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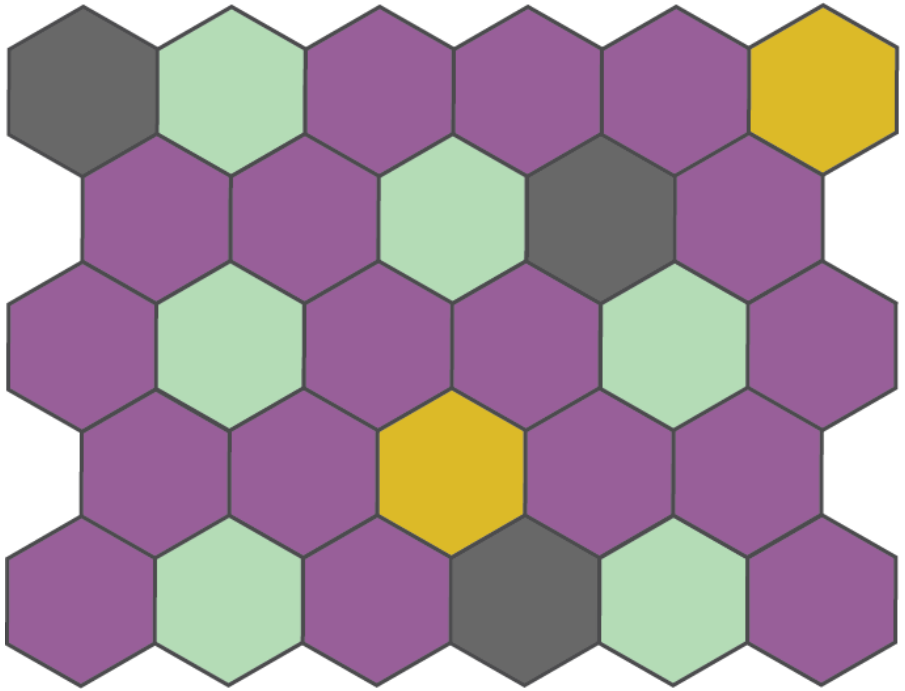
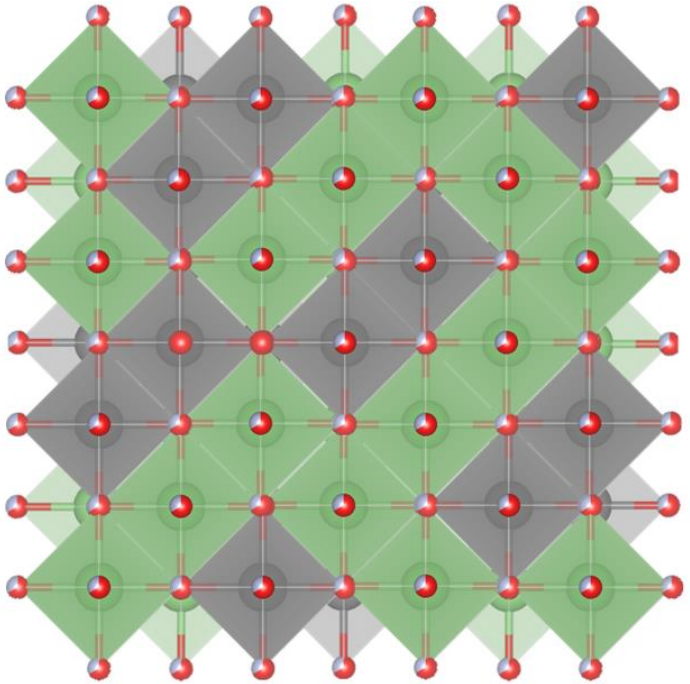
Non-equilibrium phases and cation mixing in Li-rich rock salt derived positive electrode materials





William Brant

11/05/2021

@willrbrant1

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Who Am I

Undergrad University of Sydney: 2006-2009

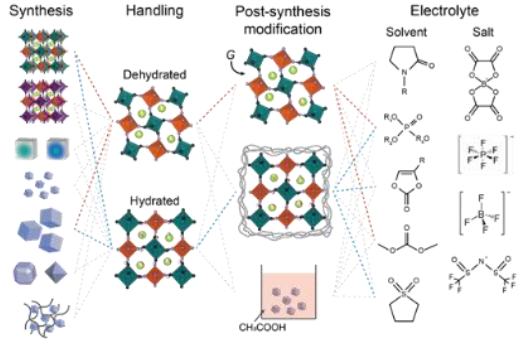
PhD USyd: 2010-2014

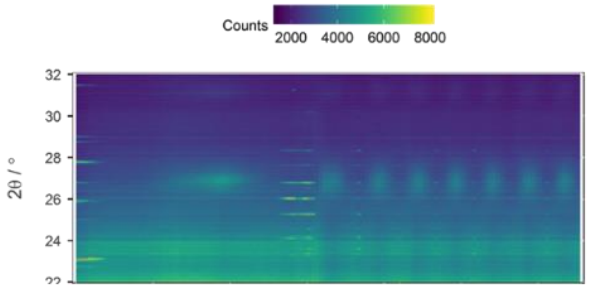
Postdoc UU: 2015-2017

Research leader UU: 2017-now

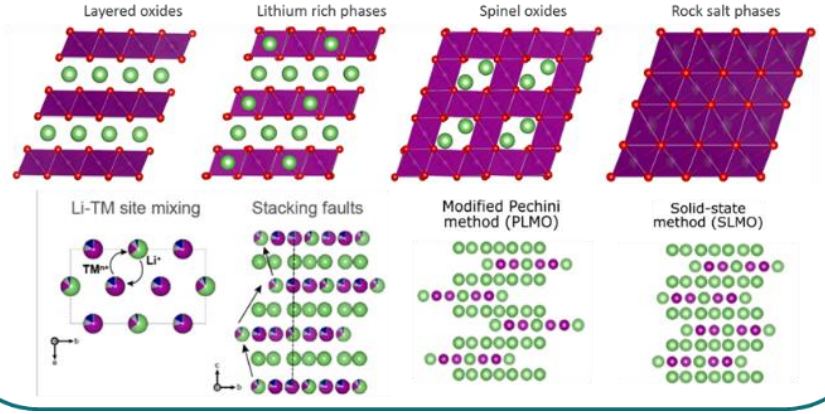
Electroactive materials under change

Advanced Synthesis and Characterisation

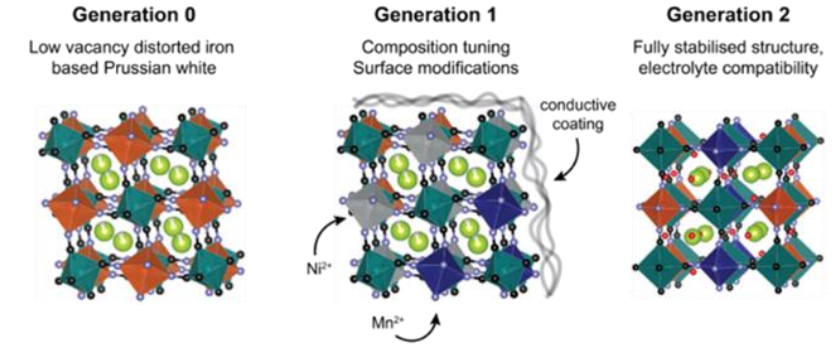




Rock Salt Oxides



Prussian Blue Analogues



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Who Does the Work

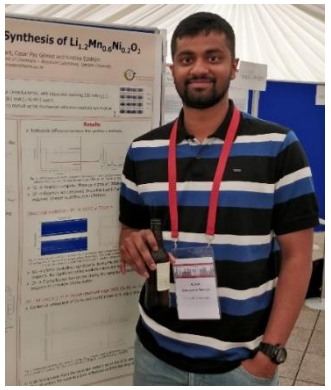
Undergrad University of Sydney: 2006-2009

PhD USyd: 2010-2014

Postdoc UU: 2015-2017

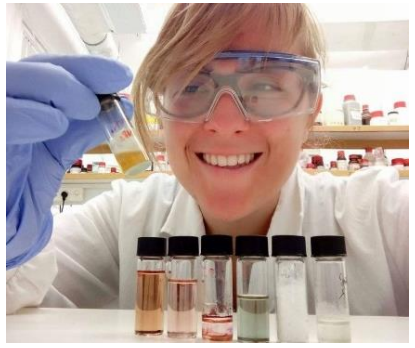
Research leader UU: 2017-now

PhDs

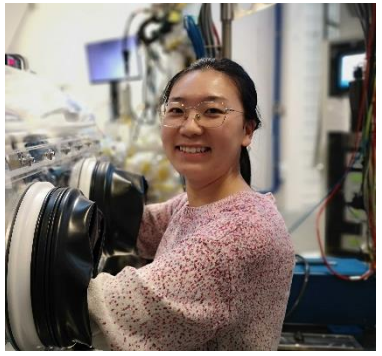


Ashok Menon

Olle Gustafsson



Djurdjija Dzodan



Heyin Chen

Postdocs

Dickson Ojwang

Adriano Pavan

Masters Students

John Corley
Said Khalil

Materials chemistry and crystallography

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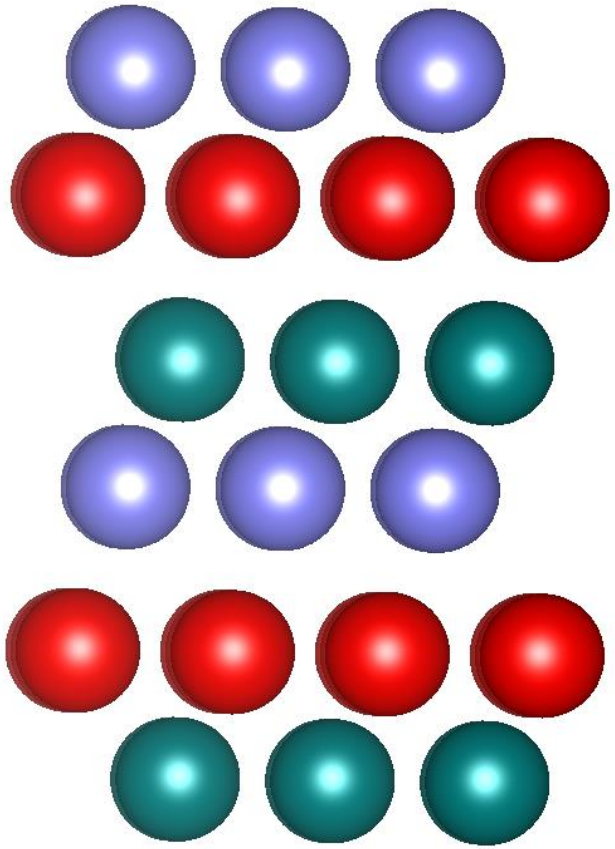
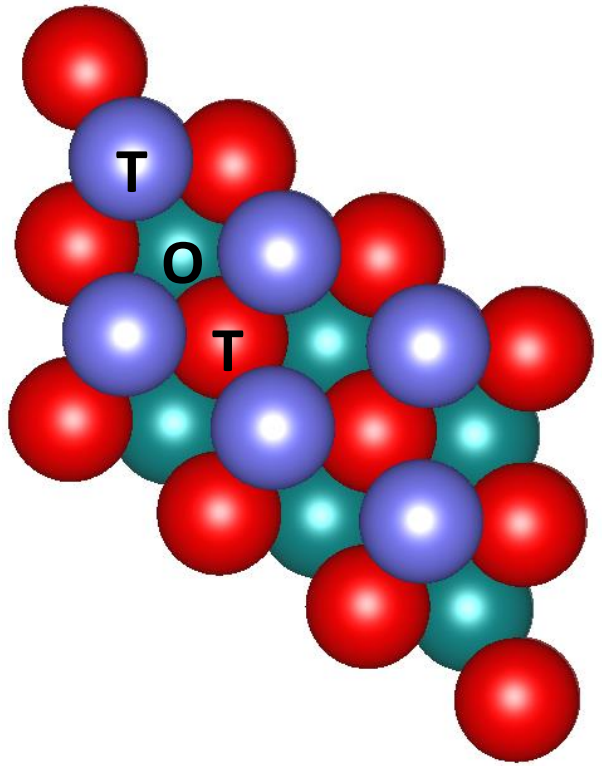
Cation order in rock salt phases

AX Cubic close packed array of anions





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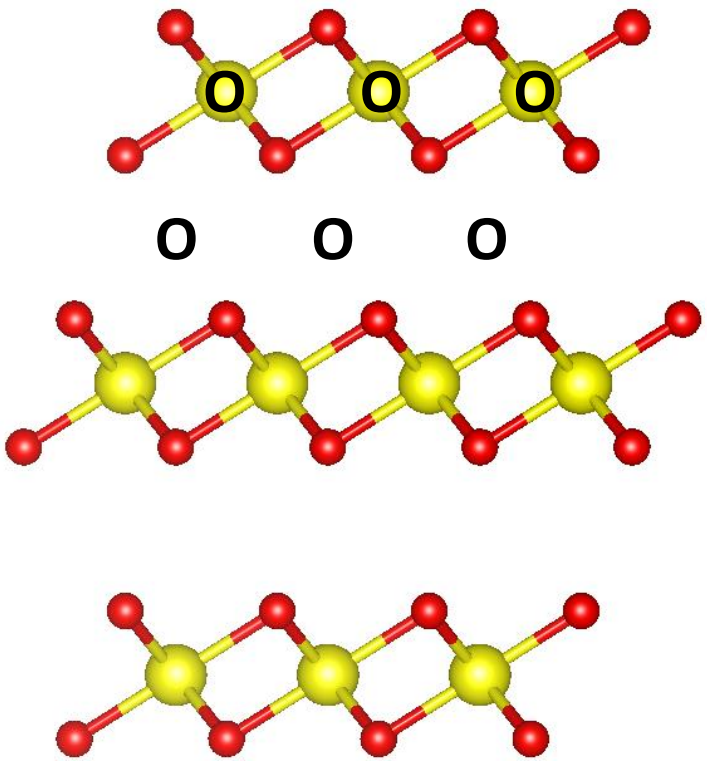
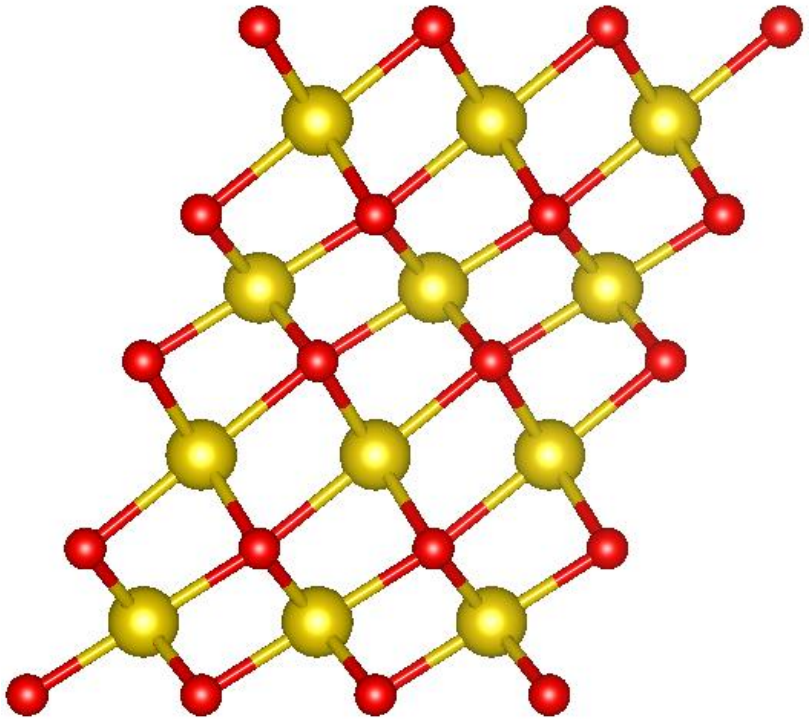
Cation order in rock salt phases

ABX_2 Cubic close packed array of anions





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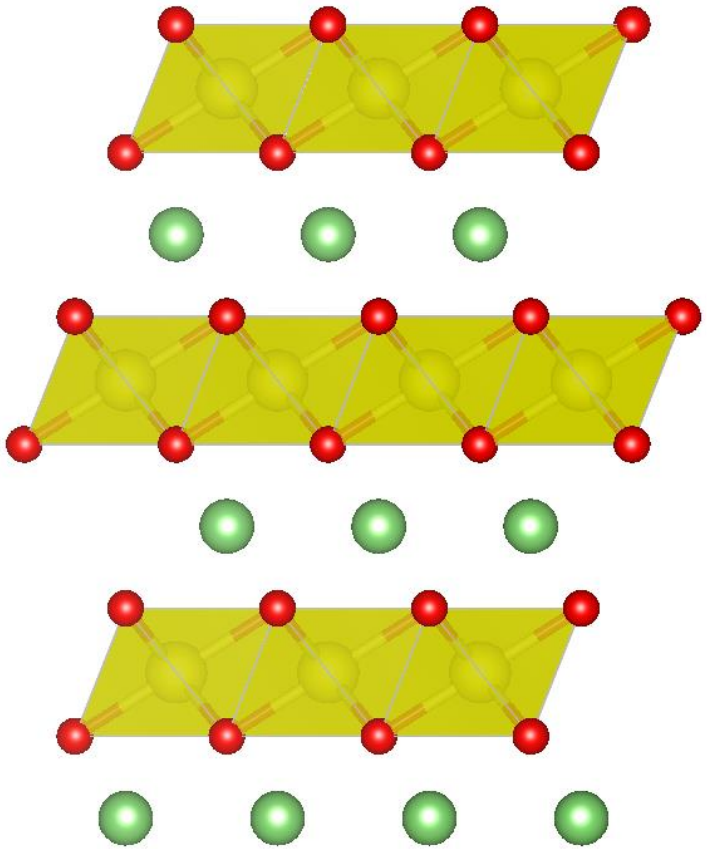
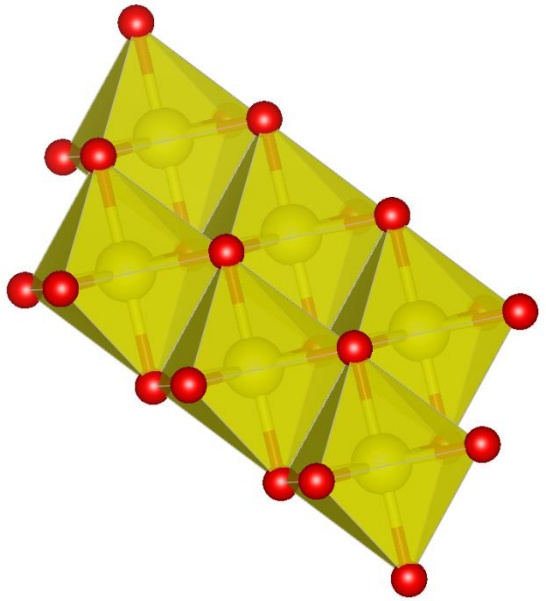
Layered rock salt phases

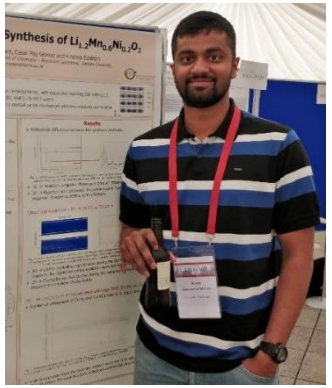
Li_xMO_2 Cubic close packed array of anions





Li Rich Layered Phases

Compositional complexity and structural analysis



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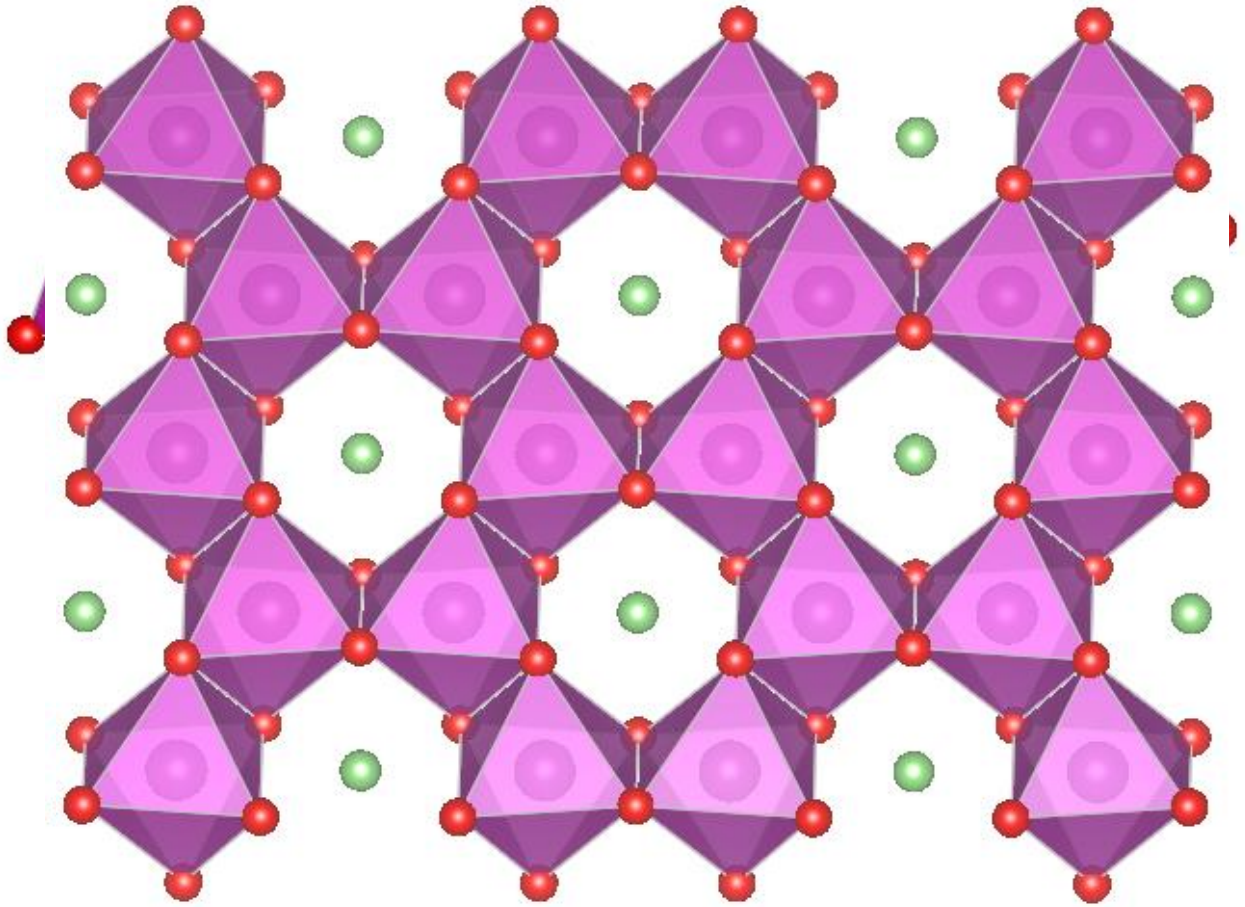
Li-rich layered rock salt phases

$Li_{1+y}M_{1-y}O_2$

Cubic close packed array of anions



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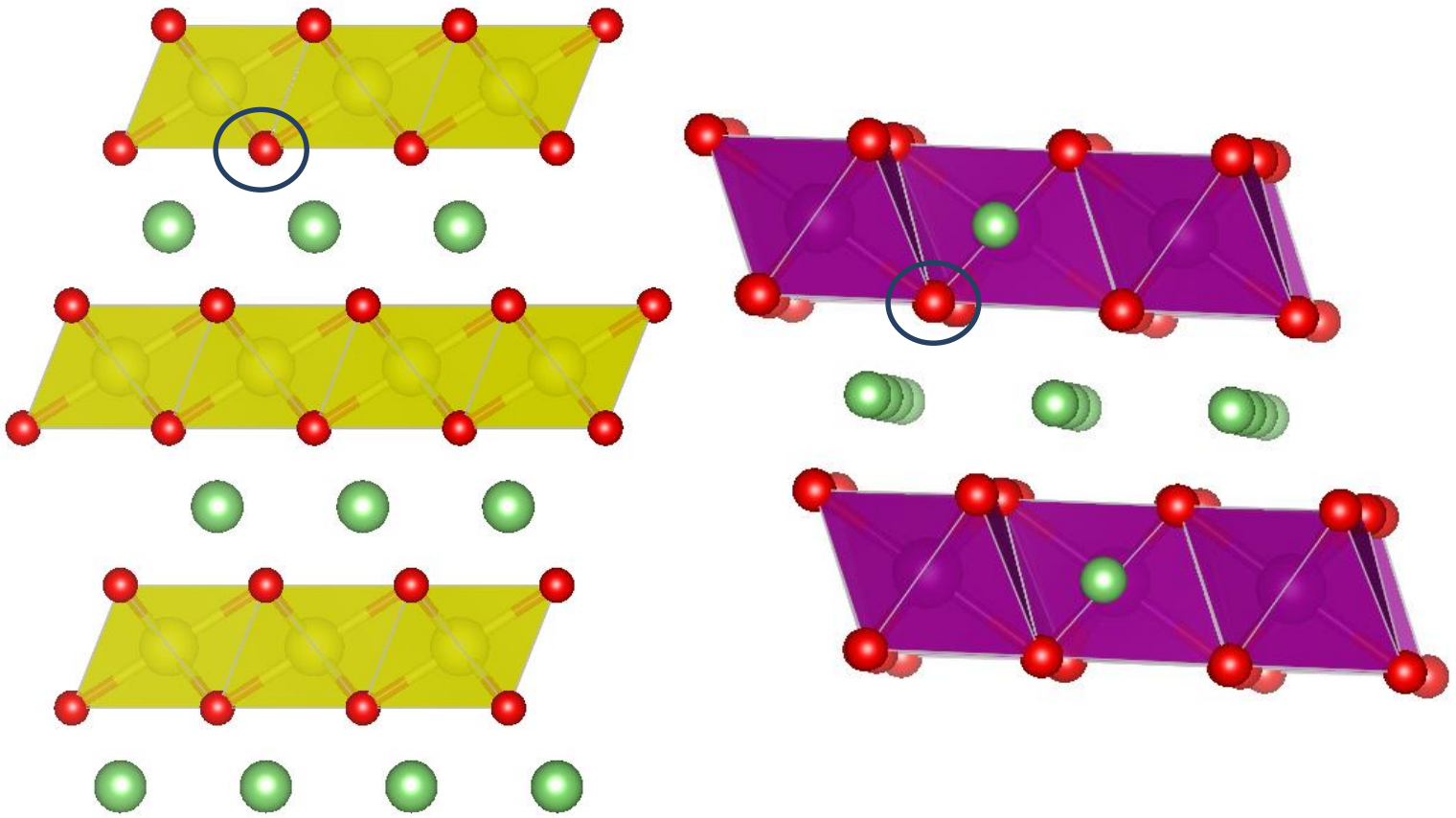
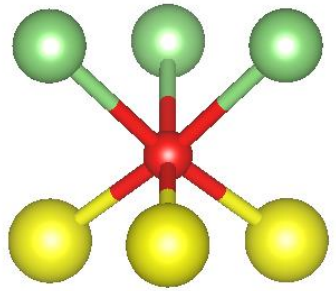
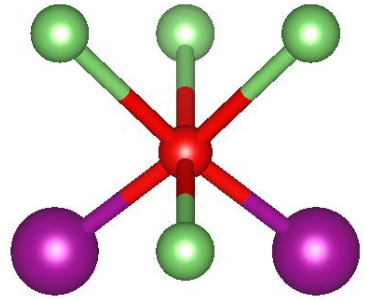
Li-rich layered rock salt phases

$Li_{1+y}M_{1-y}O_2$ Cubic close packed array of anions

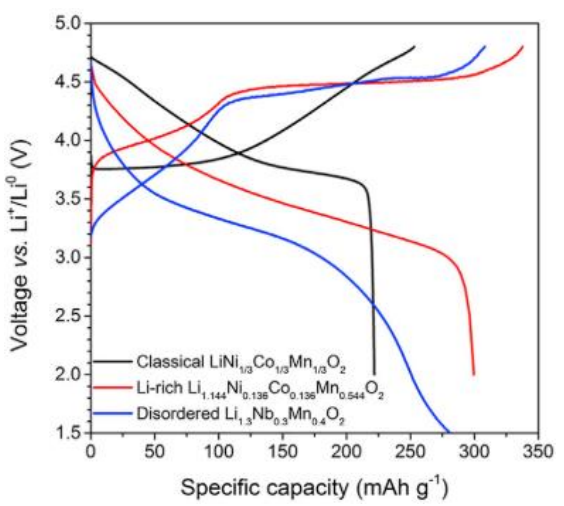


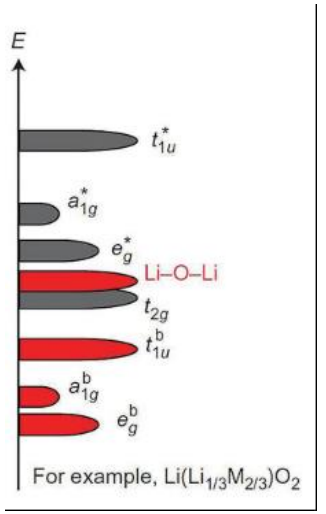


Only M-O-Li



M-O-Li *and* Li-O-Li





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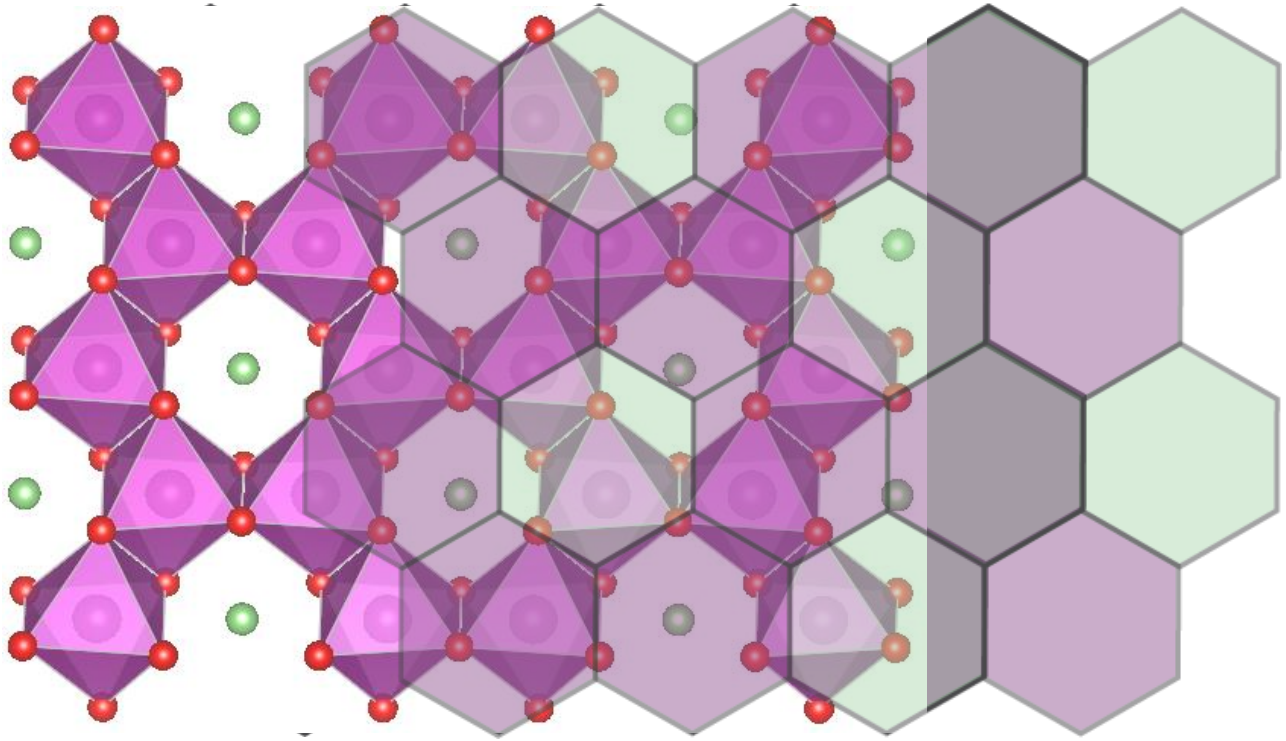
Structural Complexity in Li_2MnO_3

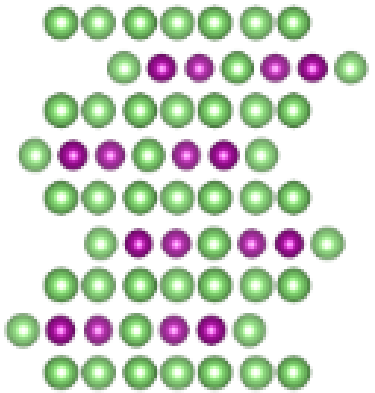
$Li_{1.33}Mn_{0.66}O_2$ – aka Li_2MnO_3

1/3 substitution → hexagonal ordering

Mn, Li



Note: Anion sublattice is unchanged



Stacking faults of the cations only

Menon, A. S.; Ojwang, D. O.; Willhammar, T.; Peterson, V. K.; Edström, K.; Gomez, C. P.; Brant, W. R., Influence of Synthesis Routes on the Crystallography, Morphology, and Electrochemistry of Li2MnO3. ACS Applied Materials & Interfaces 2020, 12 (5), 5939

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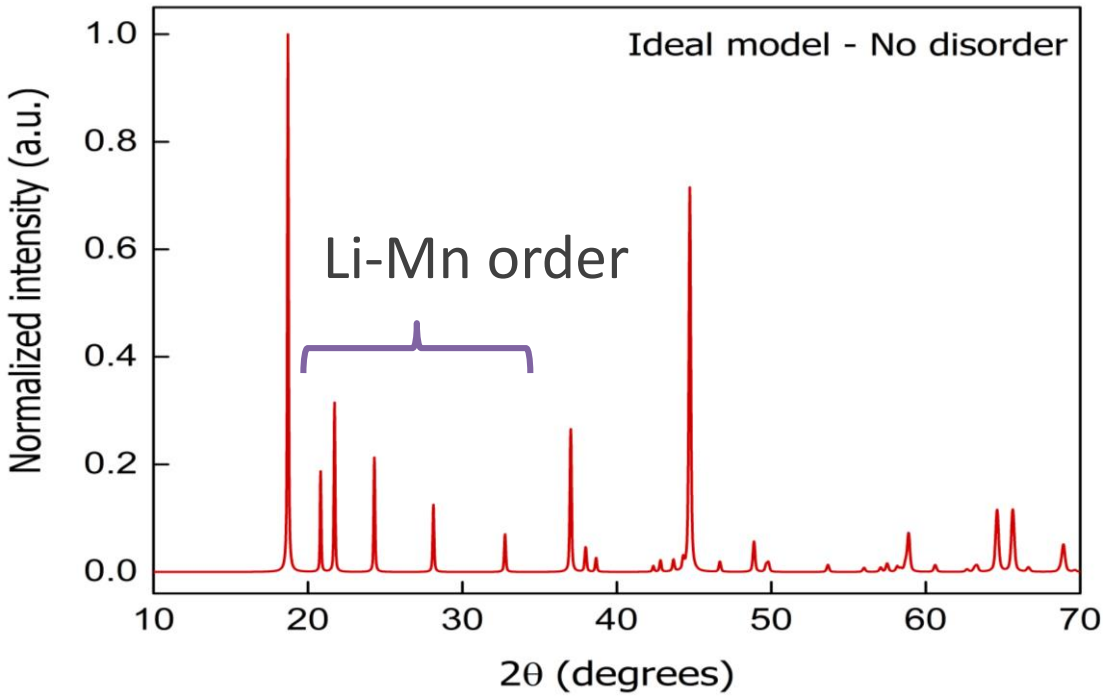
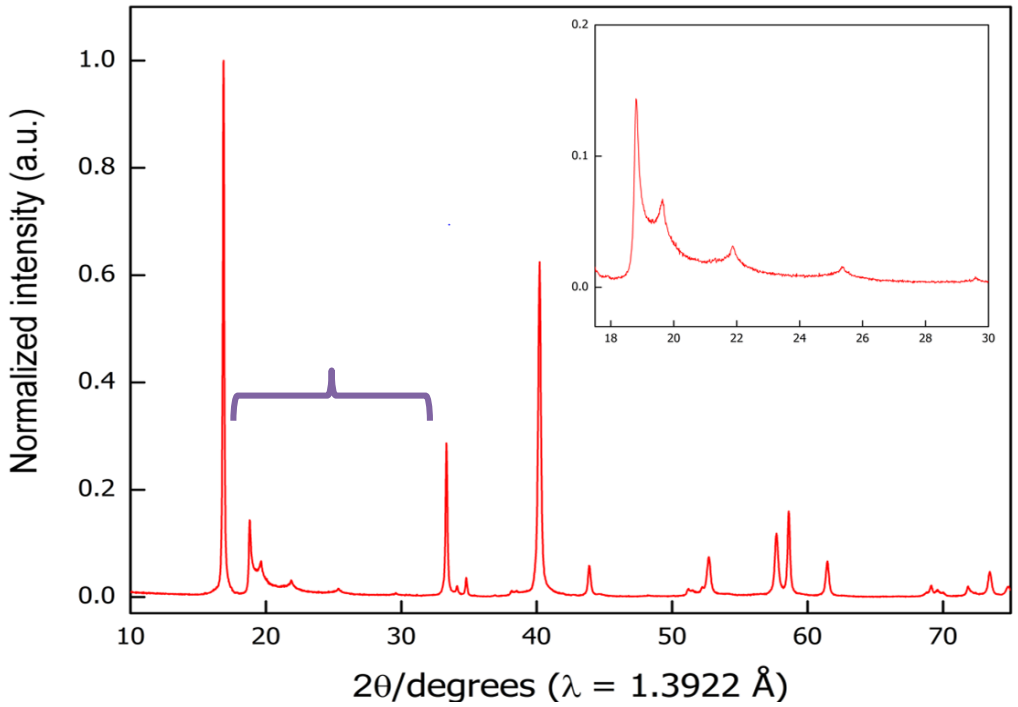
Structural Complexity in Li_2MnO_3

Can diffraction see this?





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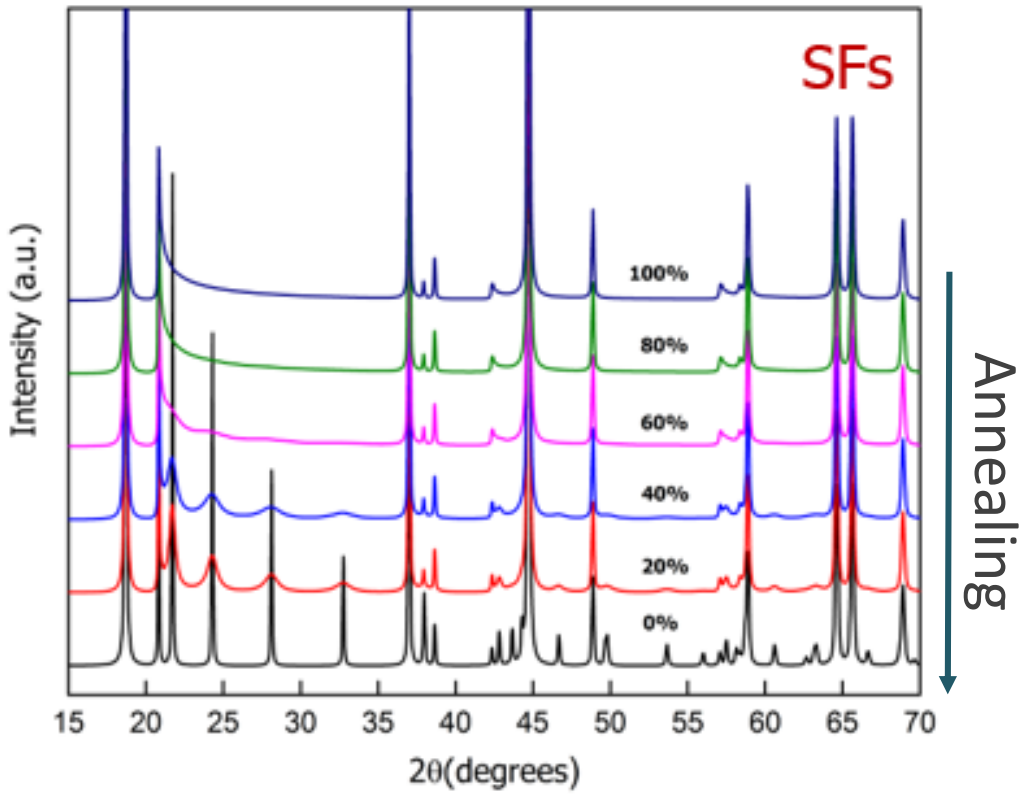
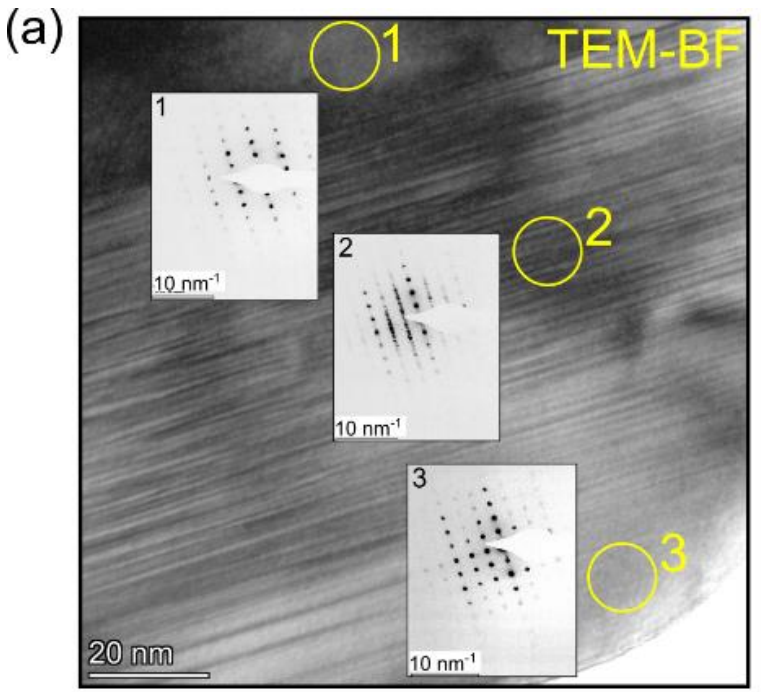
Structural Complexity in Li_2MnO_3

Remember: The anion sublattice is unchanged!



Consequence: Complete intergrowth of faulted and non-faulted domains



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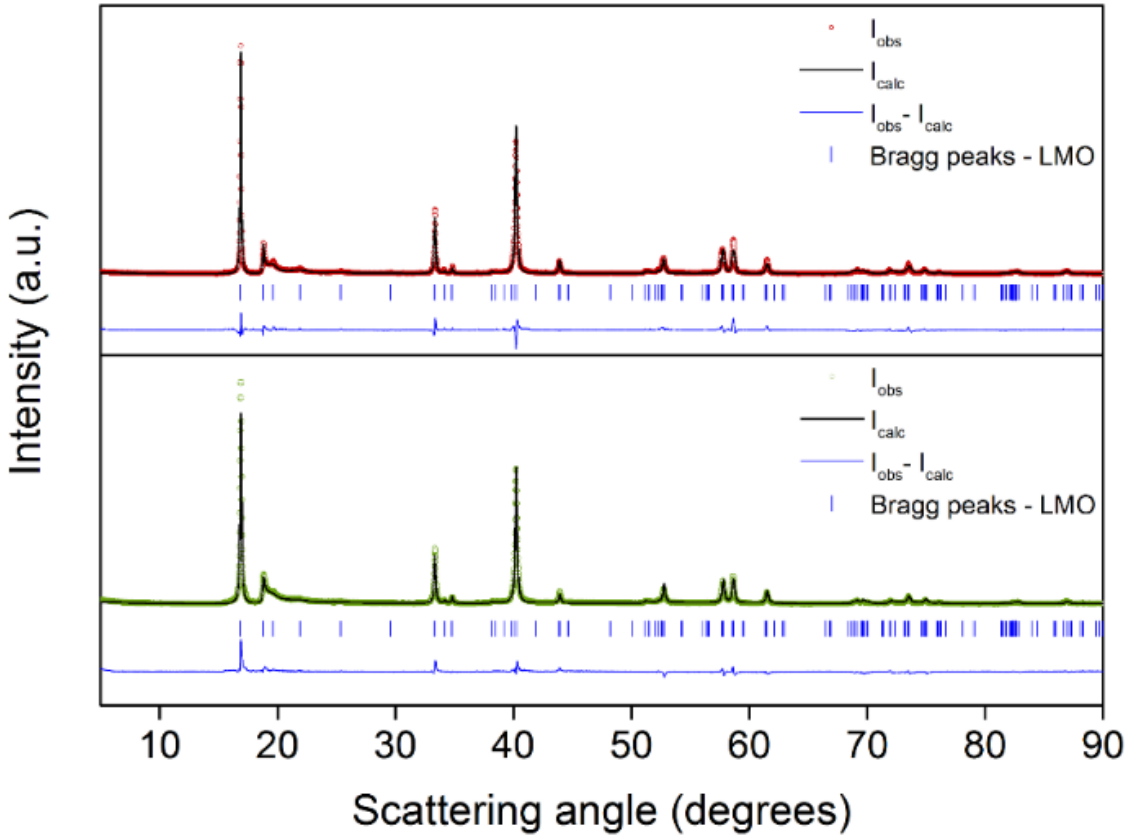
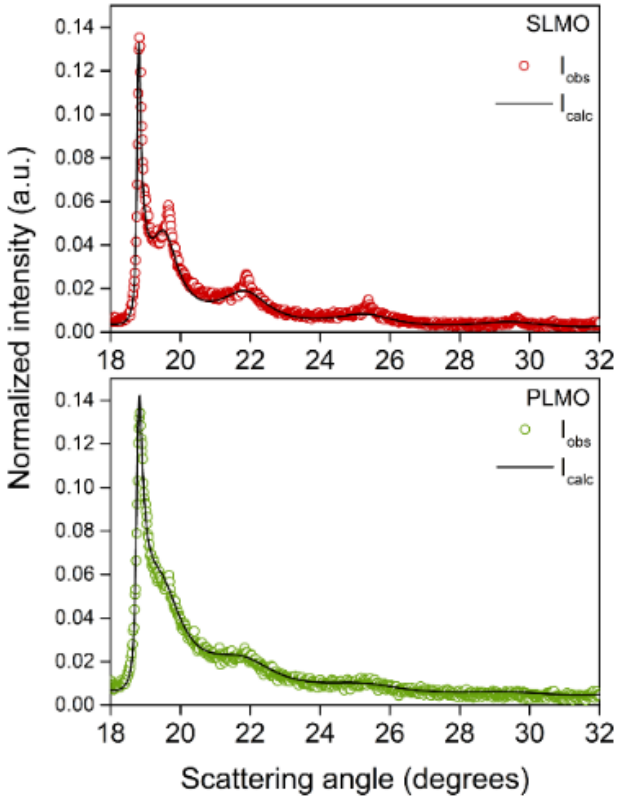
Structural Complexity in Li_2MnO_3

TEM is localised – is this a long range phenomenon? Can you tell?





Yes! If you actually model the stacking faults

Whether intergrowth occurs depends on synthesis…

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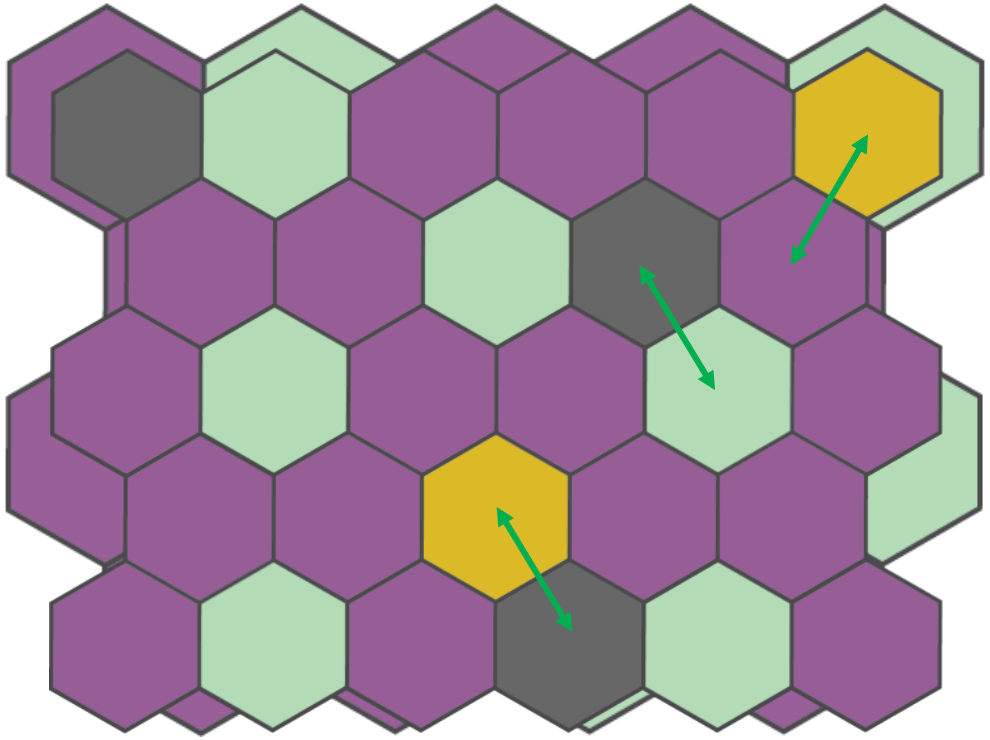
$Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$

Why does this matter? – Li_2MnO_3 ($Li_{1.33}Mn_{0.66}O_2$) is compositionally simple, LMNCO is not

→ Three length scales of disorder

Mn, Li, Ni, Co



Compositional frustration

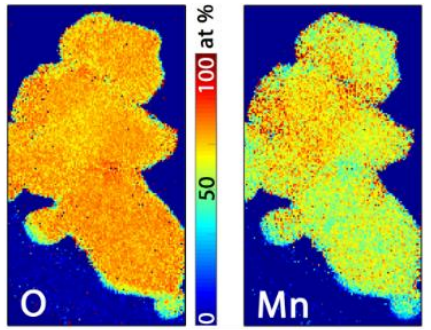
Å level – point defects

nm level – Stacking faults

µm level – Phase intergrowth

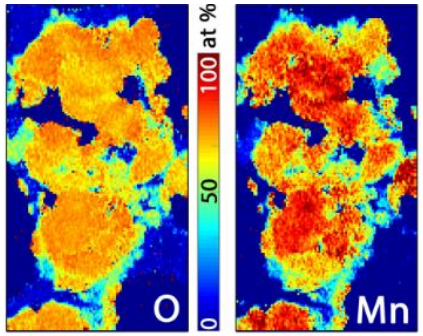
Sol gel

$Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$



Solid state

Li_2MnO_3+Li(NiMnCo)O_2



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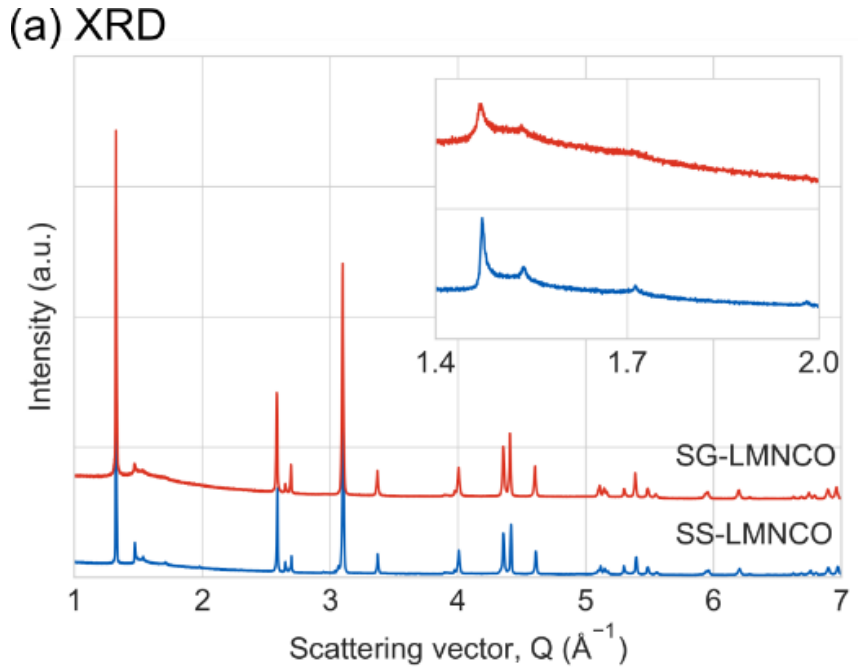
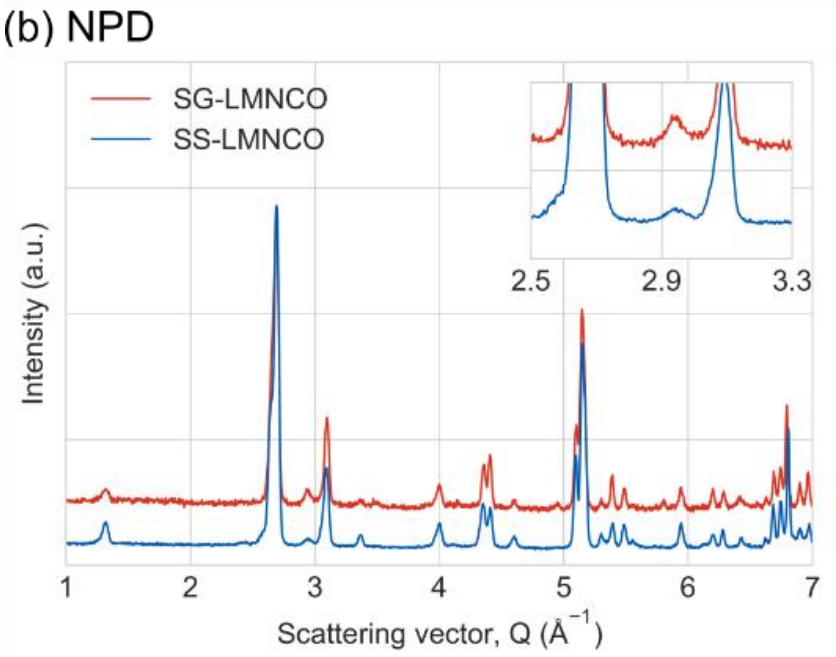
$Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$

How does the disorder manifest? When regular diffraction breaks down…





Menon, A. S.; Ulusoy, S.; Ojwang, D. O.; Riekehr, L.; Didier, C.; Peterson, V. K.; Salazar-Alvarez, G.; Svedlindh, P.; Edström, K.; Gomez, C. P.; Brant, W. R., Synthetic Pathway Determines the Nonequilibrium Crystallography of Li- and Mn-Rich Layered Oxide Cathode Materials. *ACS Applied Energy Materials* **2021,** *4* (2), 1924

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$Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$

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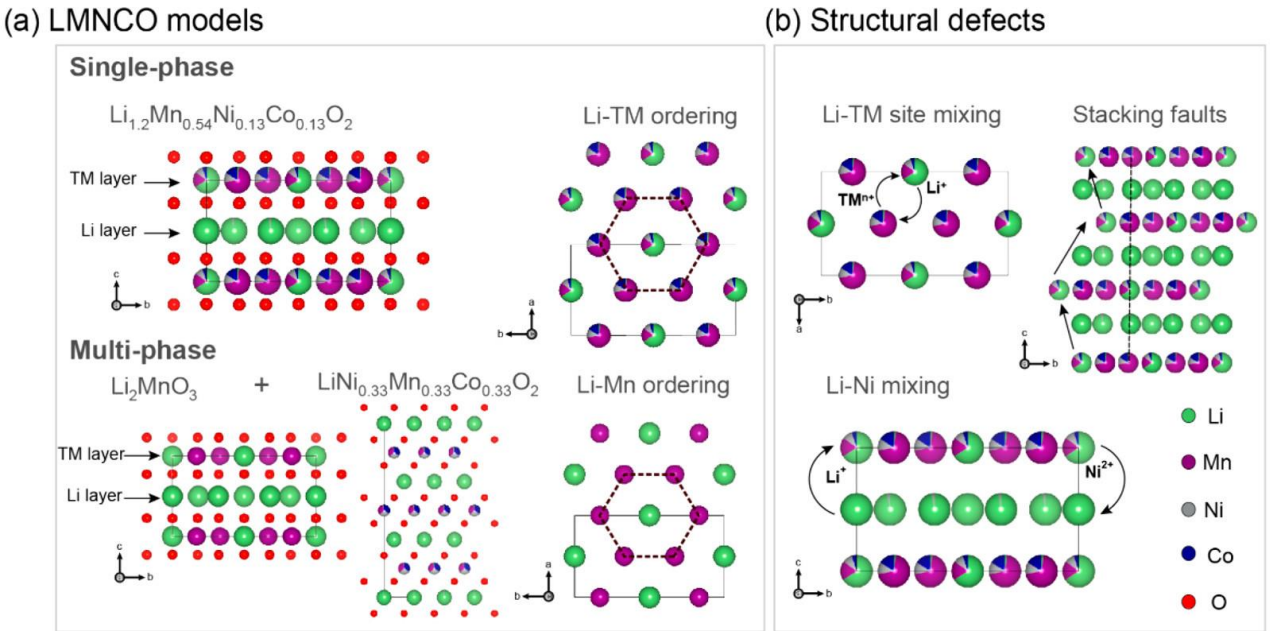

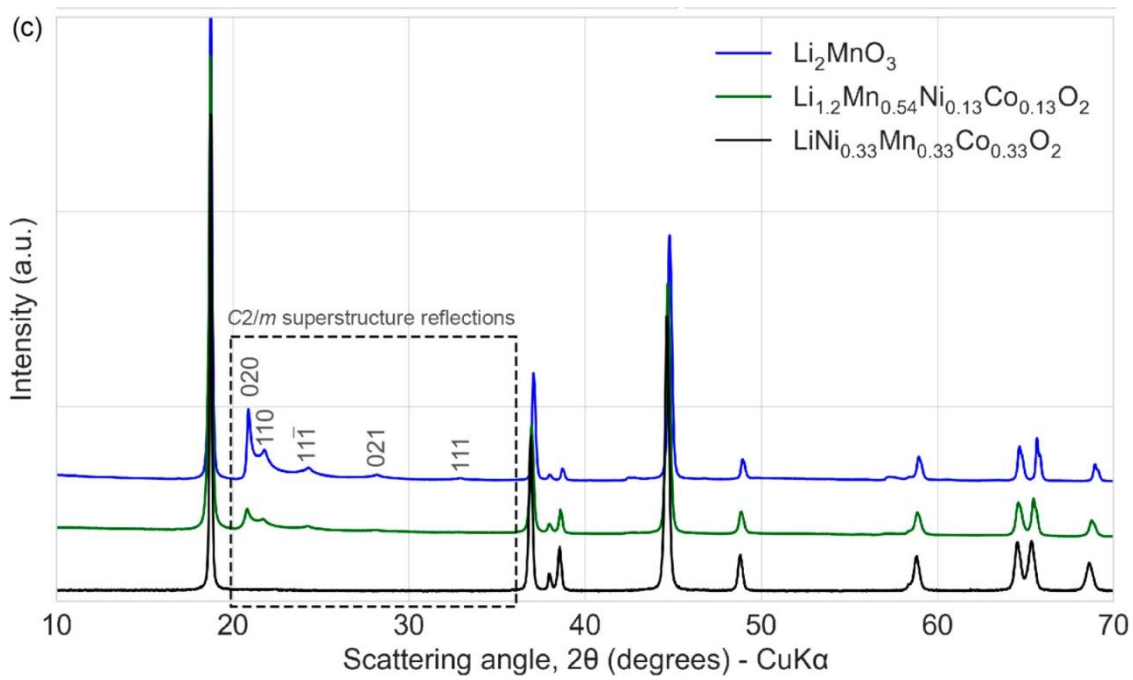

How can we accurately model these compounds?

X-ray, neutrons, total scattering

Tune into Ashoks Defence on the 14th of June to find out ☺

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Conclusions

The most functionally interesting battery materials are deceptively complex

Properties are dictated by order-disorder transitions

Degree of order and length scale over which (dis)ordering occurs determined by synthesis

Non-equilibrium phase transitions in **metastable compounds** makes predicting structural changes in a battery extremely difficult

Neutrons and X-rays are highly complementary and data should be combined for these systems

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Acknowledgements

Ashok Sreekumar Menon
Olof Gustafsson
Christian Baur

Kristina Edström
Daniel Brandell
Cesar Pay Gomez

Vetenskapsrådet

STandUP for ENERGY

Swedish Energy Agency

LiRichFCC

SwedNess