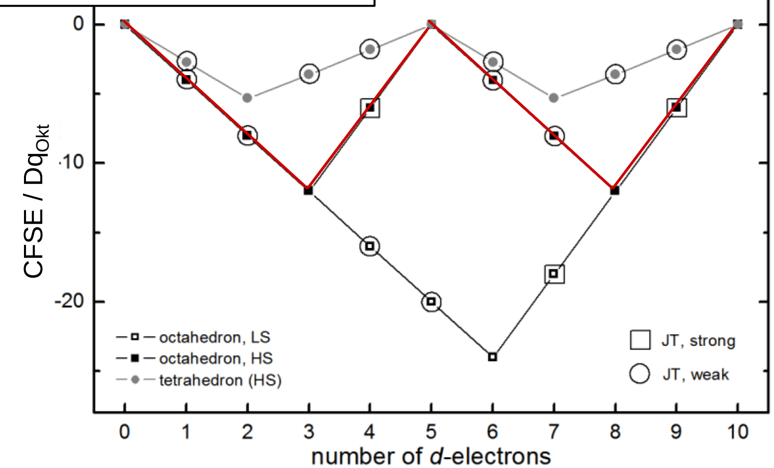
- 80% te… What is the reason for the phase transition? …nal phase

Crystal field theory

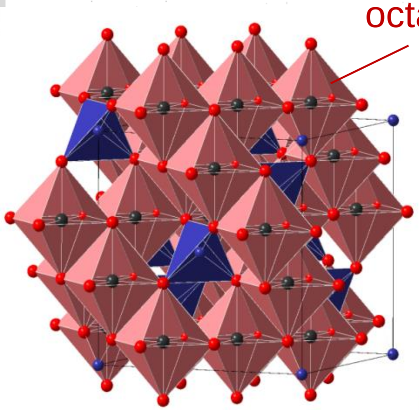
- octahedral crystal field

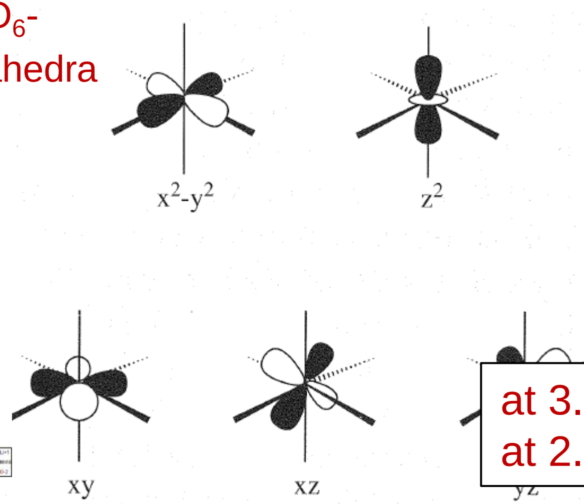


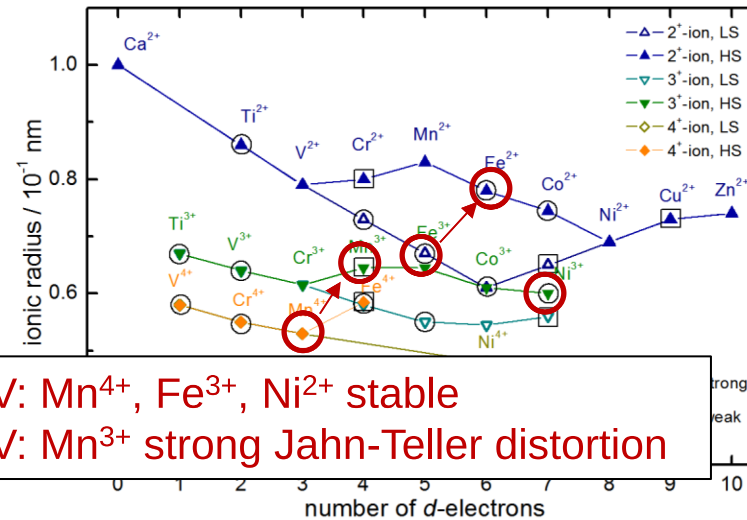
weak O-, F- ligands
-> High spin configuration



MnO_6-octahedra







at 3.5V: Mn^{4+}, Fe^{3+}, Ni^{2+} stable
at 2.0V: Mn^{3+} strong Jahn-Teller distortion

E. Riedel, Moderne Anorg. Chemie, (1999)

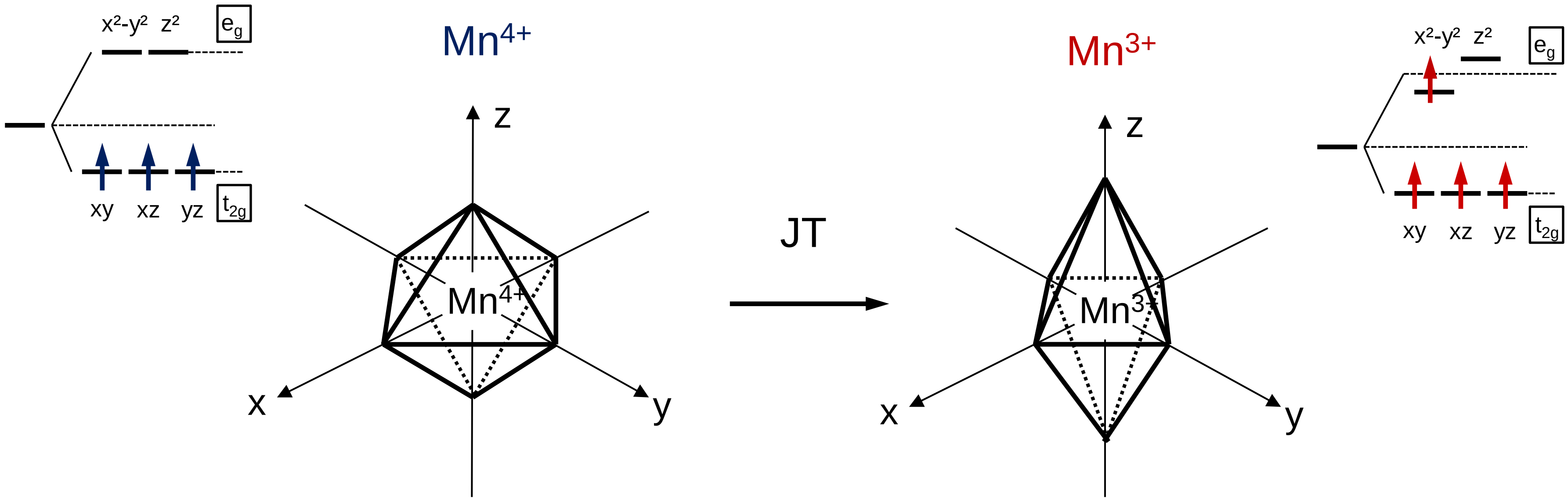
acc. to X. Shannon et. al., Acta Cryst., ***A32*** *(1976), 751*

Jahn-Teller distortion

- Hermann Arthur Jahn, Edward Teller, 1937:

  Jahn-Teller theorem

  „any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy thereby removing the degeneracy"



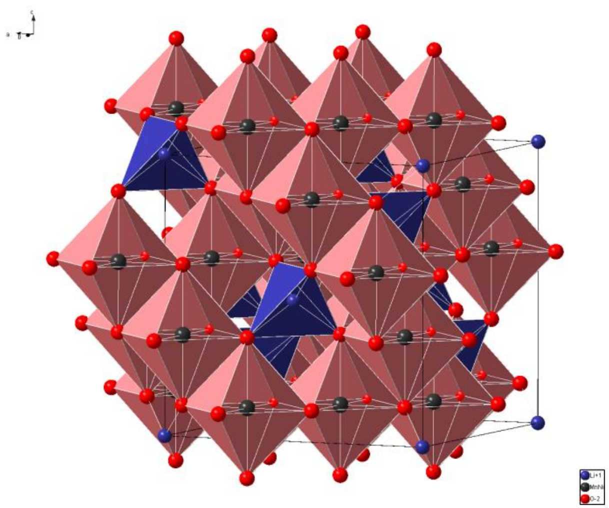
$Fd\bar{3}m$ (cubic) O_h D_{4h} $I4_1/a\,m\,d$ (tetragonal)

$Li_1Ni_{0.5}\overset{+4}{Mn}_{1.5}O_4$: $\xrightarrow{+x_{Li}}$ $\overset{+1}{Li}_{1+x}Ni_{0.5}\overset{+3}{Mn}_x\overset{+4}{Mn}_{1.5-x}O_4$:

Change of the crystal structure

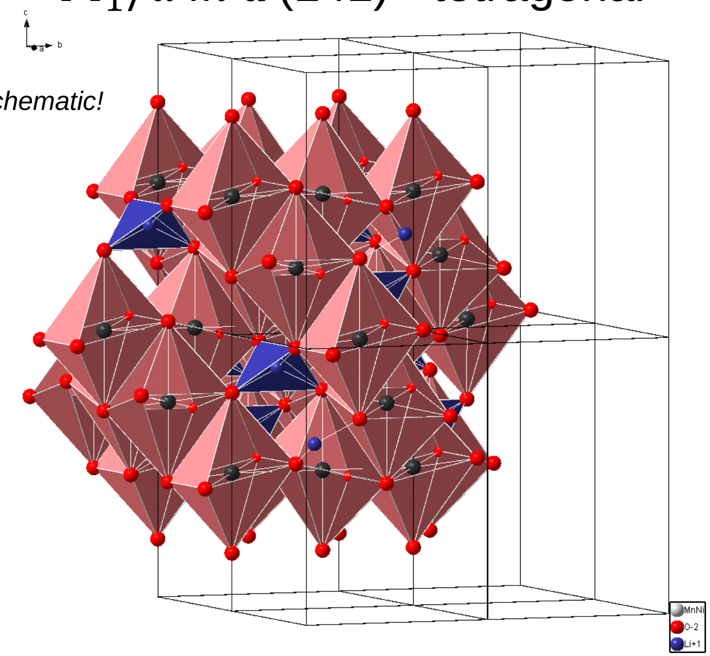
- The ideal spinel structure $Li_{1+x}Ni_{0.5}Mn_{1.5}O_4$, x_{Li} = 0, rewritten in the tetragonal space group:

$Fd\bar{3}m$ (227) - cubic



$I4_1/a\,m\,\mathrm{d}$ (141) - tetragonal

schematic!



3.5V

a = b = c = 8.18 Å

V = 547 Å³ Z=8

2V $Li_{0.96}Ni_{0.40}Fe_{0.08}Mn_{1.56}O_4$ $Li_{0.95}Ni_{0.50}Fe_{0.07}Mn_{1.47}O_{3.91}F_{0.09}$

c
a
V

less volume change
and less distortion with F-doping!

$\Delta V/V_{Cub,\ 100\%\ tetr.}$ = 5% $\Delta V/V_{Cub,\ 100\%\ tetr}$ = 4%

$c/a_{undistorted}$ = 1.414 c/a = 1.524 c/a = 1.506

New series: $LiNi_{0.5-x}Fe_{0.1}Ti_{0.02}Mn_{1.5-y}O_{4-z}F_z$

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- Synthesis

$Li(CH_3COO)\cdot 2H_2O$
$Ni(CH_3COO)_2\cdot 4\ H_2O$
$Mn(CH_3COO)_2\cdot 4\ H_2O$
$Fe(NO_3)_3\cdot 9\ H_2O$
CF_3COOH

↓

aqueous solution

↓

spray drying

↓

calcination T_1

↓

milling

↓ ← **LTO-Sol**

spray granulation

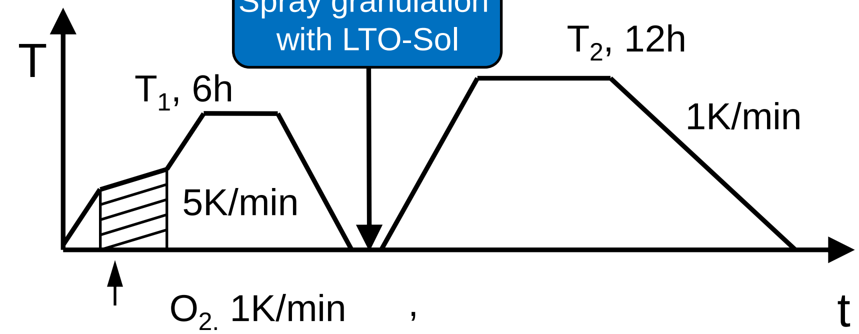
↓

temperature treatment T_2

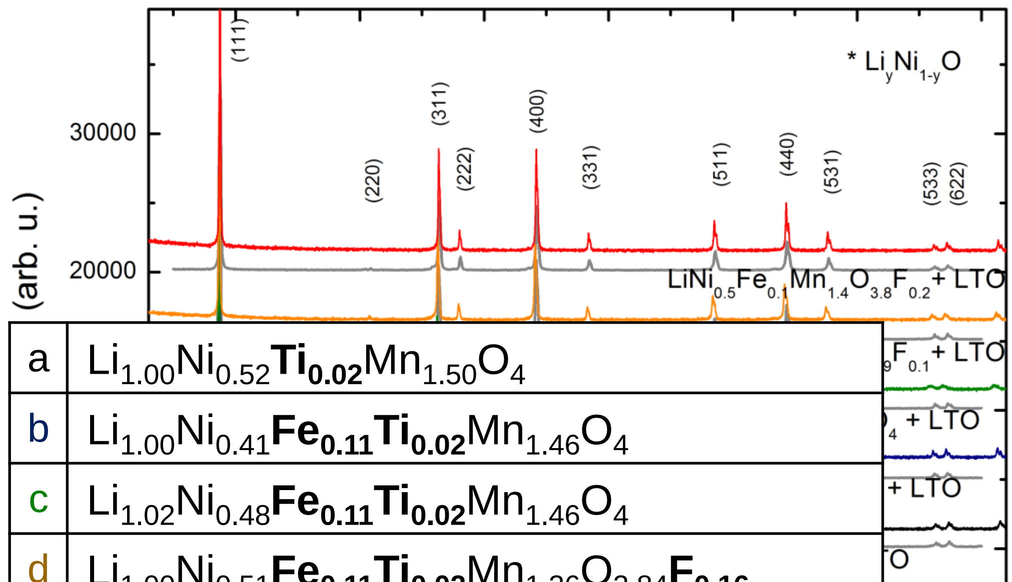
↓

homogenization

- temperature profile:



- XRD:



a	$Li_{1.00}Ni_{0.52}\mathbf{Ti_{0.02}}Mn_{1.50}O_4$
b	$Li_{1.00}Ni_{0.41}\mathbf{Fe_{0.11}Ti_{0.02}}Mn_{1.46}O_4$
c	$Li_{1.02}Ni_{0.48}\mathbf{Fe_{0.11}Ti_{0.02}}Mn_{1.46}O_4$
d	$Li_{1.00}Ni_{0.51}\mathbf{Fe_{0.11}Ti_{0.02}}Mn_{1.36}O_{3.84}\mathbf{F_{0.16}}$
e	$Li_{1.02}Ni_{0.51}\mathbf{Fe_{0.11}Ti_{0.02}}Mn_{1.35}O_{3.73}\mathbf{F_{0.27}}$

C. Adelhelm
T. Bergfeldt

Morphology of $LiNi_{0.5-x}Fe_{0.1}Ti_{0.02}Mn_{1.5-y}O_{4-z}F_z$

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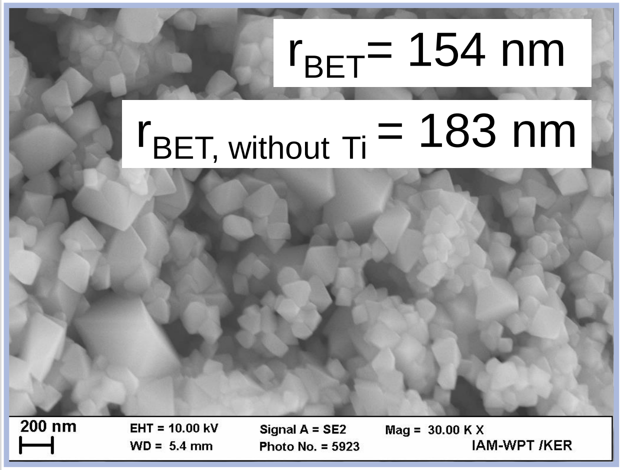
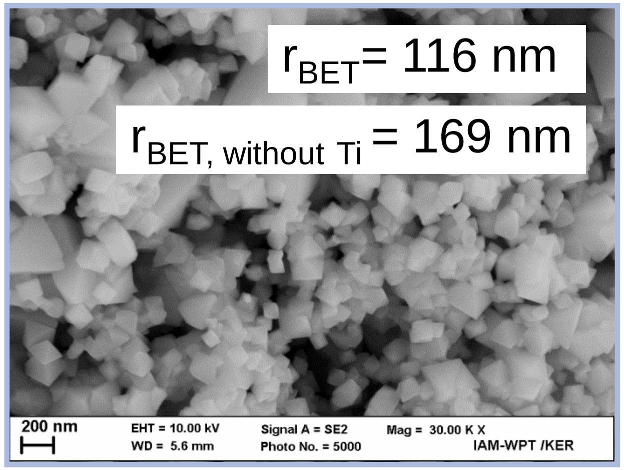
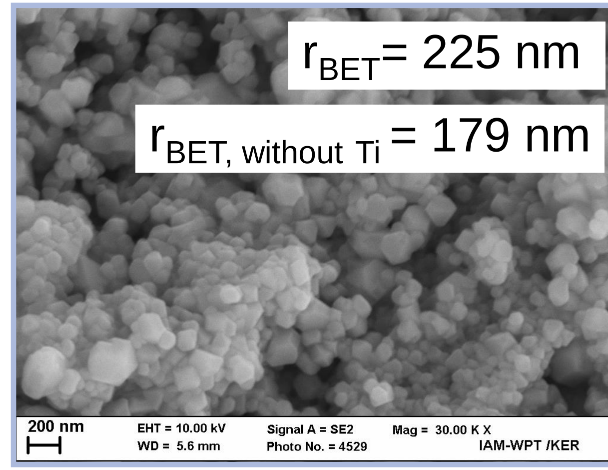
$Li_{1.00}Ni_{0.52}Ti_{0.02}Mn_{1.50}O_4$



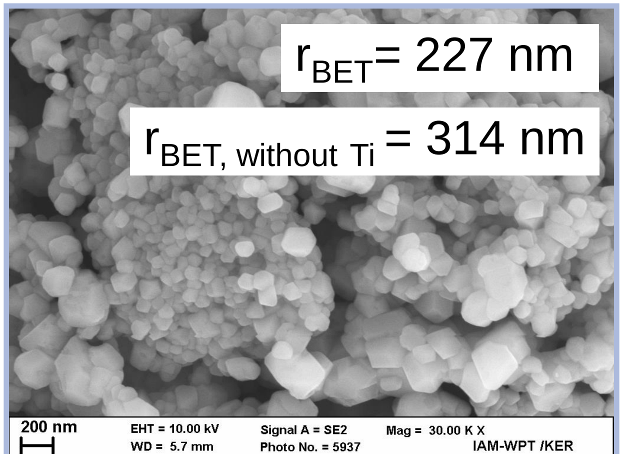
$Li_{1.00}Ni_{0.41}Fe_{0.11}Ti_{0.02}Mn_{1.46}O_4$



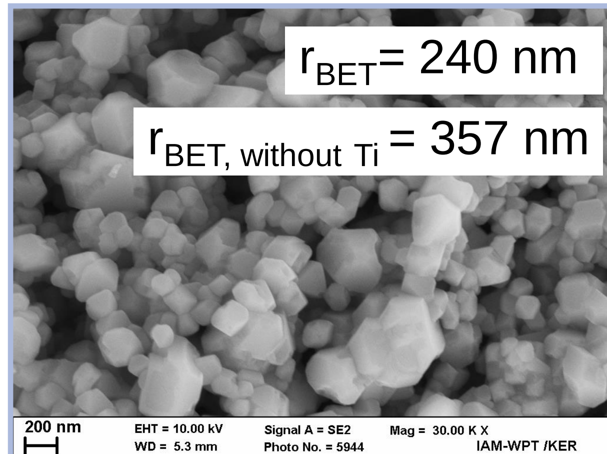
$Li_{1.02}Ni_{0.48}Fe_{0.11}Ti_{0.02}Mn_{1.46}O_4$



$Li_{1.00}Ni_{0.51}Fe_{0.11}Ti_{0.02}Mn_{1.36}O_{3.84}F_{0.16}$



$Li_{1.02}Ni_{0.51}Fe_{0.11}Ti_{0.02}Mn_{1.35}O_{3.73}F_{0.27}$



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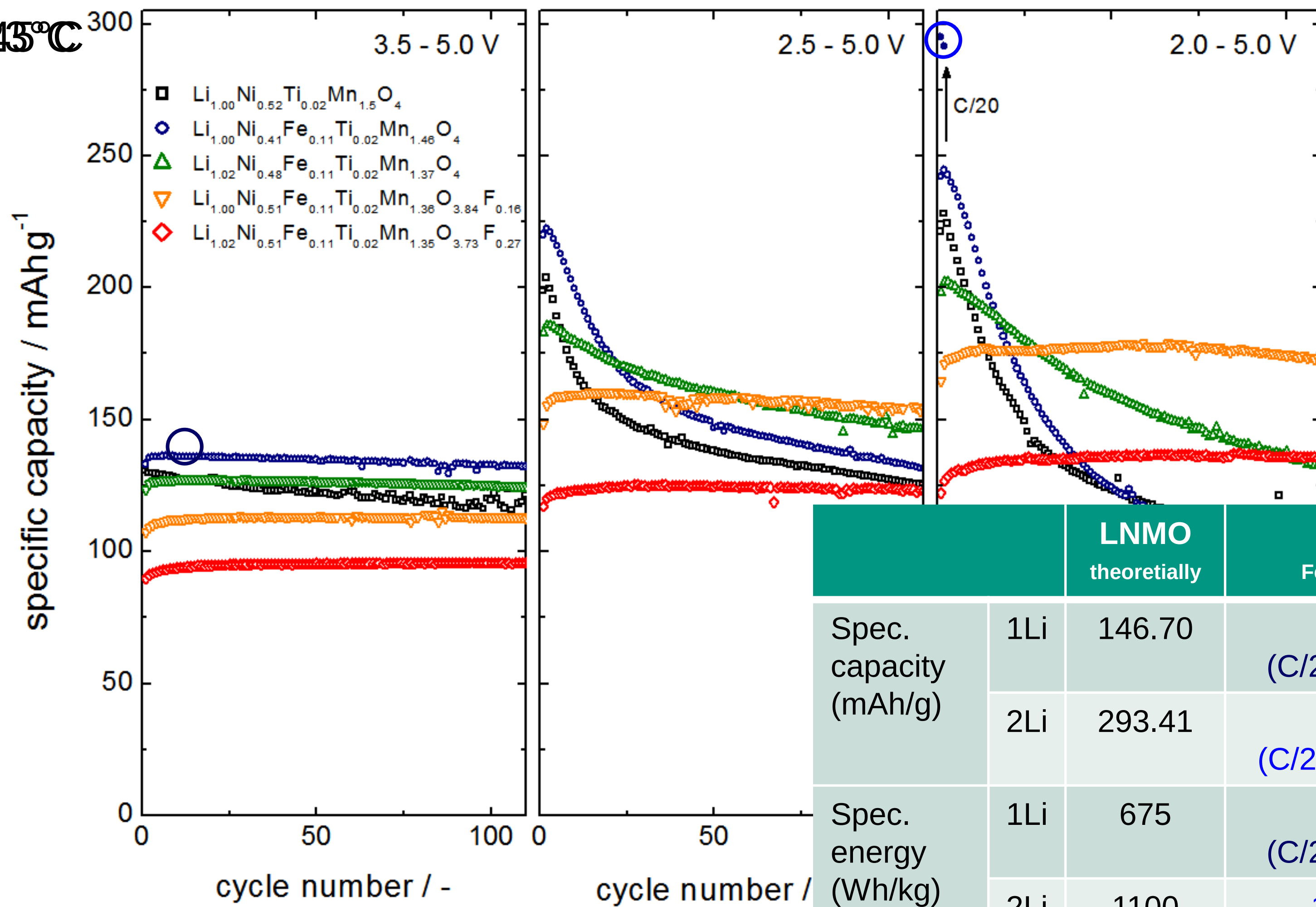
U. Maciejewski

Cycleability of $LiNi_{0.5-x}Fe_{0.1}Mn_{1.5-y}O_{4-z}F_z$

- 45°C

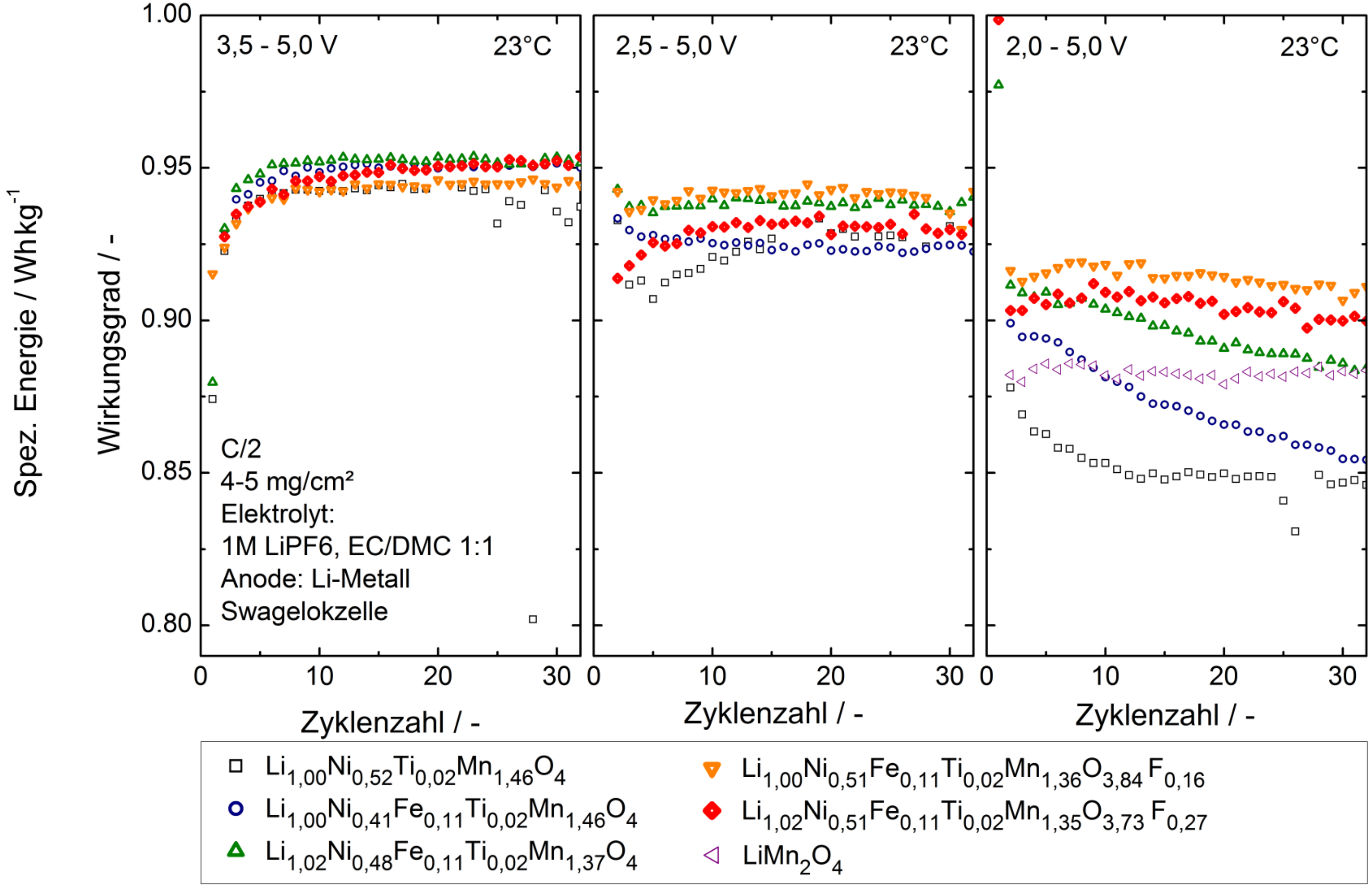


		LNMO theoretically	LNMO Fe,Ti- doped
Spec. capacity (mAh/g)	1Li	146.70	135.14 (C/2, 6. cycle)
	2Li	293.41	294.84 (C/20, 1. cycle)
Spec. energy (Wh/kg)	1Li	675	616.95 (C/2, 6. cycle)
	2Li	1100	1045.39 (C/20, 1. cycle)

- Ti doping increases spec. capacities

Cycleability of $LiNi_{0.5-x}Fe_{0.1}Mn_{1.5-y}O_{4-z}F_z$

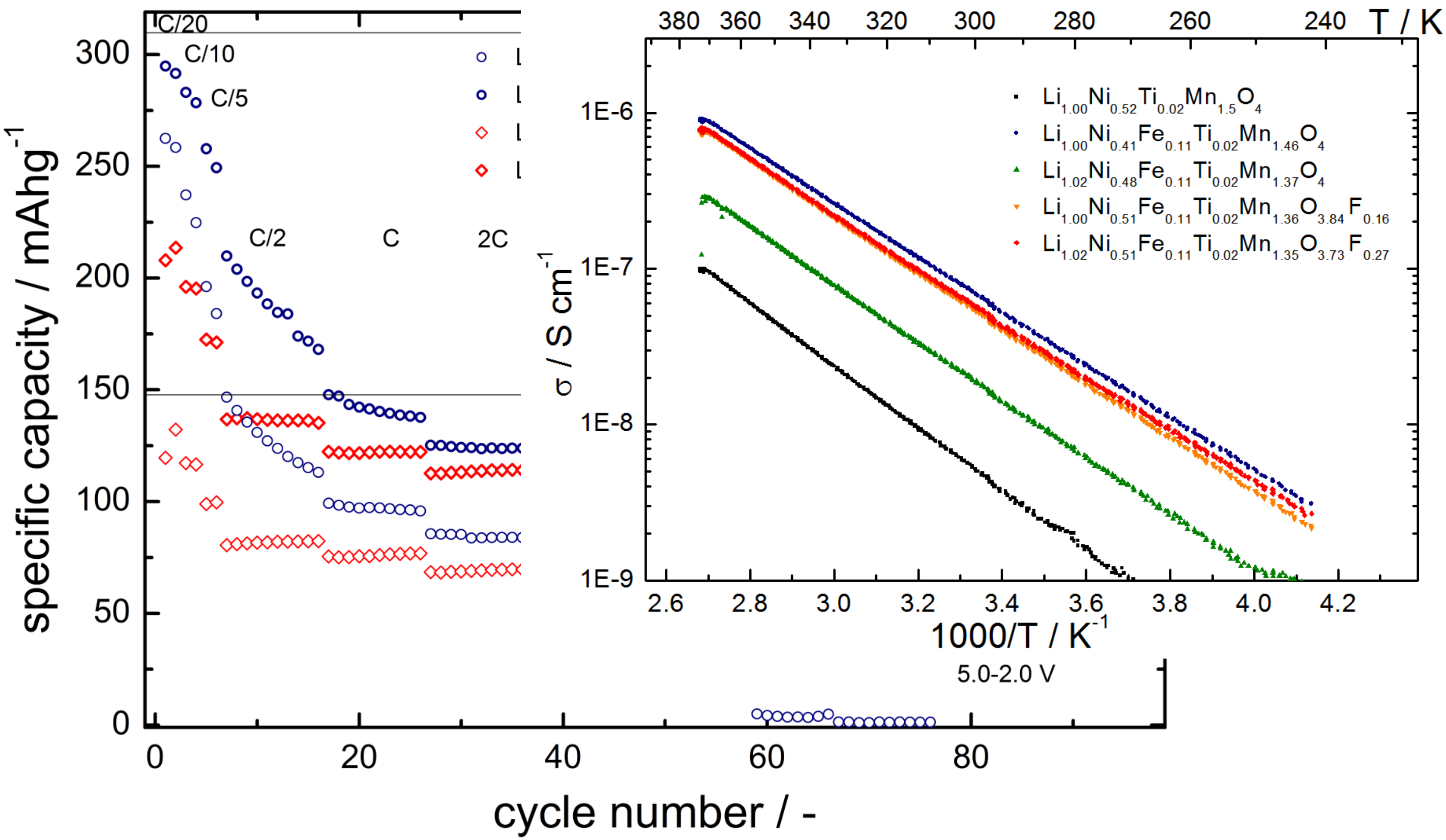
- energy efficiency



- F doping reduces side reactions at the cathode electrolyt interface

Comparison: Fe-, F- and Fe-, Ti-, F-doping

- performance test
- electronic conductivity

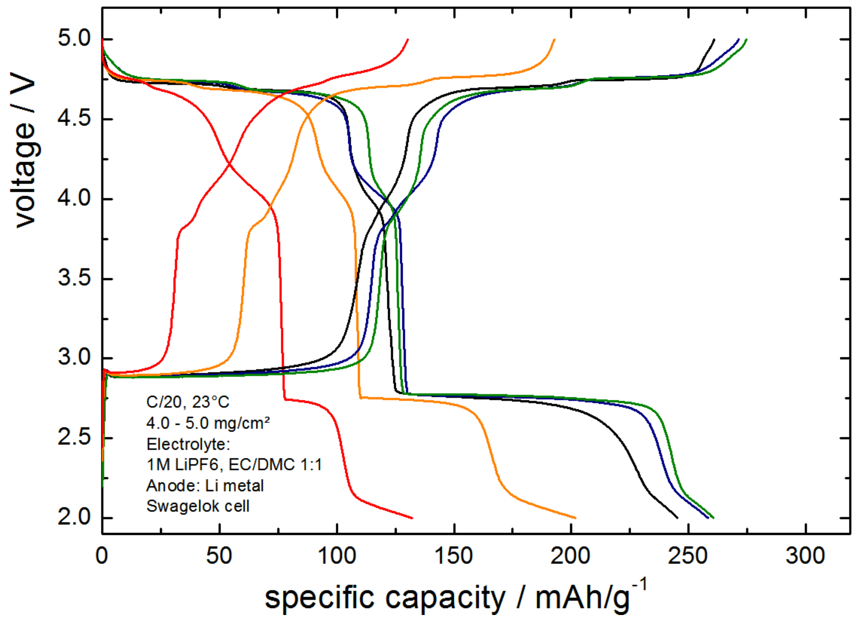


⇒ *F-,Fe- and Ti-doped* $LiNi_{0.5}Mn_{1.5}O_4$ *retains almost 100 mAh/g at 10C*

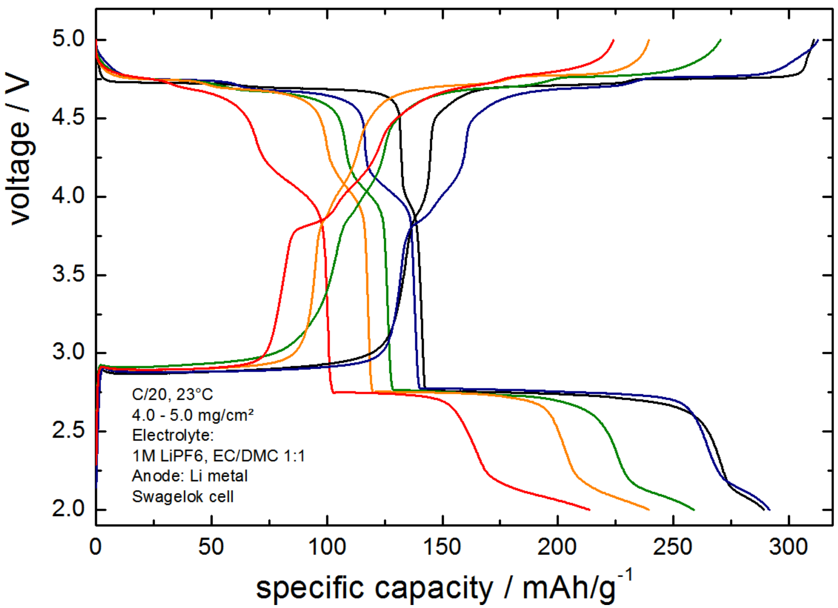
Comparison: Fe-, F- and Fe-, Ti-, F-doping

- Voltage profiles (C/20, cycle 2)

Fe-, F- series



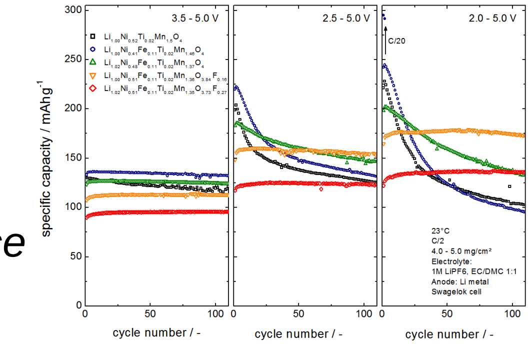
Fe-, Ti-, F- series



- Tetragonal phase transformation of Fe-, Ti-, F- doping samples less prohibited than for Fe-, F-doping
- Determination of the cell parameters of Fe-, Ti-, F- doped phases needed

Conclusion

- **Full 2 Li per formula cycled** with *Fe- and Ti-doped $LiNi_{0.5}Mn_{1.5}O_4$ (294 mAh/g, 2. cycle)*
- Energy density up to **1 kWh/kg**
- Doping improves the high voltage spinel *$LiNi_{0.5}Mn_{1.5}O_4$*:
  - ***F doping**: better temperature and electrolyte stability,*
  - ***Fe doping**: Less impurity phase, better electr. conductivity*
  - ***Ti doping**: higher capacity, better conductivity and performance*
  - *Together: **improved wide operation voltage capabablity***



- *F-,Fe- and Ti-doped $LiNi_{0.5}Mn_{1.5}O_4$ retains almost 100 mAh/g at 10C*
- *Lithium containing anodes (2V) and a more stable electrolyte (5V) needed*

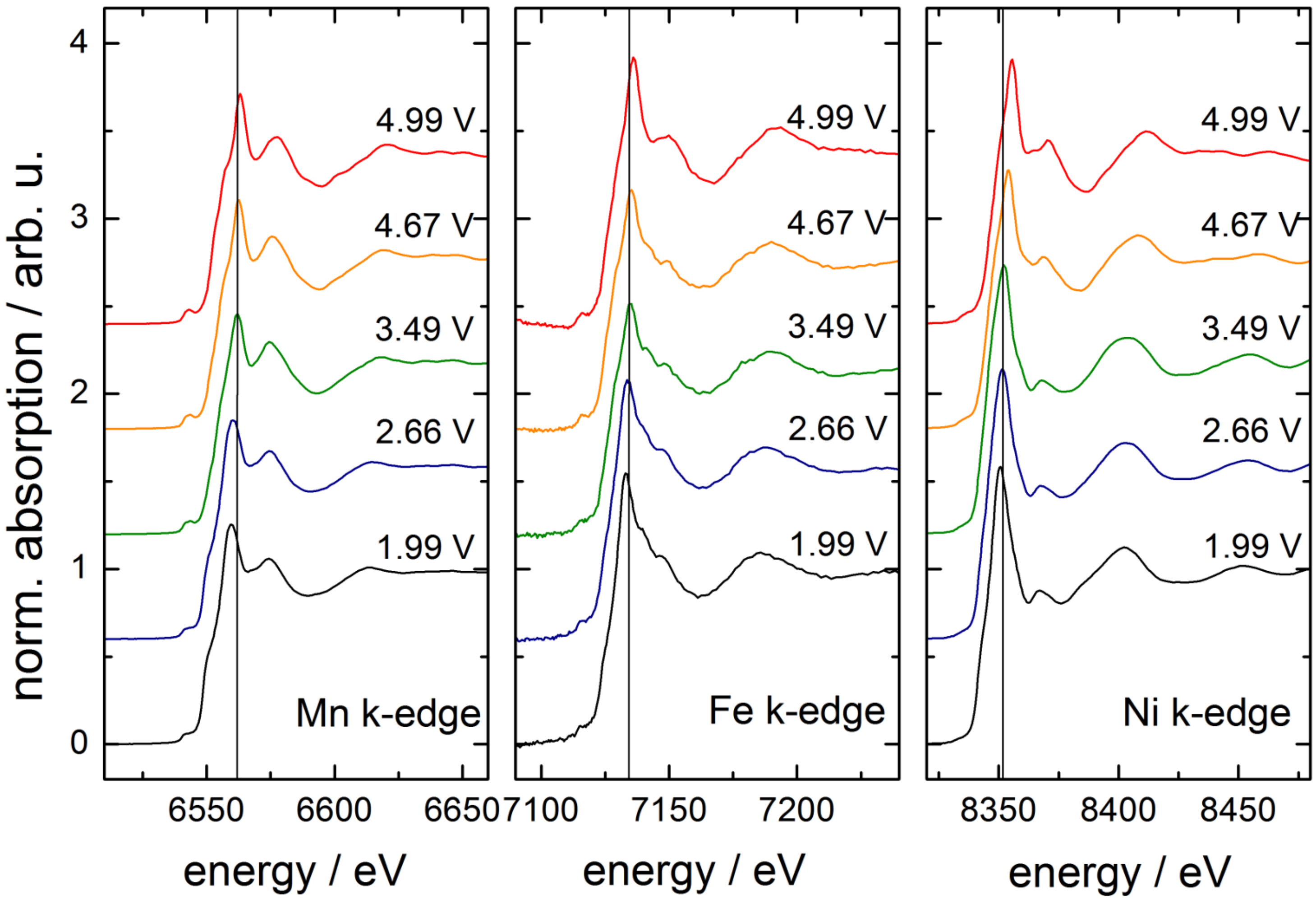
Further experiments necessary:

- *insitu* x-ray diffraction of the Ti doped samples

Thank you for your attention!

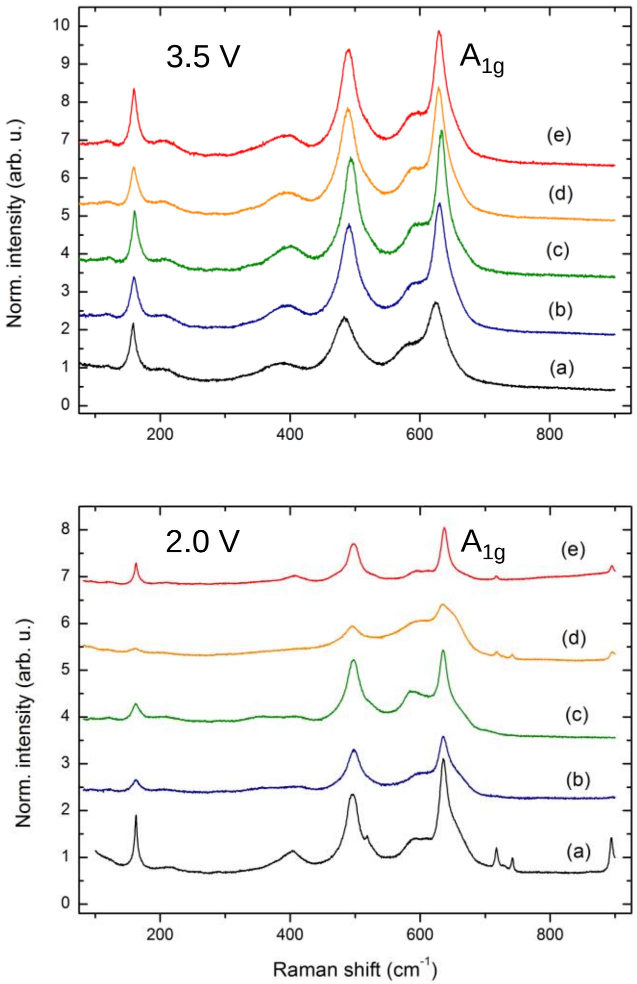
The financial support from the Helmholtz Gesellschaft and the state Baden-Württemberg is gratefully acknowledged.

EXAFS - $LiNi_{0.4}Fe_{0.1}Mn_{1.5}O_4$

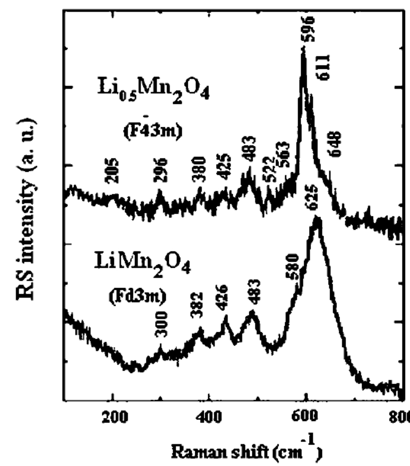


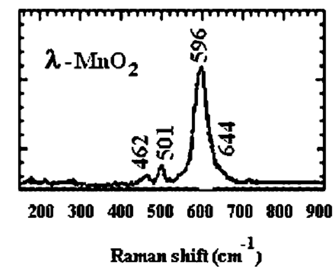
S. Glatthaar

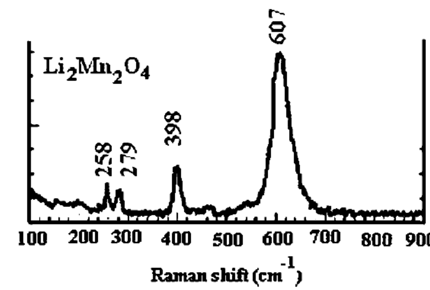
Raman spectra



a	$LiNi_{0.5}Mn^{3+}_{0.0}Mn^{4+}_{1.5}O_4$
b	$LiNi_{0.4}Mn^{3+}_{0.1}Mn^{4+}_{1.4}Fe_{0.1}O_4$
c	$LiNi_{0.45}Mn^{3+}_{0.0}Mn^{4+}_{1.45}Fe_{0.1}O_4$
d	$LiNi_{0.5}Mn^{3+}_{0.0}Mn^{4+}_{1.5}Fe_{0.1}O_{3.9}F_{0.1}$
e	$LiNi_{0.5}Mn^{3+}_{0.1}Mn^{4+}_{1.4}Fe_{0.1}O_{3.8}F_{0.2}$







Thackeray, M. M.; Johnson, P.; De Piciotto, L.; Bruce, P. G.; Goodenough, J. B. Mater. Res. Bull. ***1984****, 19, 179*

- Raman spectra do not show significant change of local structure, A_{1g}: 625-637 cm^{-1}