Performance and Safety of Olivines and Layered Oxides

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Project ID: ES069

Overview

Timeline

- Start date: October 1, 2009 (new project)
- End date: September 31, 2010
- Complete: 30%

Budget

- Total project funding
  - FY10 $300K

Barriers Addressed

- Energy density
- Cycle life
- Safety

Partners

- Collaborations: Grey (Stony Brook), Ceder (MIT), Richardson, Kostecki, Doeff, Cabana (LBNL), Gabrisch (UNO), NCEM, ALS, SSRL
- Project lead: John Newman

Objectives\Milestones

Objectives

- Investigate phase transition mechanisms and explore kinetic barriers of high-energy cathode materials.
- Establish direct correlations between crystal structure, composition, morphology, performance, and stability.
- Provide guidelines to design and develop electrode materials with improved energy density, rate capability, and safety, especially with regard to thermal stability.

Milestones

- Report thermal stability and performance evaluation of the modified $LiMnPO_4$.
- Report results on the synthesis of layered oxide crystals.

Approach

- Prepare well-formed crystals of cathode materials with various crystal structures, chemical compositions, sizes, and morphologies.

- Characterize physical properties and investigate solid state chemistry of the crystals using chemical and electroanalytical methods, synchrotron based spectroscopies and spectromicroscopies, x-ray and neutron diffractions, vibrational spectroscopies, scanning calorimetry, and electron microscopic techniques.

- Optimize synthesis and processing conditions, improve performance and safety of the cathode materials based on the structural and mechanistic understandings.

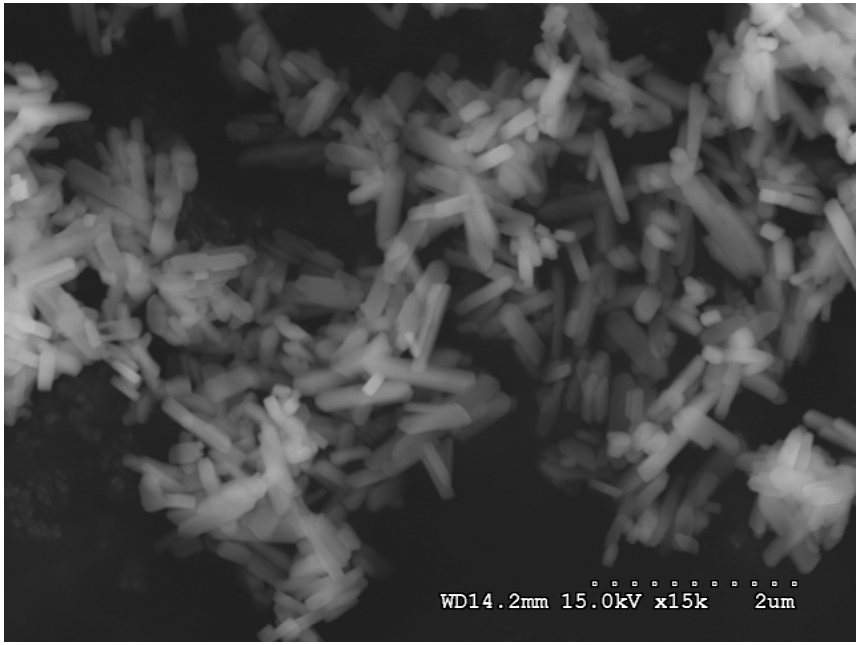
Olivines

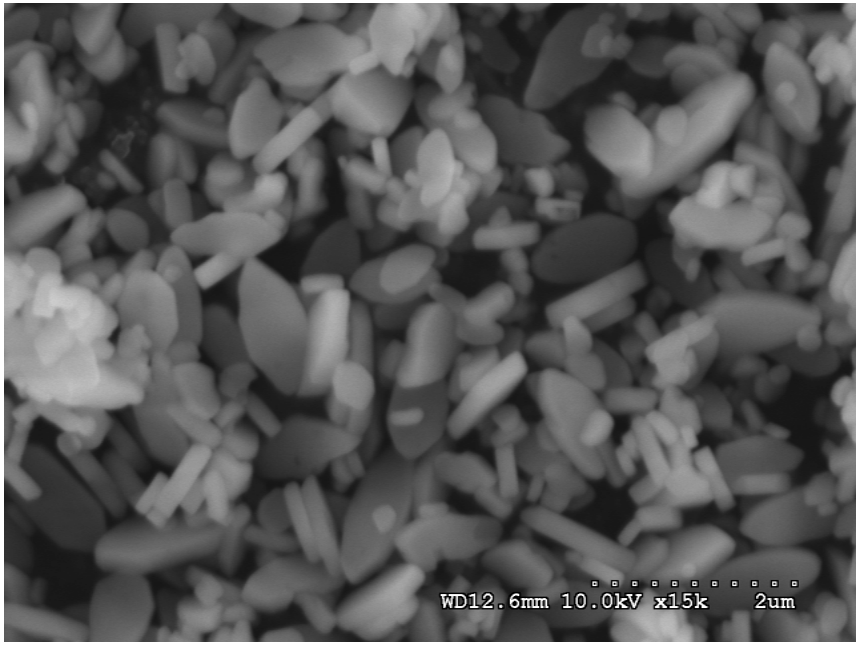
- $LiMnPO_4$ has high theoretical energy density but low effective energy density. Delithiated $LiMnPO_4$ has poor chemical and thermal stabilities.

- What makes $LiMnPO_4$ kinetically slow and thermally unstable?
- How do chemical composition, crystal size and morphology, and surface treatment affect performance and safety?
- What can be done to make the olivine phosphates ($LiMPO_4$, M=Mn, Co and Ni) practical high-energy cathodes?

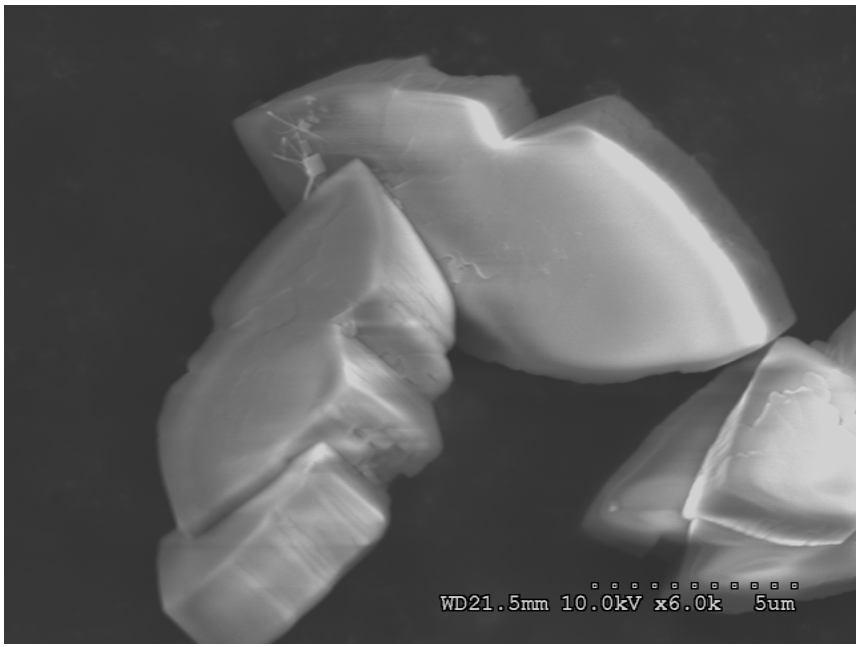
- Prepare pristine and substituted $LiMnPO_4$ with controlled morphologies.
- Investigate the effect of size and morphology on the phase transformation process.
- Investigate the effects of substitution and surface treatment on structure, kinetics and stabilities (physical, chemical and thermal).
- Explore other approaches to producing better-performing $LiMPO_4$.

Crystal Synthesis





- Single crystals of pristine and substituted $LiMnPO_4$ were prepared by the hydrothermal method.
- Particle size and morphology were controlled by synthesis conditions.



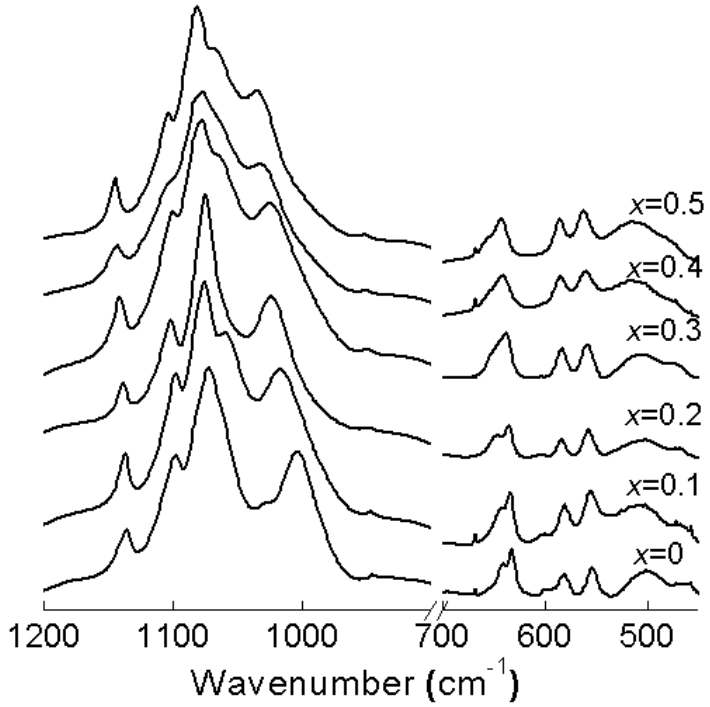
Improved Kinetics

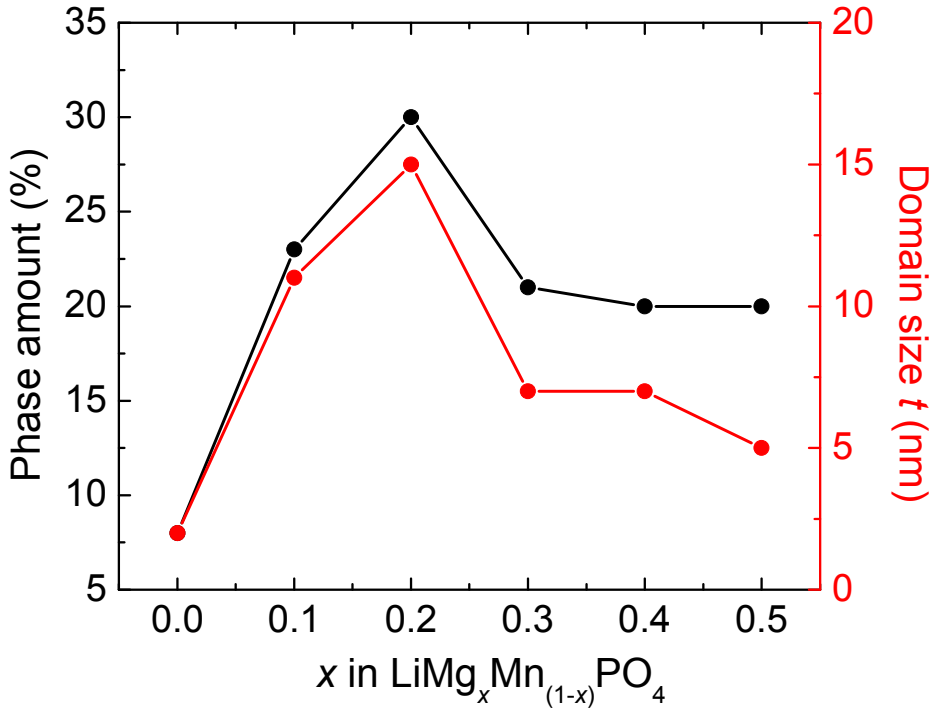
Chemical Delithiation (y=0.5)

$LiMg_xMn_{(1-x)}PO_4 + y(1-x)NO_2BF_4 \rightarrow$

$(1-y)LiMg_xMn_{(1-x)}PO_4 + yLi_xMg_xMn_{(1-x)}PO_4 + y(1-x)NO_2 + y(1-x)LiBF_4$

$E_{NO2}{}^{+}/_{NO2} \approx 5.1$ V vs. Li/Li^{+}

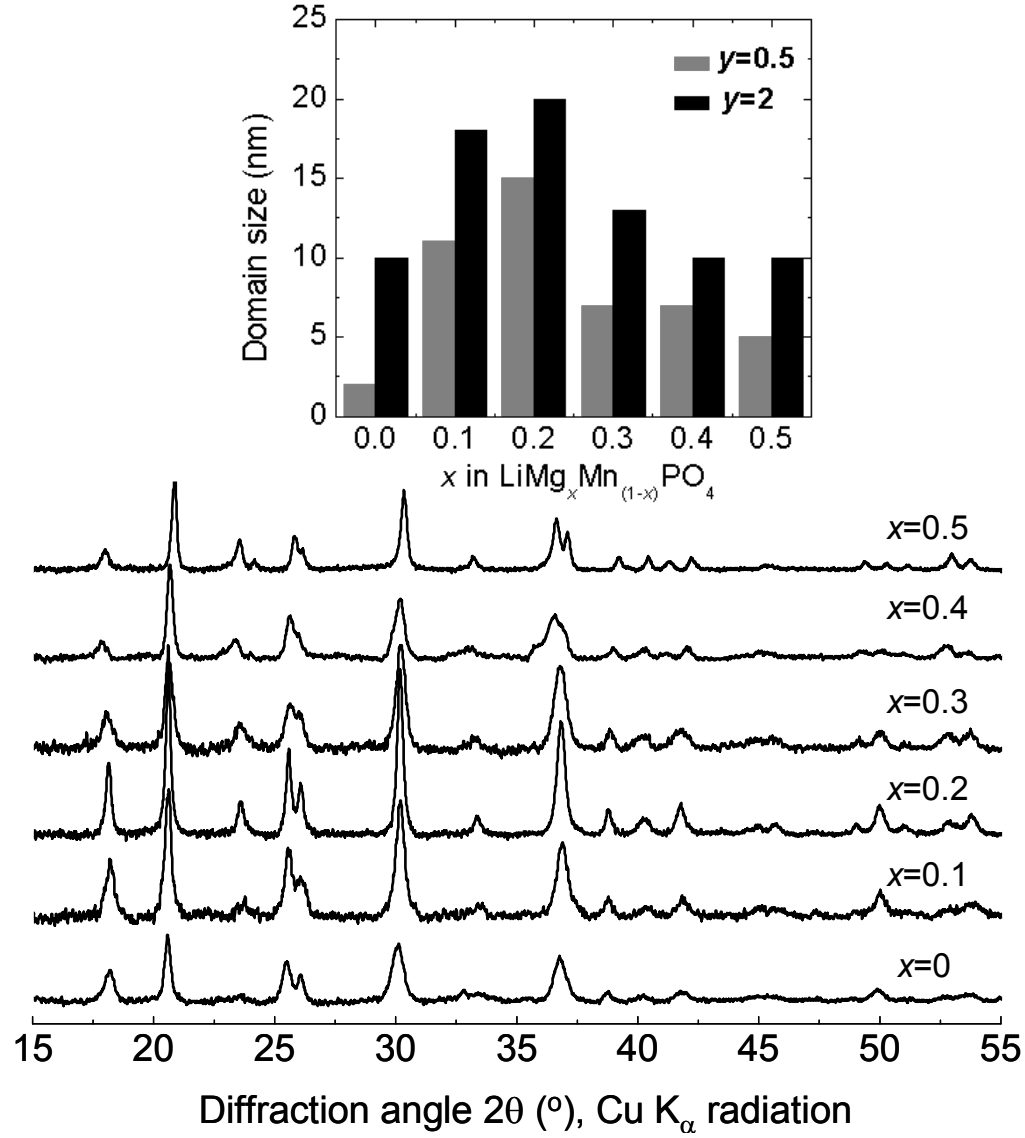


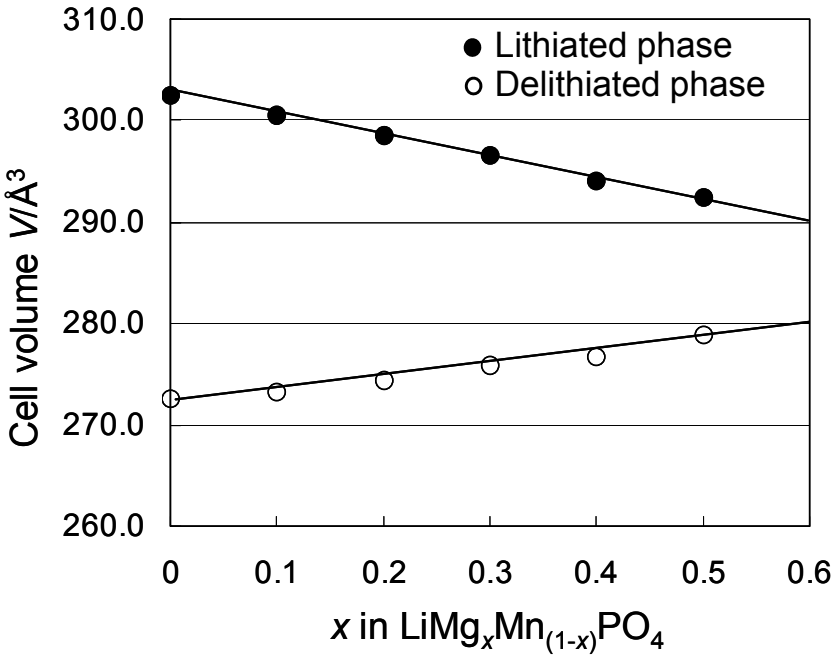


- Mg substitution improves delithiation efficiency and phase crystallinity.
- Best performance obtained with 20% Mg substitution.

Improved Kinetics

Chemical Delithiation (y=2)



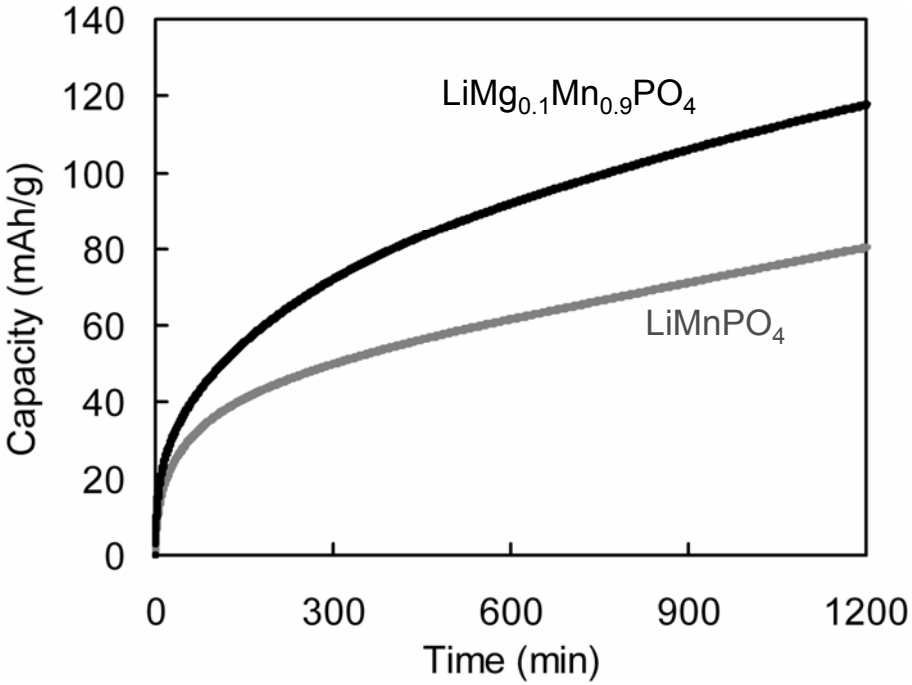


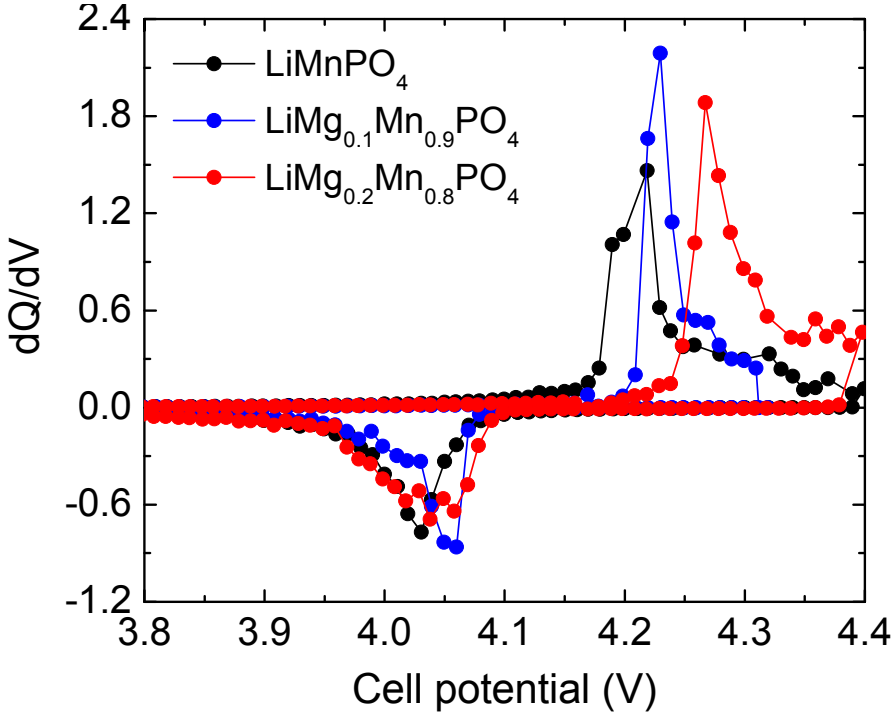
- Internal strain limits the growth of the delithiated domain upon further oxidation.

- Mg substitution decreases volume mismatch at the phase boundary.

Improved Kinetics

Electrochemical Studies

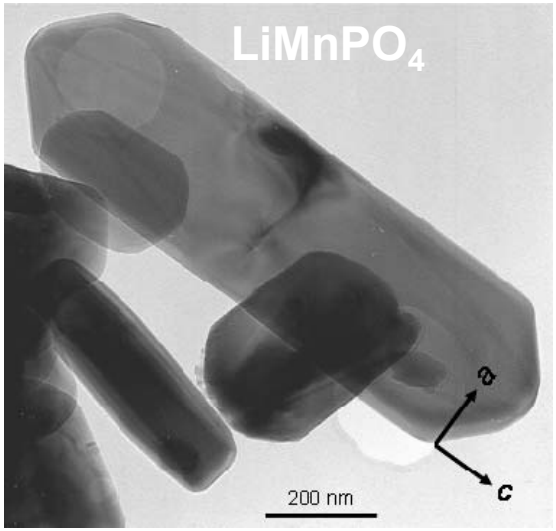


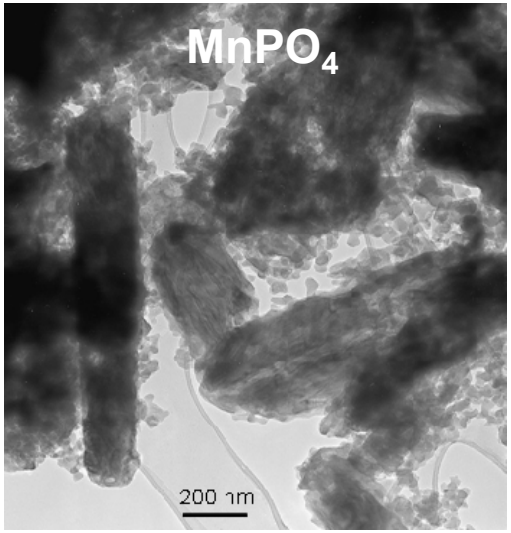


- Mg substitution improves electrochemical charge kinetics.

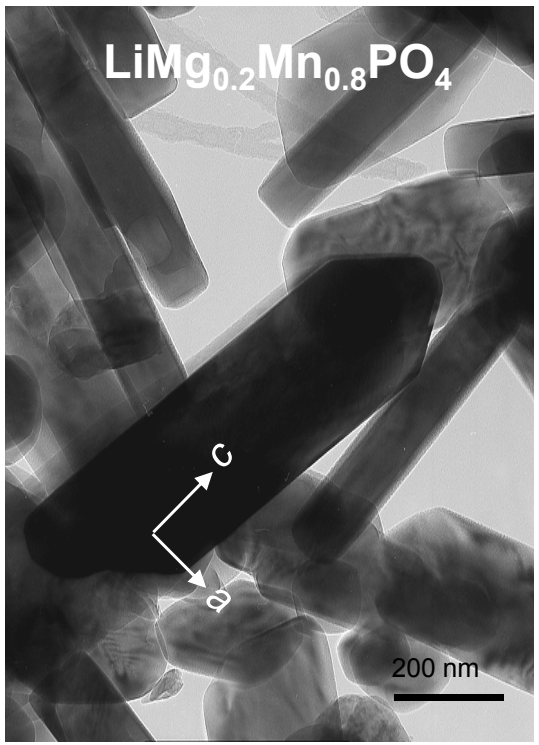
- Mg substitution raises charge and discharge potentials.

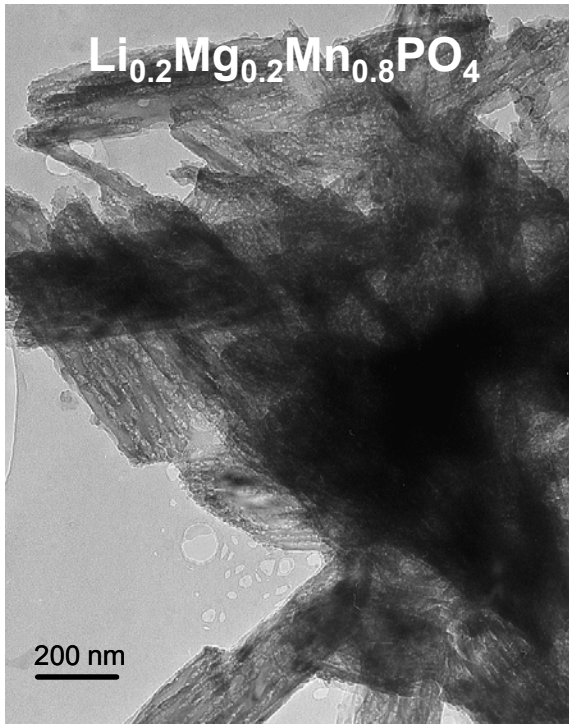
Improved Physical Stability





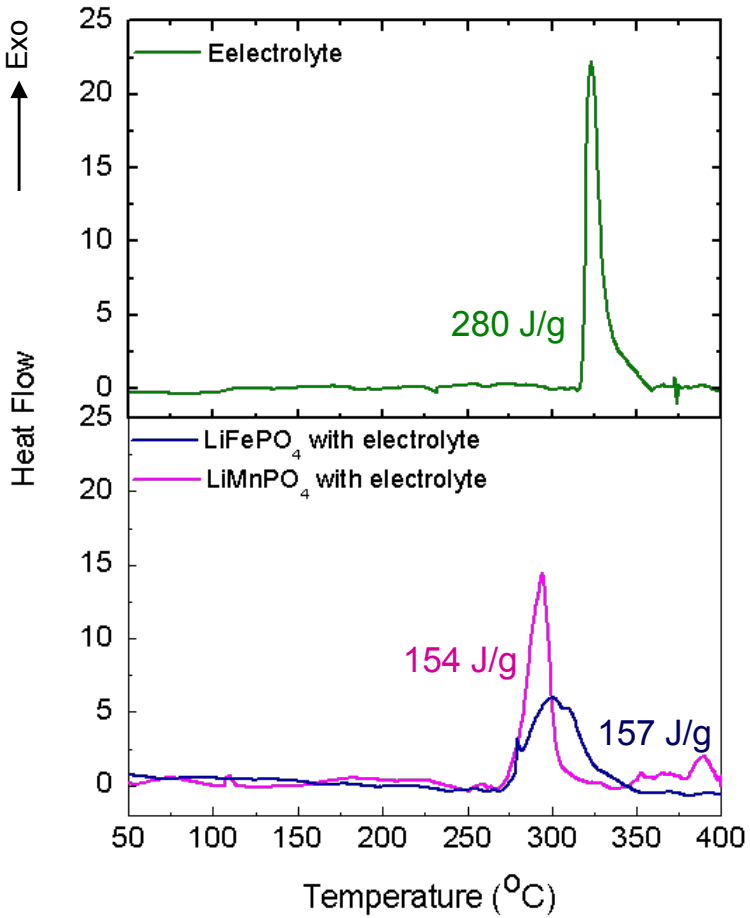
- Internal strain and large volume mismatch at the phase boundary result in crystal decrepitation when Li is removed.
- Morphological instability contributes to poor phase transition kinetics in $LiMnPO_4$.

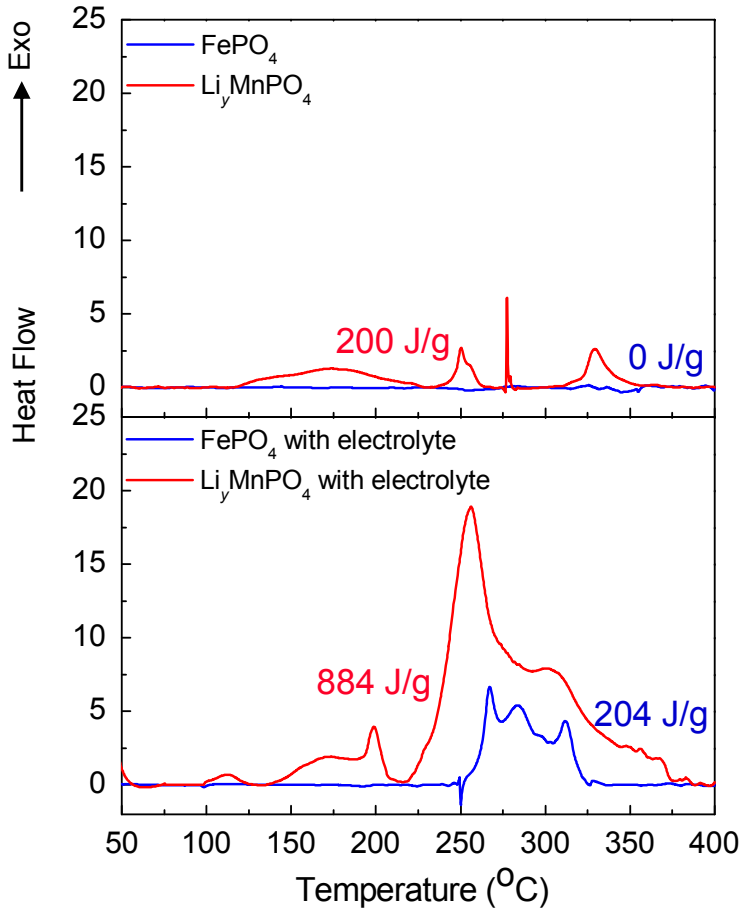




- Mg substitution dilutes the Jahn -Teller ion (Mn^{3+}) in the structure and reduces volume mismatch.
- Crystals retain physical integrity after delithiation.

Improved Thermal Stability





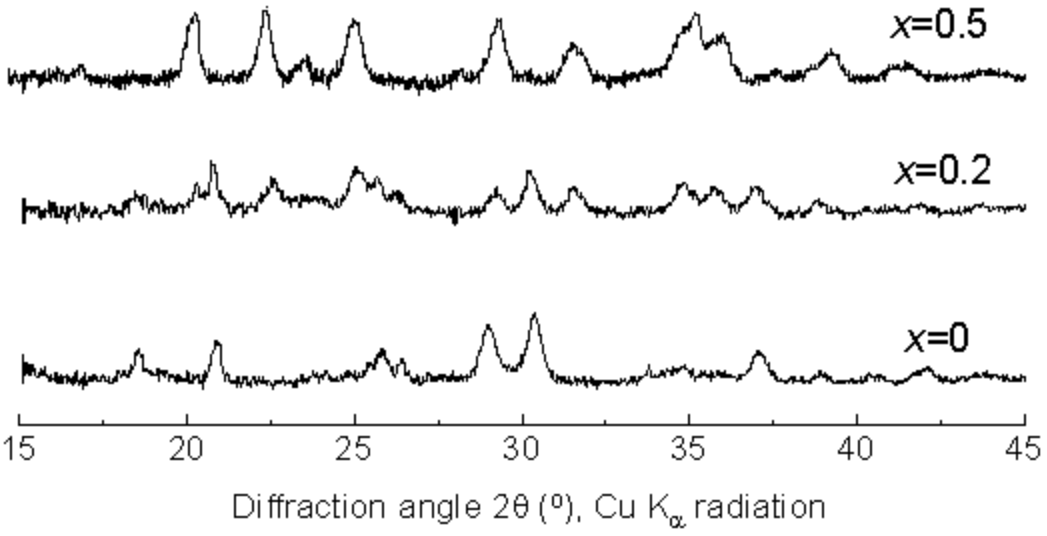
- Unlike $FePO_4$, delithiated $LiMnPO_4$ decomposes and releases O_2 around 150 °C.
- The reaction with the electrolyte produces a large amount of heat similar to that of charged $LiCoO_2$.

Improved Thermal Stability

$$2Li_xMg_xMn_{1-x}PO_4 \rightarrow 2xLiMgPO_4 + (1-x)Mn_2P_2O_7 + 0.5(1-x)O_2$$

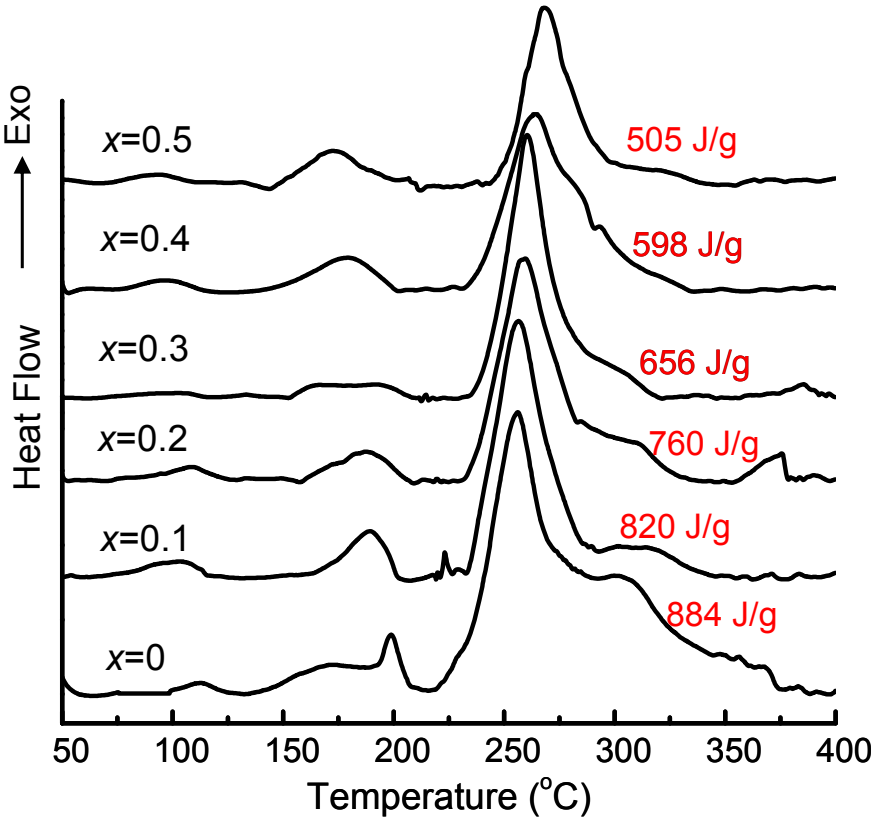
$$3Li_xMg_xMn_{1-x}PO_4 \rightarrow 3xLiMgPO_4 + (1-x)Mn_3(PO_4)_2 + 0.5(1-x)P_2O_5 + 0.75(1-x)O_2$$

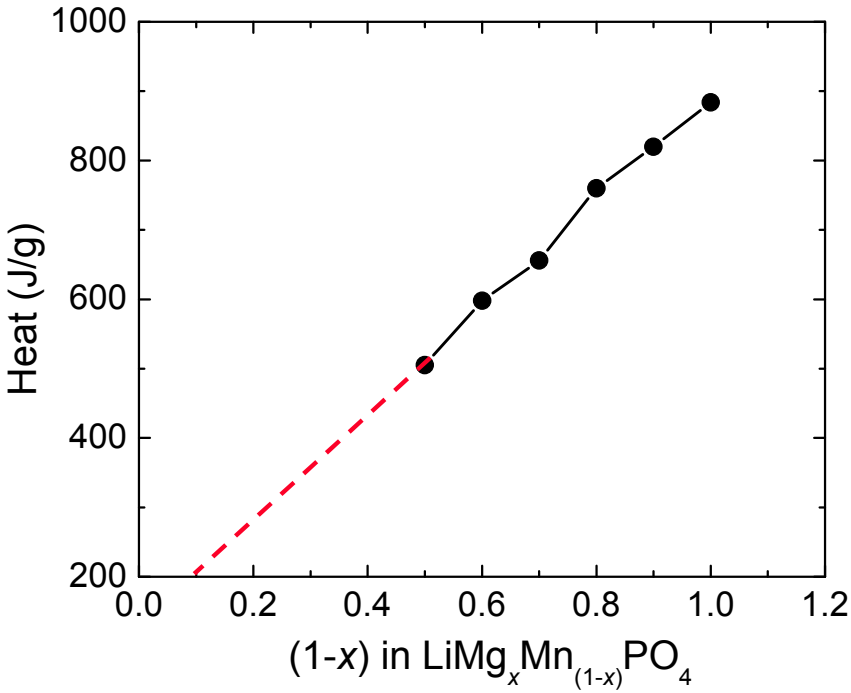
XRD of heat-treated $Li_xMg_xMn_{(1-x)}PO_4$ crystals:



- Unsubstituted phosphate (x=0) decomposes to $Mn_2P_2O_7$ and releases 0.25 mole O_2 per mole phosphate.
- Substituted phosphate (x=0.5) decomposes to $Mn_3(PO_4)_2$ and releases 0.125 mole O_2.
- Both $Mn_2P_2O_7$ and $Mn_3(PO_4)_2$ were formed in the samples with $0<x<0.5$.

Improved Thermal Stability





- Released oxygen and generated heat decrease with the decrease of Mn content in the phosphates.
- Total heat evolved: 136 ± 3 kJ per mole of Mn in the phosphates.

Layered Oxides, $Li_{1+x}M_{1-x}O_2$

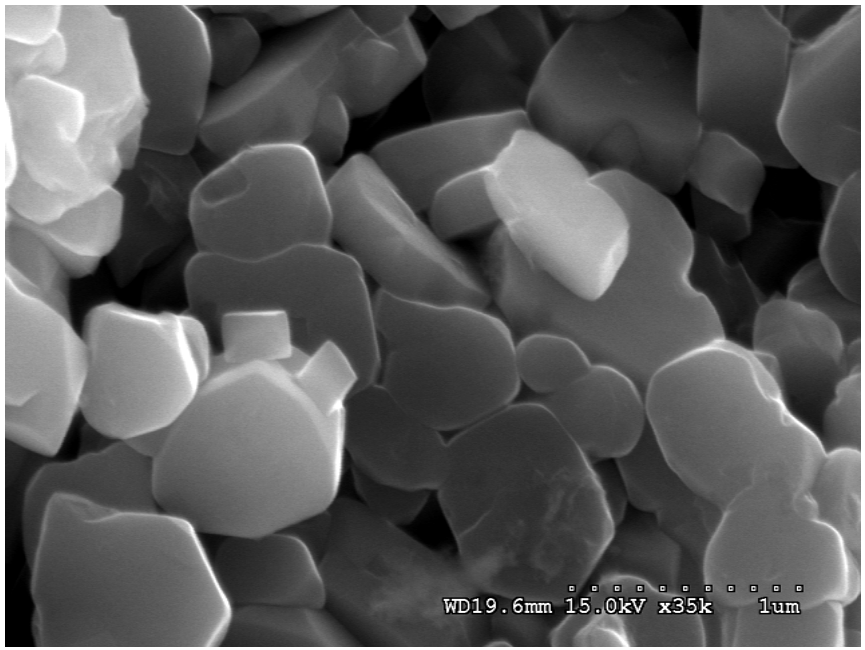
- Layered $Li_{1+x}M_{1-x}O_2$ (M = Ni, Mn and Co) has over 200 mAh/g capacity. Structure and ordering scheme key to the performance but poorly understood from the studies on aggregated oxide particles.

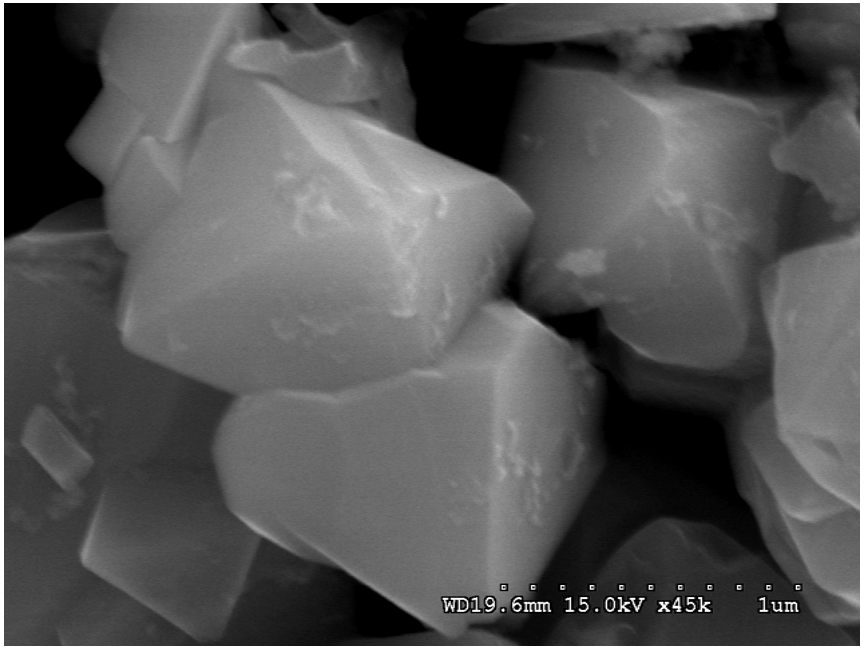
- At the single crystallite level, how do the local and long-range orders in the oxides correlate to their performance and safety?
- What is the mechanism for oxygen evolution at high voltages? What causes the irreversible capacity loss in the material?
- Is there phase transformation during delithiation and relithiation? What are the mechanisms?
- What is the optimum composition?
- What is the optimum particle morphology?

- Synthesize $Li_{1+x}M_{1-x}O_2$ (M = Ni, Mn and Co) single crystals with controlled morphologies.
- Evaluate performance and investigate the effect of Li stoichiometry, transition metal ratios, delithiation and relithiation processes (both chemical and electrochemical) on local and long-range orders.
- Explore synthesis conditions to produce desired structure and ordering scheme for optimum performance and safety.

Crystal Synthesis

- Single crystals were synthesized by the molten salt method.
- Particle size and morphology can be controlled by synthesis conditions.

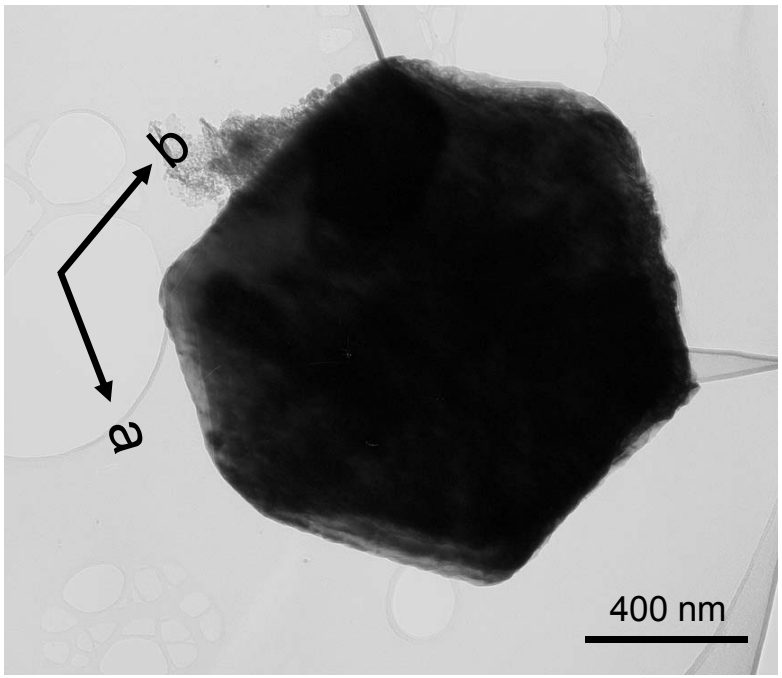




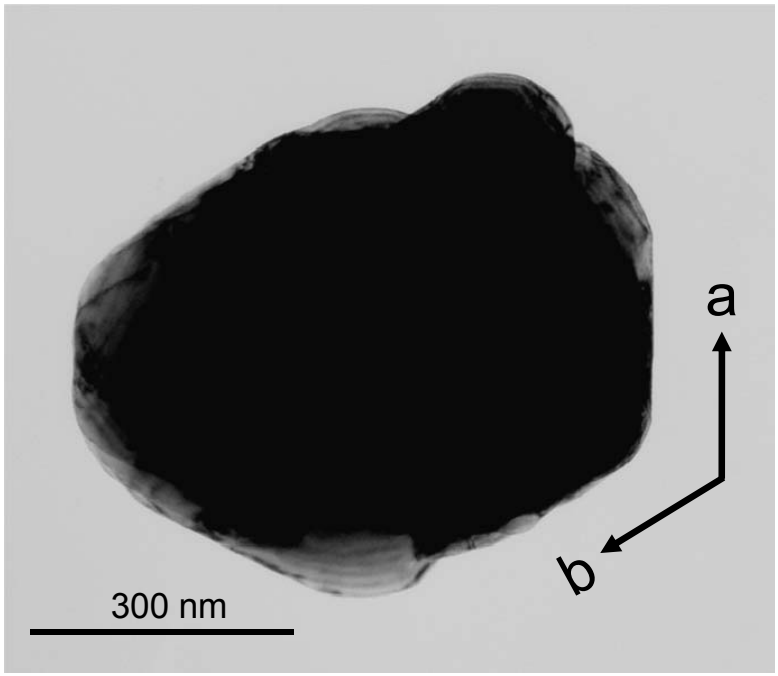
Crystal Synthesis

- Plate-shaped crystals of “Li-excess” and “Li-stoichiometric” oxides, $Li_{1+x}(Ni_{0.33}Mn_{0.33}Co_{0.33})_{1-x}O_2$ (NMC333), were prepared.
- x = 0.14 and 0 based on ICP analysis.

“Li-excess” NMC333 (x=0.14)

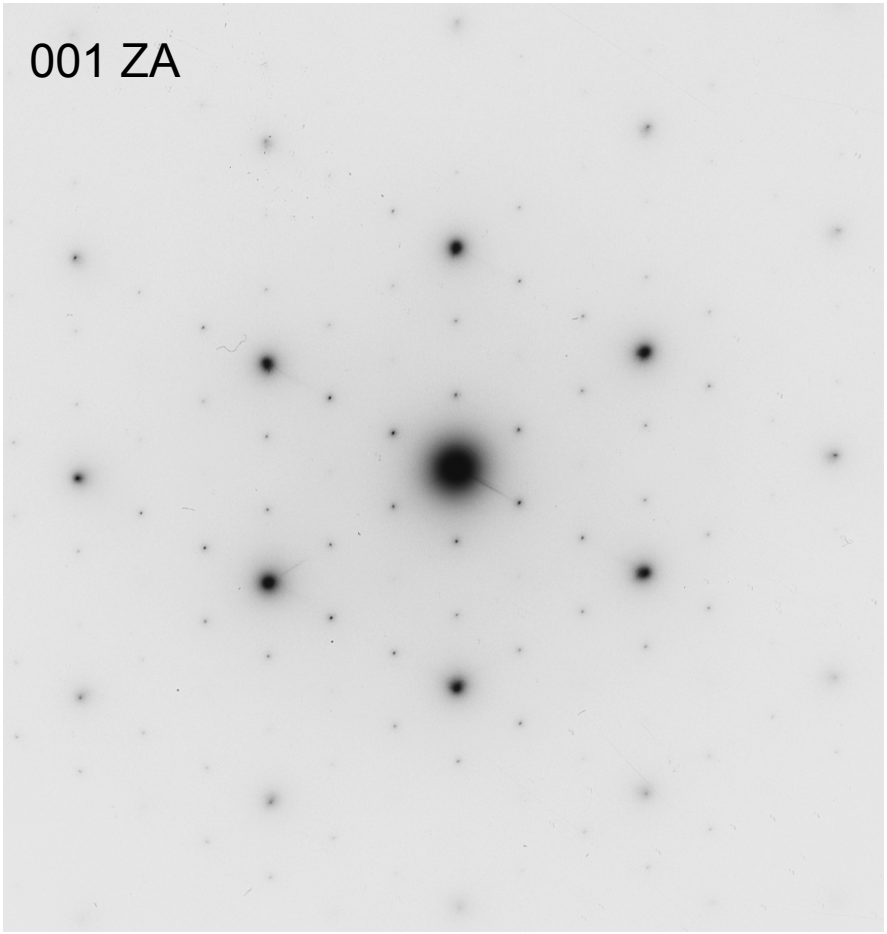


“Li-stoichiometric” NMC333 (x=0)

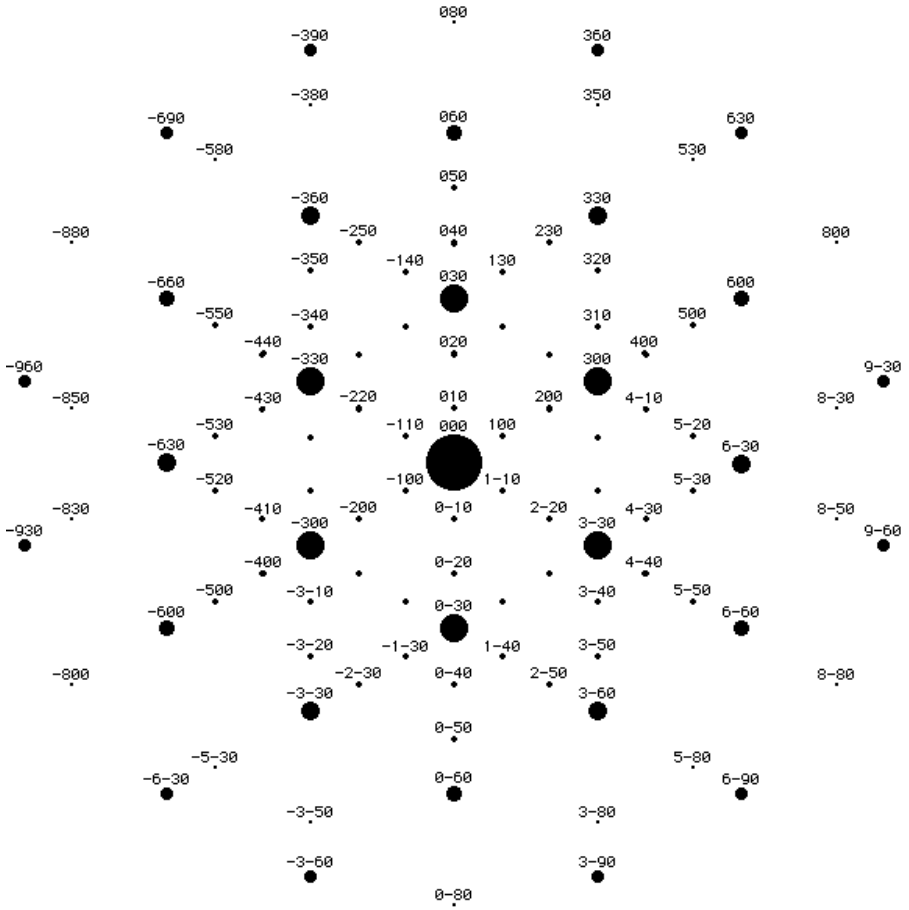


Electron Diffraction

"Li-excess" NMC333 Crystals

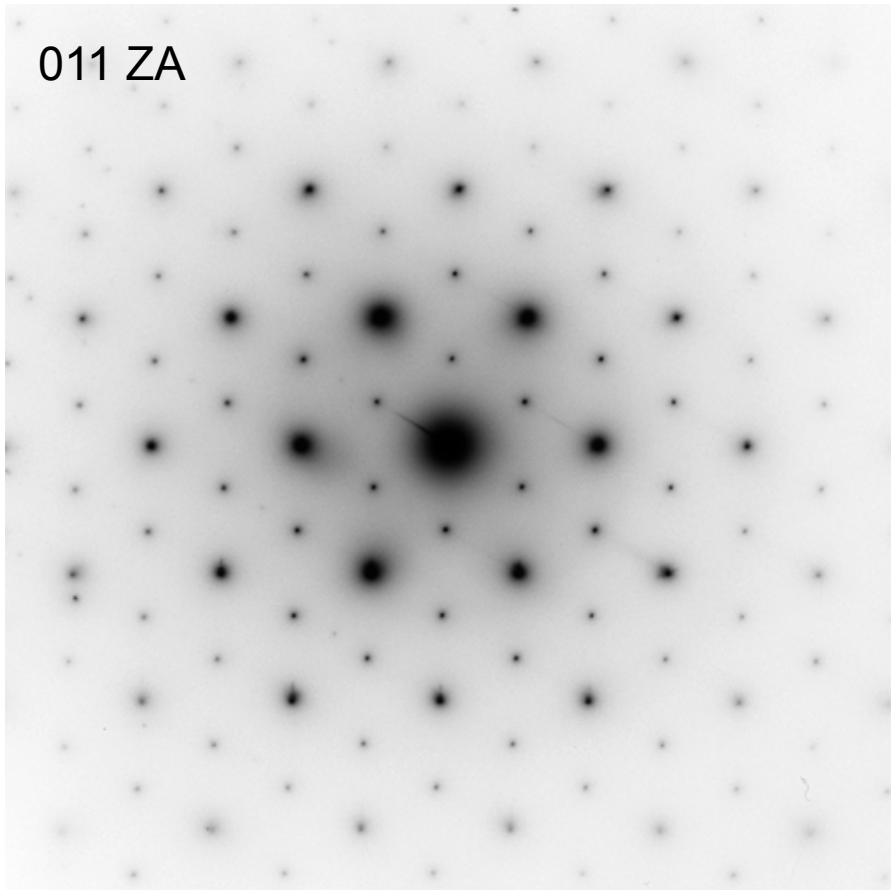


Simulated pattern from $P3_112$ (001 ZA)

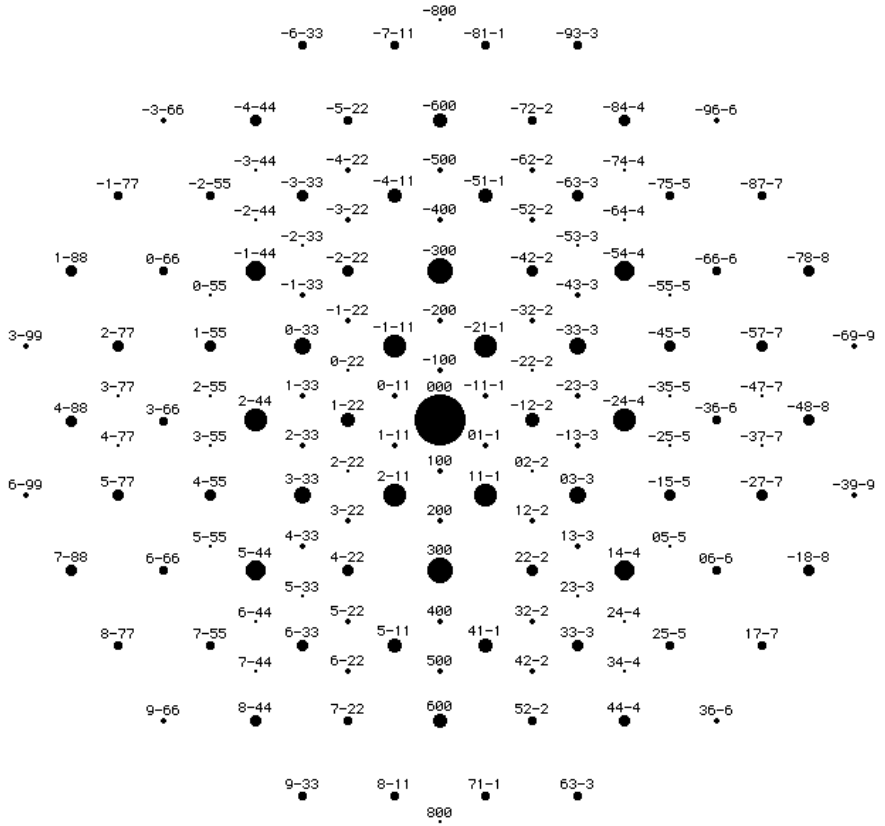


Electron Diffraction

"Li-excess" NMC333 Crystals



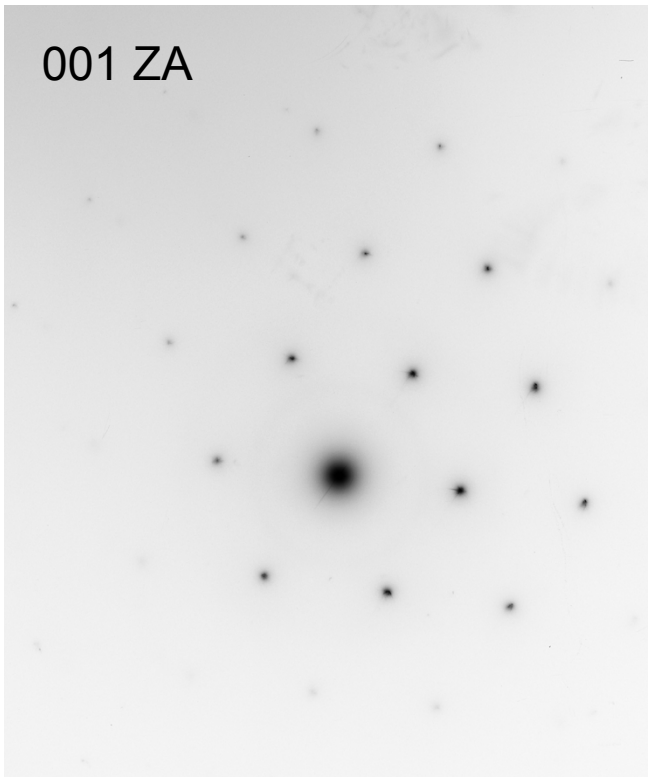
Simulated pattern from $P3_112$ (011 ZA)



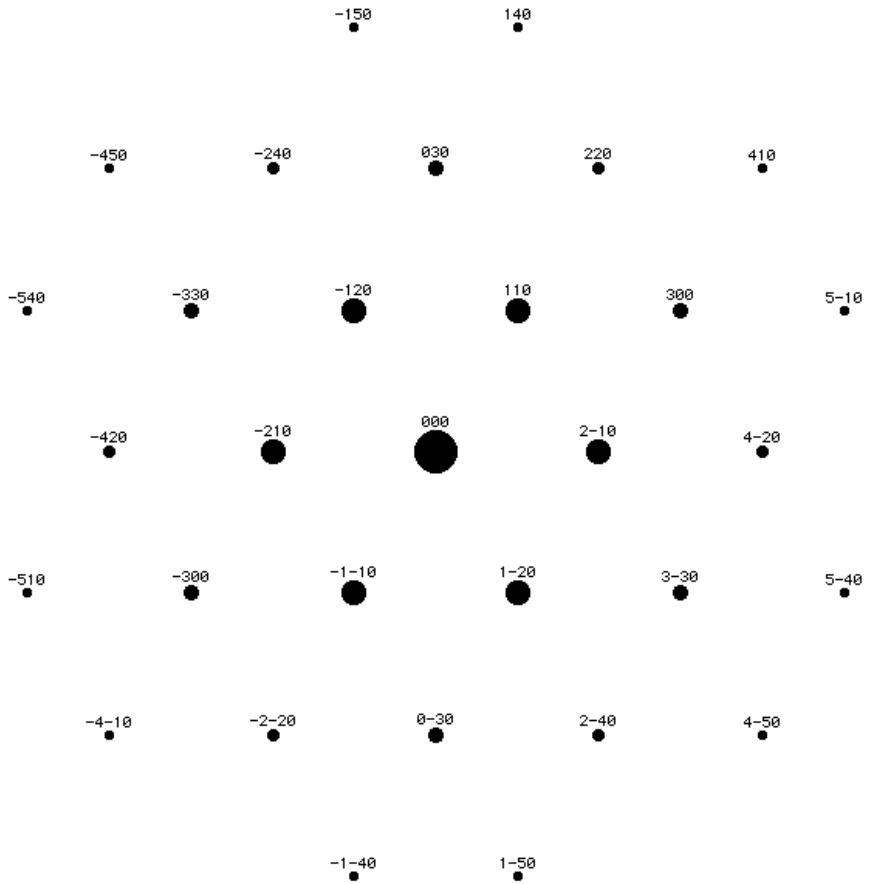
- Strong superlattice reflections suggest the presence of superstructures with $\sqrt{3}a_{hex.} \times \sqrt{3}a_{hex}$ unit cell.
- Diffraction patterns match the patterns simulated from $P3_112$ cell.

Electron Diffraction

"Li-stoichiometric" NMC333 Crystals



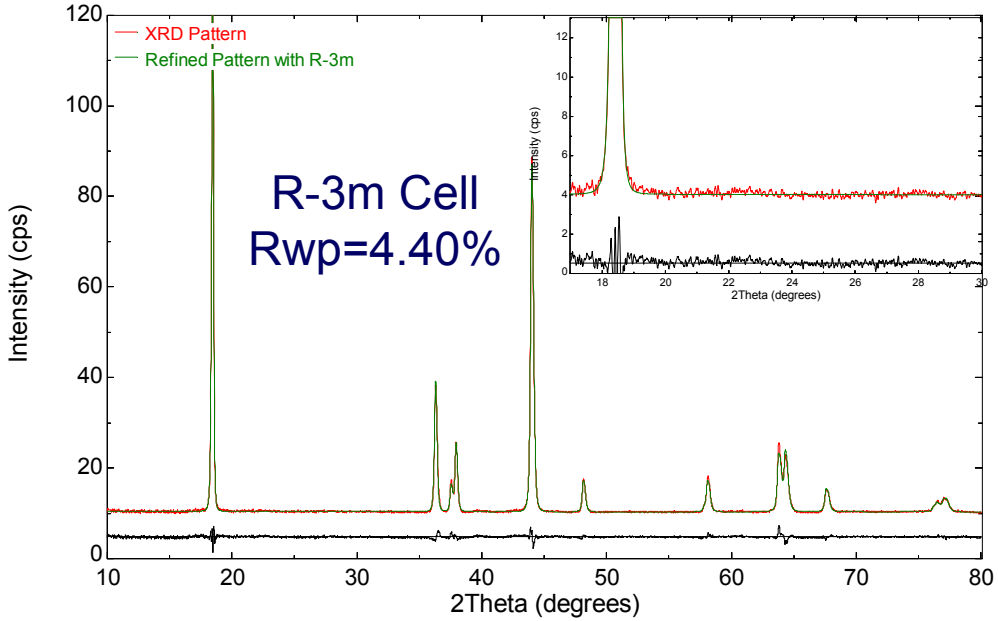
Simulated pattern from R-3m



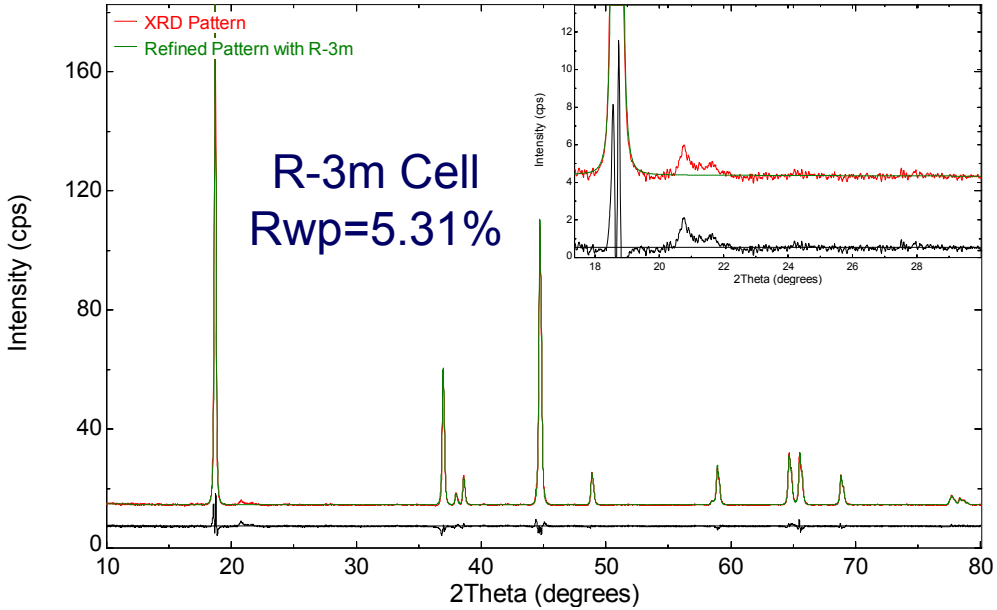
- Lack of superlattice reflections suggests weak or no superstructure.
- Diffraction patterns match the patterns simulated from R-3m cell.

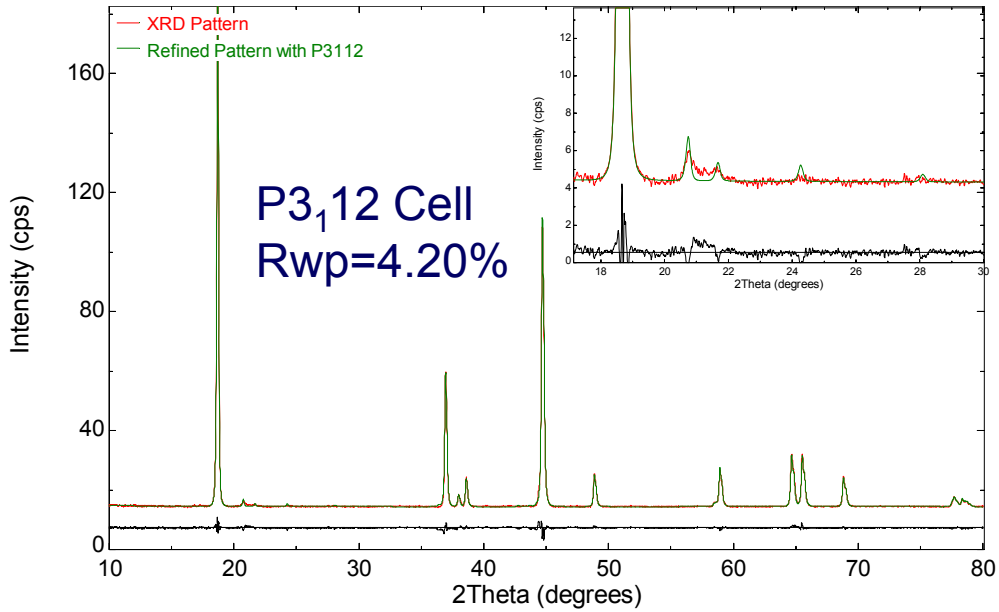
Rietveld Refinements

***x*=0**



***x*=0.14**



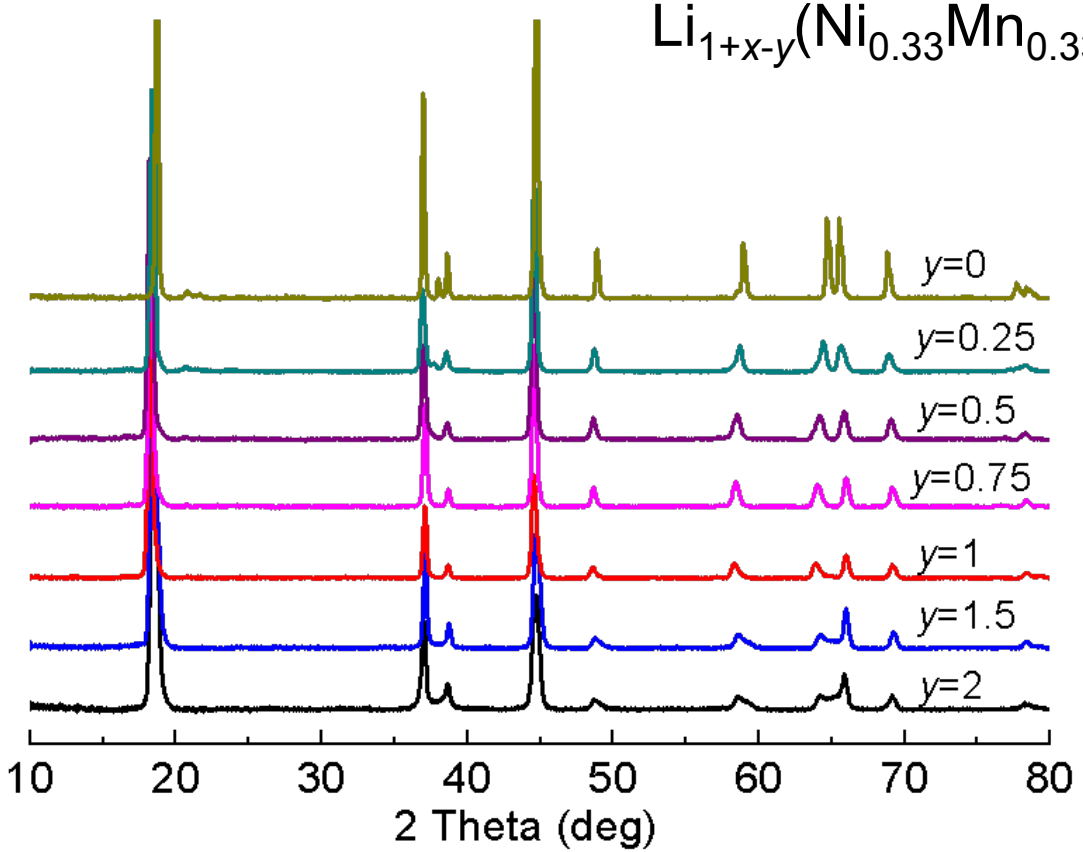


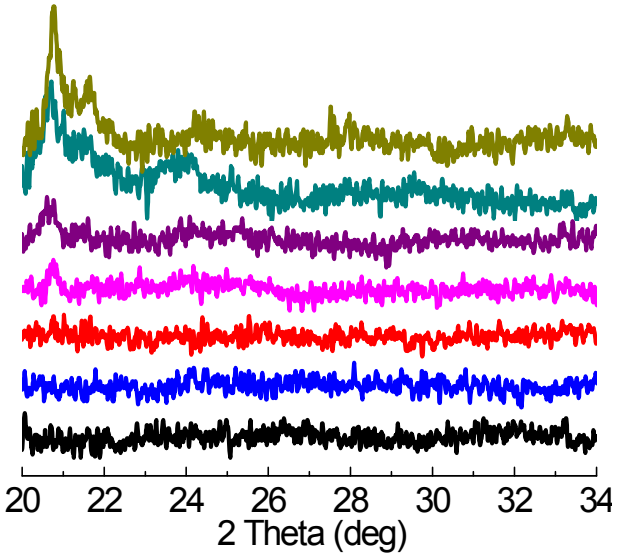
- For *x*=0, no additional peaks in the range $20 \leq 2\theta \leq 28$. The pattern is indexed with R-3m structure.
- For *x*=0.14, the pattern is indexed with $P3_112$ structure to fit the superstructure peaks in the range $20 \leq 2\theta \leq 28$.

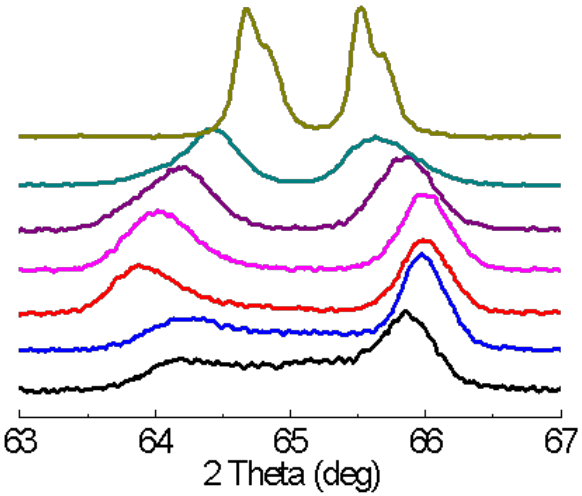
Chemical Delithiation

"Li-excess" NMC333

$Li_{1+x}(Ni_{0.33}Mn_{0.33}Co_{0.33})_{1-x}O_2 + yNO_2BF_4 \rightarrow$
$Li_{1+x-y}(Ni_{0.33}Mn_{0.33}Co_{0.33})_{1-x}O_2 + yNO_2 + yLiBF_4$



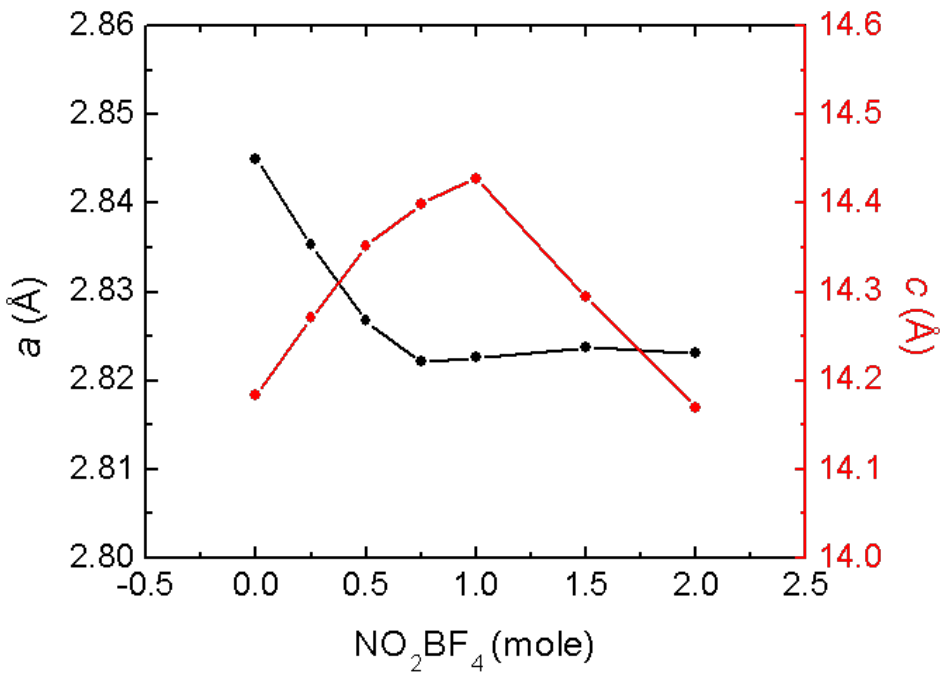


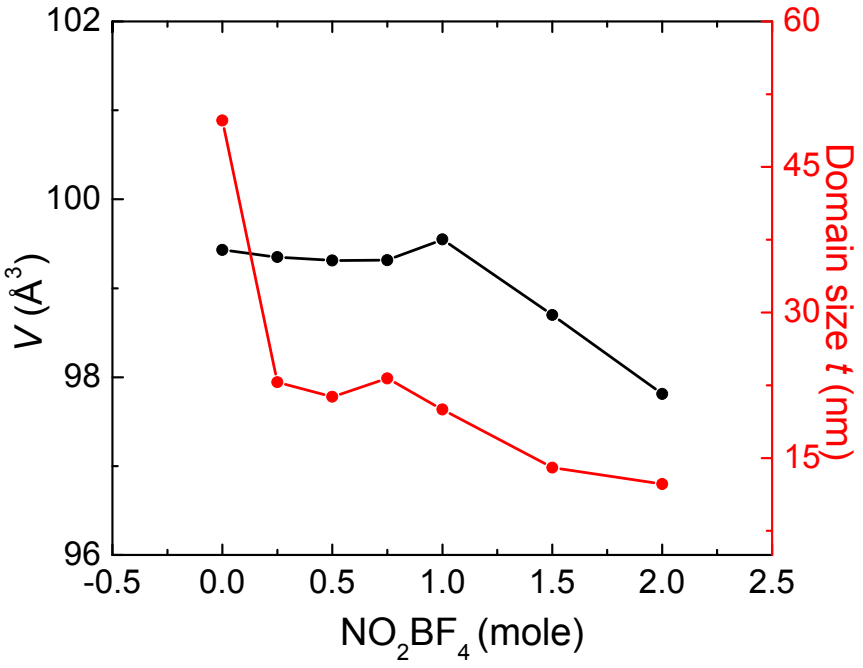


- Intensity of the superlattice peaks gradually decreased upon delithiation. The peaks completely disappeared at *y*=1.
- Phase transition from O3 (R-3m) to P3 (R3m) occurred when y>1.

Chemical Delithiation

"Li-excess" NMC333

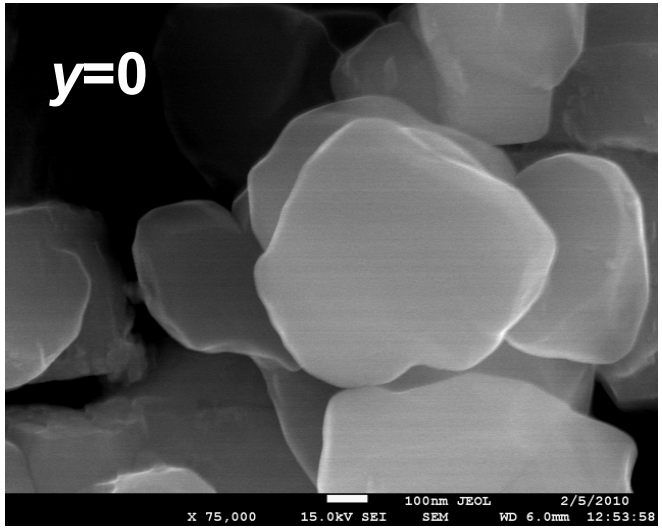


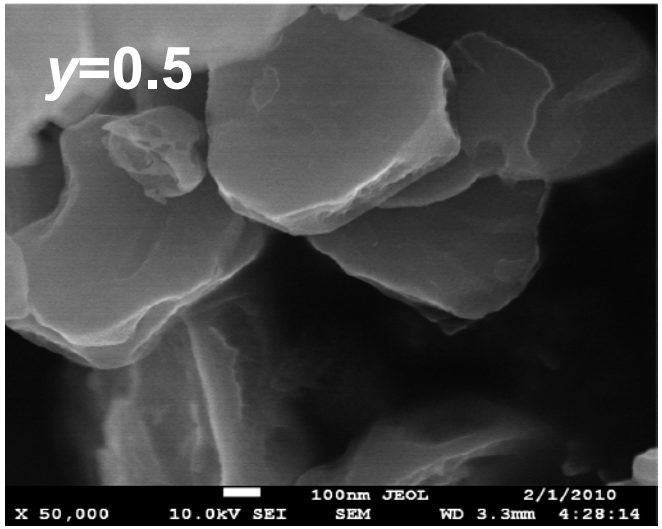


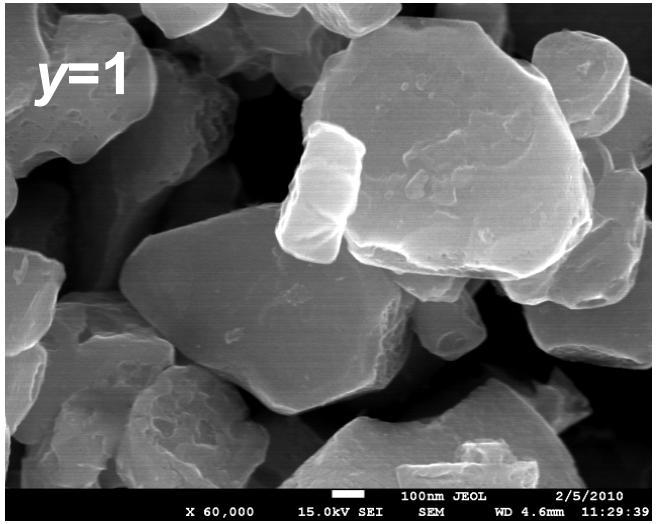
- Upon delithiation, the unit cell shrinks and then stabilizes in the *a* direction. It expands and then shrinks in the *c* direction.
- The overall cell volume remains nearly constant up to y=1.
- Phase crystallinity decreases with chemical delithiation.

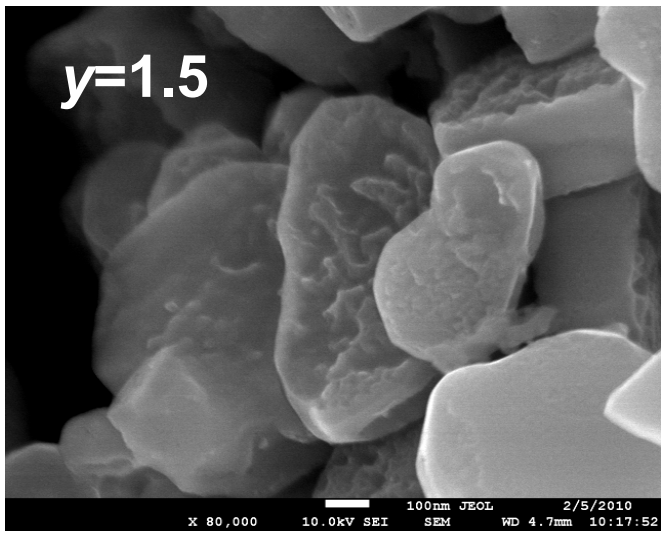
Chemical Delithiation

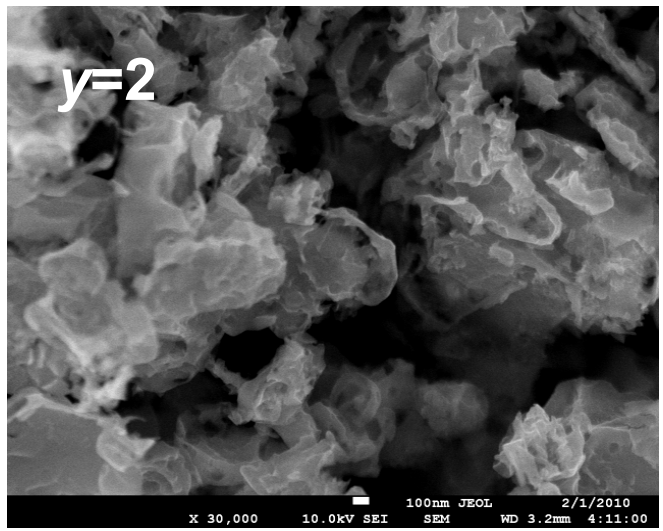
"Li-excess" NMC333









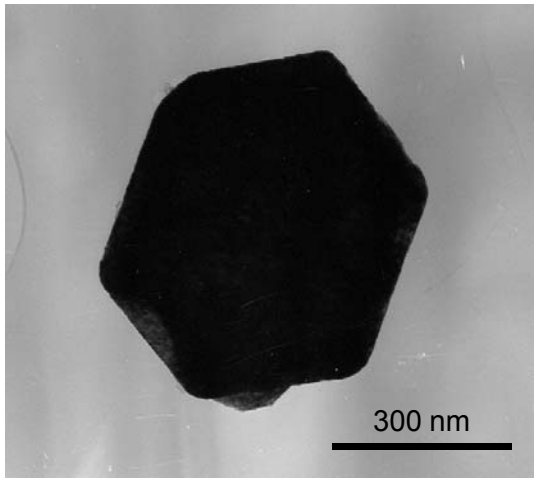


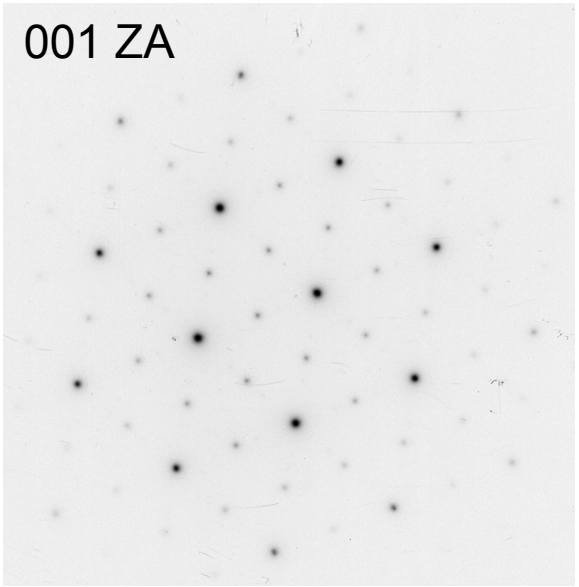
- Upon delithiation, crystals lose physical integrity even when the volume change is negligible.
- Morphological evolution indicates the loss of mass upon delithiation, possibly as Li_2O.

Chemical Delithiation

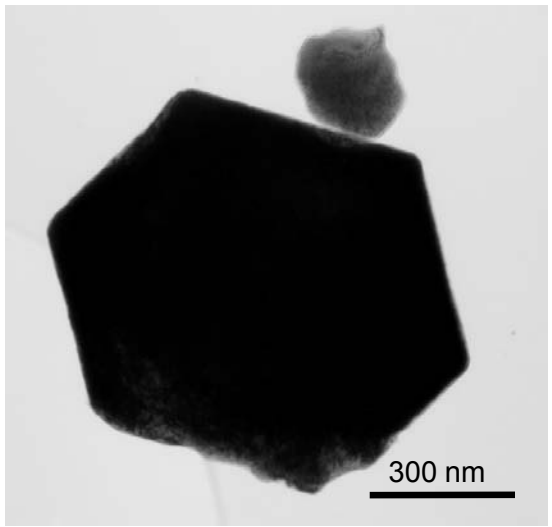
"Li-excess" NMC333

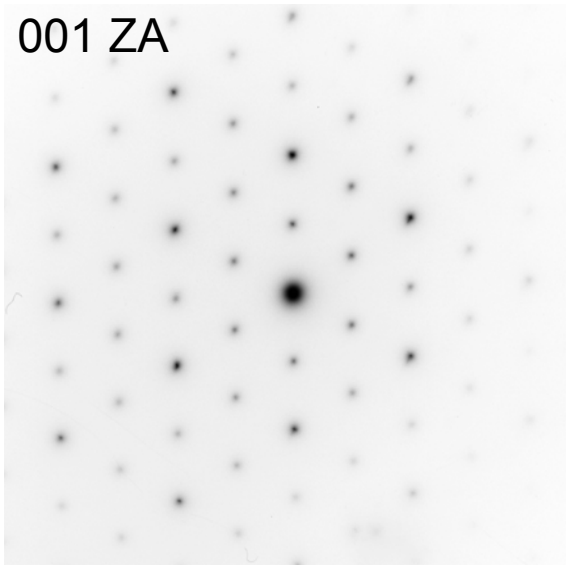
***y*=0.5**





***y*=1**



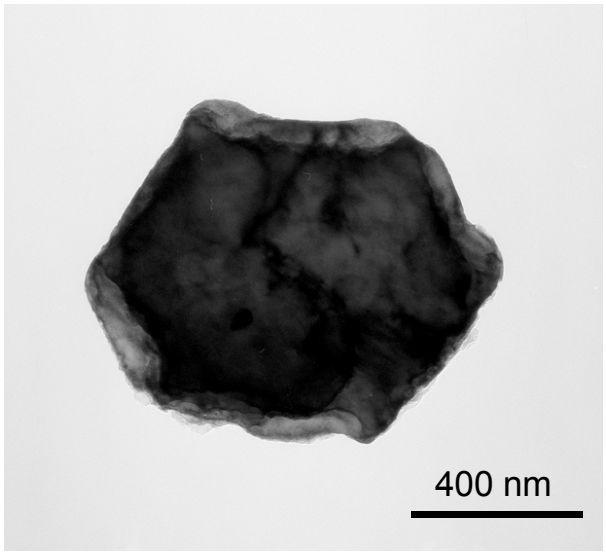


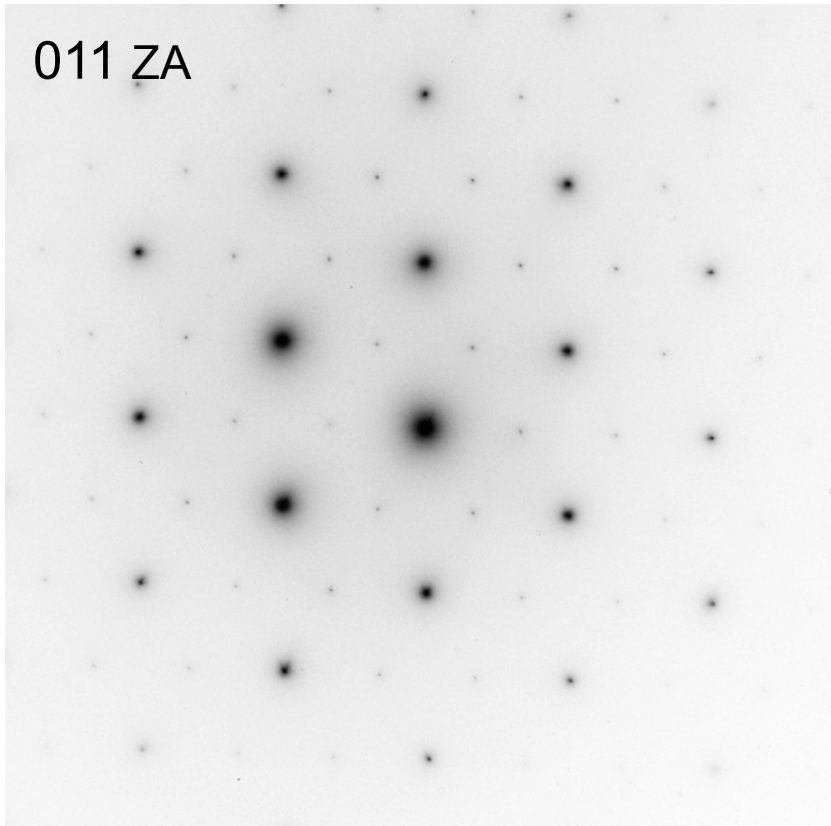
- $\sqrt{3}a_{hex.} \times \sqrt{3}a_{hex}$ super cell reflections disappear when Li is removed from the structure.

- The appearance of new superlattice reflections indicate the change of in-plane ordering in the delithiated crystals.

Chemical Relithiation

"Li-excess" NMC333

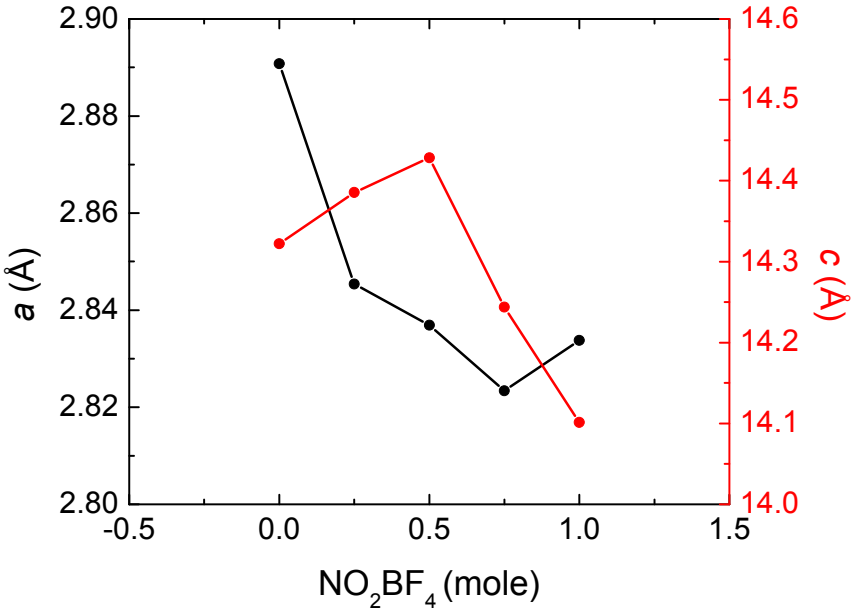


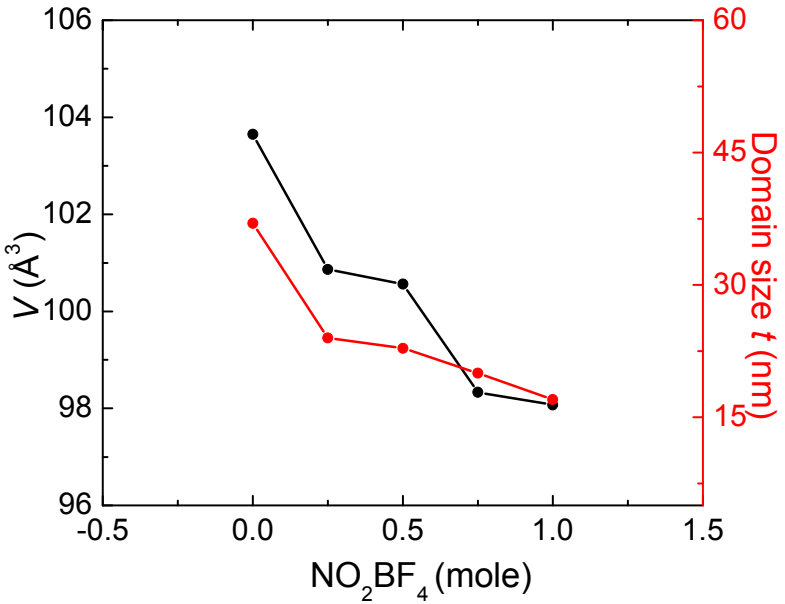


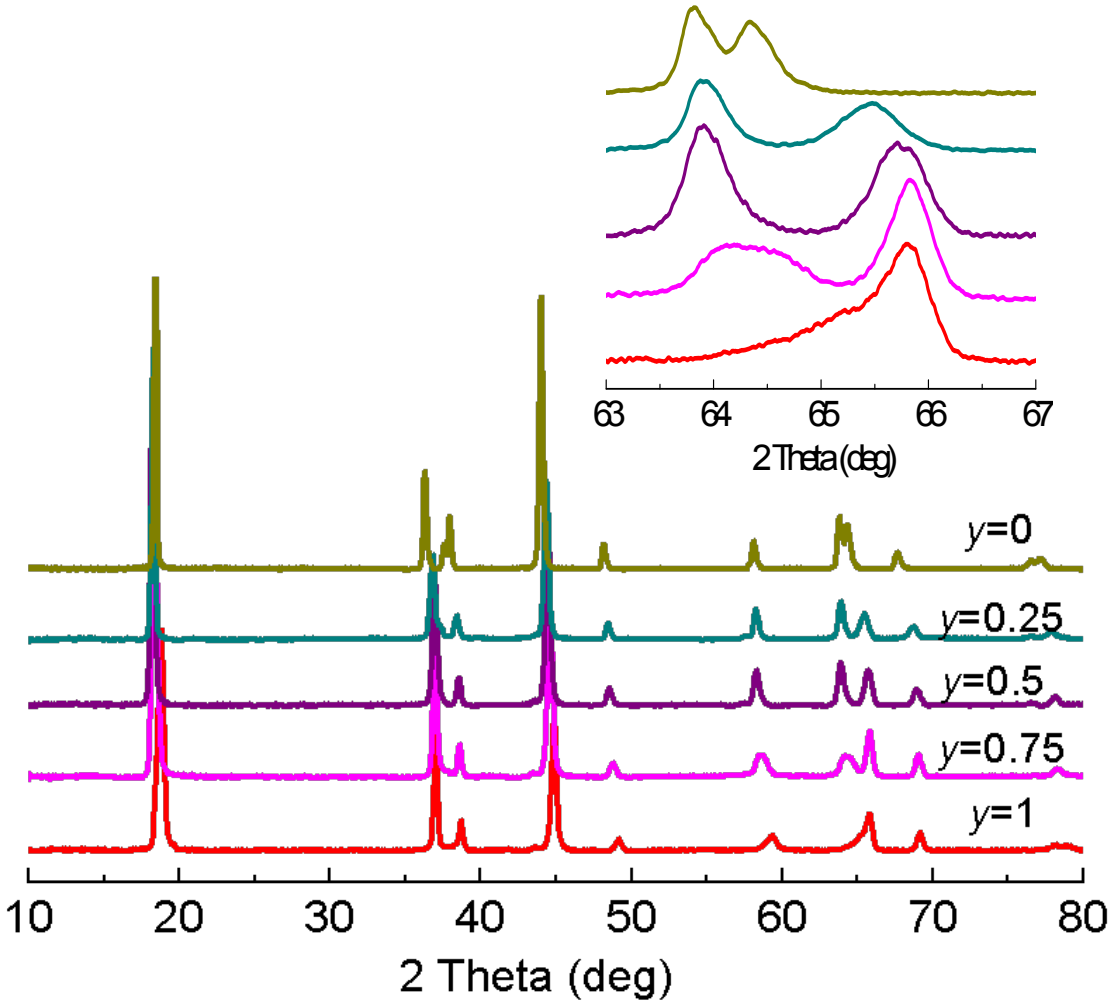
- Crystals were delithiated with 0.5 mole of NO_2BF_4 and then relithiated with 2 mole of LiI.
- Original superlattice reflections reappeared on relithiation, indicating the restore of $\sqrt{3}a_{hex.} \times \sqrt{3}a_{hex}$ super cell structure.

Chemical Delithiation

"Li-stoichiometric" NMC333



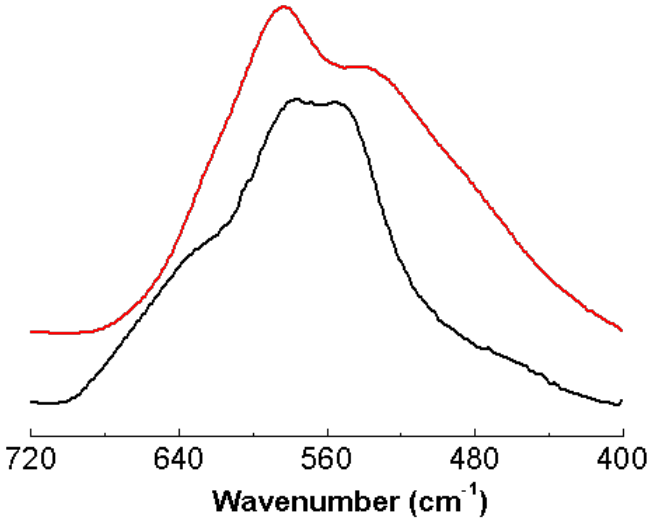


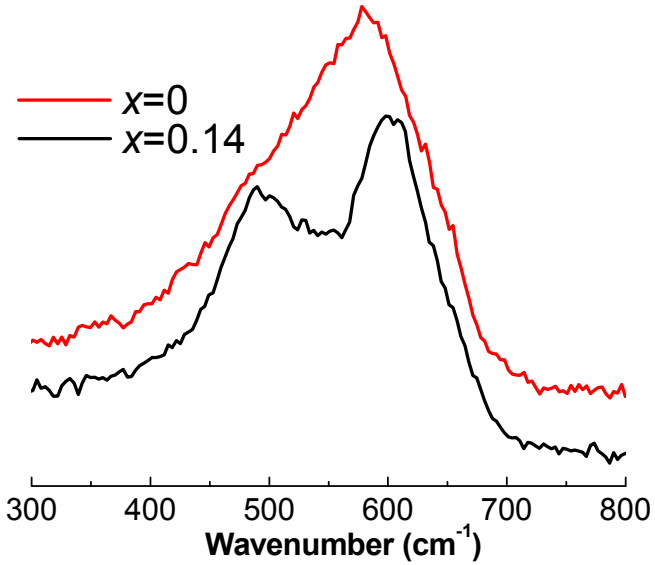


- Phase transition from O3 to P3 occurred at oxidation level of y=0.75 instead of 1.
- Cell volume decreased 5.4% at y=1.

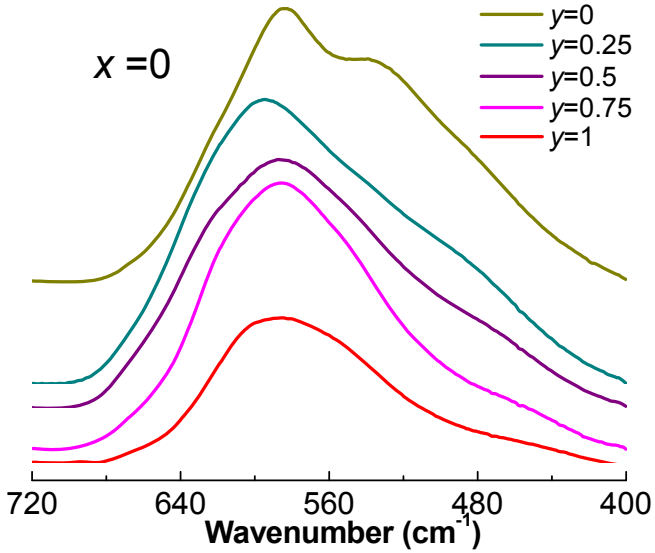
Chemical Delithiation

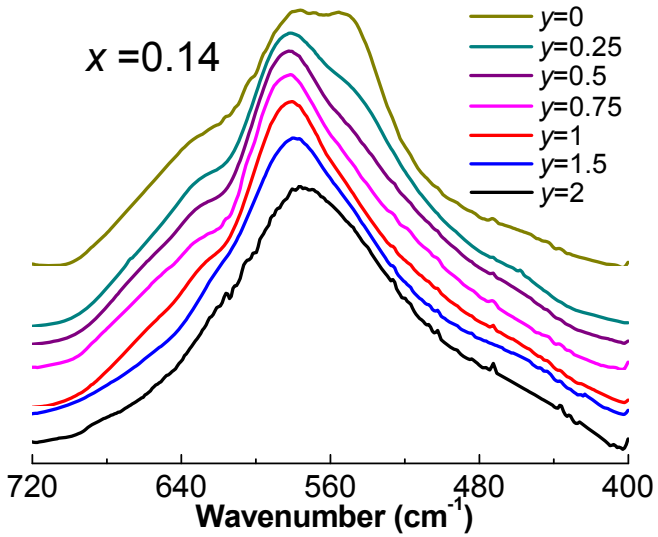
Vibrational Spectroscopies





- FTIR and Raman of fresh crystals: significant difference in local structure due to excess Li.





- FTIR of delithiated crystals: larger shift toward higher frequency in x=0 series. Consistent with the larger decrease in unit cell dimension.

Collaborations

- Tom Richardson (LBNL) – Material Synthesis and Characterization
- Clare Grey, Jordi Cabana (Stony Brook) – NMR Spectroscopy
- Heike Gabrisch (U. New Orleans) – TEM study of iron phosphates
- Gerbrand Ceder (MIT) – Theory on hydrothermal synthesized crystals
- Martin Kunz, Nobumichi Tamura (ALS), Sumohan Misra (SSRL) – *in situ* X-ray diffraction and absorption
- Robert Kostechi (LBNL) – Raman and FTIR Spectroscopy
- John Kerr (LBNL) – TGA and DSC
- Vince Battaglia (LBNL) – ICP
- Marca Doeff (LBNL) – Electrode Fabrication

Future Work

- **Olivines:**
  - Investigate the effect of size, morphology, surface modifications, other cation and anion substituents on rate capability and stability of $LiMnPO_4$.
  - Investigate phase transformation mechanism and phase stability of mixed transition metal olivine crystals ($LiMPO_4$, M=Fe, Mn, Co and Ni).
- **$Li_{1+x}M_{1-x}O_2$:**
  - Further analyze the chemical delithiated series – Li and O contents, metal ratio distribution on the crystals, the change of ordering, and the possibility of proton insertion in the structure.
  - Compare the structural change during electrochemical charge and discharge. Investigate O_2 evolution mechanism.
  - Prepare well-formed oxide crystals with other Li content and metal ratios. Investigate the structure and evaluate the performance.
  - Investigate the effect of size and morphology on performance.

Summary

- Delithiated $LiMnPO_4$ has low thermal stability comparable to the charged $LiCoO_2$.
- Mg substitution in $LiMnPO_4$ improves kinetics, physical and thermal stabilities of the phosphate.
- The effect of excess Li on structure and performance of $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC333) crystals has been investigated.
- Structure of "Li-excess" NMC333 is well ordered with $\sqrt{3}a_{hex.} \times \sqrt{3}a_{hex}$ super cells. In-plane ordering scheme changes upon chemical delithiation and restores upon relithiation. Delithiation causes the crystals to disintegrate even with negligible volume change.
- "Li-stoichiometric" NMC333 lacks the same $\sqrt{3}a_{hex.} \times \sqrt{3}a_{hex}$ ordering in the structure. There is a larger decrease in unit cell volume upon delithiation.
- O3 structure transforms to P3 in both samples, but occurs at a much higher oxidation state in the "Li-excess" sample.