

Neutron Diffraction Application

Ashfia Huq

Oak Ridge National Laboratory

Research carried out at the Spallation Neutron Source at Oak Ridge National Laboratory is supported by the Division of Scientific User Facilities, Office of Basic Energy Sciences, U.S. Department of Energy.



Who Am I?



**BA: Physics and Computer Science
Mount Holyoke College**



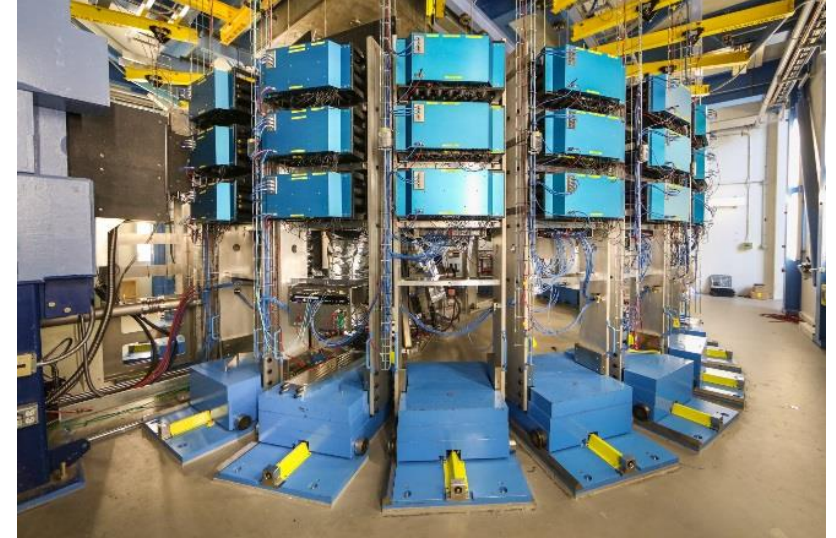
Post Doc: IPNS, ANL, IL

**Hydrogen Storage Materials, Catalysis,
Correlated electron materials.**



**Ph.D: Physics SUNY Stony Brook (NSLS, BNL), NY
Structure property of Alkali doped fullerenes,
Ab initio structure solution from powder
diffraction.**

Who Am I?

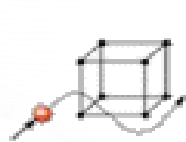


- Instrument Scientist(2006-present):
SNS, ORNL, TN
 - Neutron Instrumentation and SE development
 - Electrochemistry
 - In-situ Neutron Diffraction
 - Correlated electron materials.



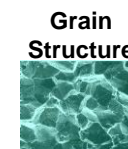
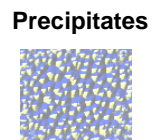
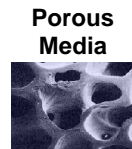
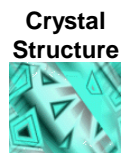
Where are the atoms?

We need wavelength (λ) \sim Object size (for most structural material of interest, that is \AA)



$$q = \frac{4\pi \sin(\theta)}{\lambda} = \frac{2\pi}{d}$$

Neutron
WAVELENGTHS are
similar to atomic scale
dimensions



X-ray

λ : 0.1 \AA - 10 \AA

$$\lambda[\text{\AA}] = 12.398/E_{\text{ph}}[\text{keV}]$$

Source:

- Lab diffractometers
- Synchrotron Sources

Neutron

thermal λ : 1 - 4 \AA

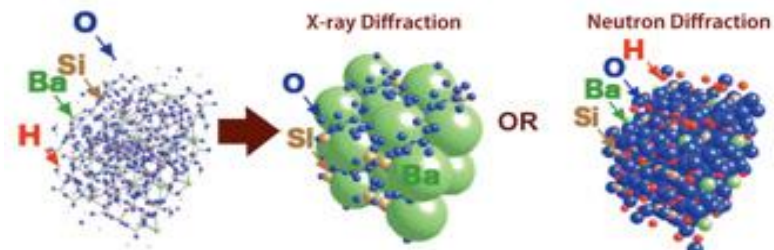
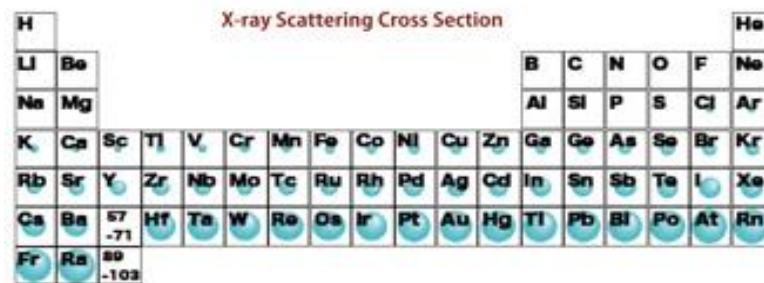
$$E_n[\text{meV}] = 81.89/\lambda^2[\text{\AA}]$$

Source:

- Reactors (fission)
- Spallation Source

Why Neutrons ?

- ❑ Detects light atoms even in the presence of heavy atoms (organic crystallography) – H is special!
- ❑ Distinguishes atoms adjacent in Periodic table and even isotopes of the same element (changing scattering picture without changing chemistry)
- ❑ Electrically neutral; penetrates centimeters of bulk material (allows non-destructive bulk analysis). Ease of *in-situ* experiments, e.g. variable temperature, pressure, magnetic field, chemical reaction etc.
- ❑ Magnetic moment (magnetic structure)



Before You Start

<https://www.ncnr.nist.gov/resources/n-lengths/>

Neutron scattering lengths and cross sections							
Isotope	conc	Coh b	Inc b	Coh xs	Inc xs	Scatt xs	Abs xs
Li	---	-1.90	---	0.454	0.92	1.37	70.5
⁶ Li	7.5	2.00-0.261i	-1.89+0.26i	0.51	0.46	0.97	940.(4.)
⁷ Li	92.5	-2.22	-2.49	0.619	0.78	1.4	0.0454

<https://www.ncnr.nist.gov/resources/activation/>

Material

Neutron Activation

For rabbit system

Thermal flux	Cd ratio	Thermal/fast ratio
<input type="text" value="1e8"/>	<input type="text" value="0"/>	<input type="text" value="0"/>
Mass	Time on beam	Time off beam
<input type="text" value="1"/>	<input type="text" value="10"/>	<input type="text" value="1 y"/>

Absorption and Scattering

Density	Thickness	<input type="button" value="Calculate"/>
<input type="text" value="3.5"/>	<input type="text" value="1"/>	
Source neutrons	Source X-rays	
<input type="text" value="1 Ang"/>	<input type="text" value="Cu Ka"/>	

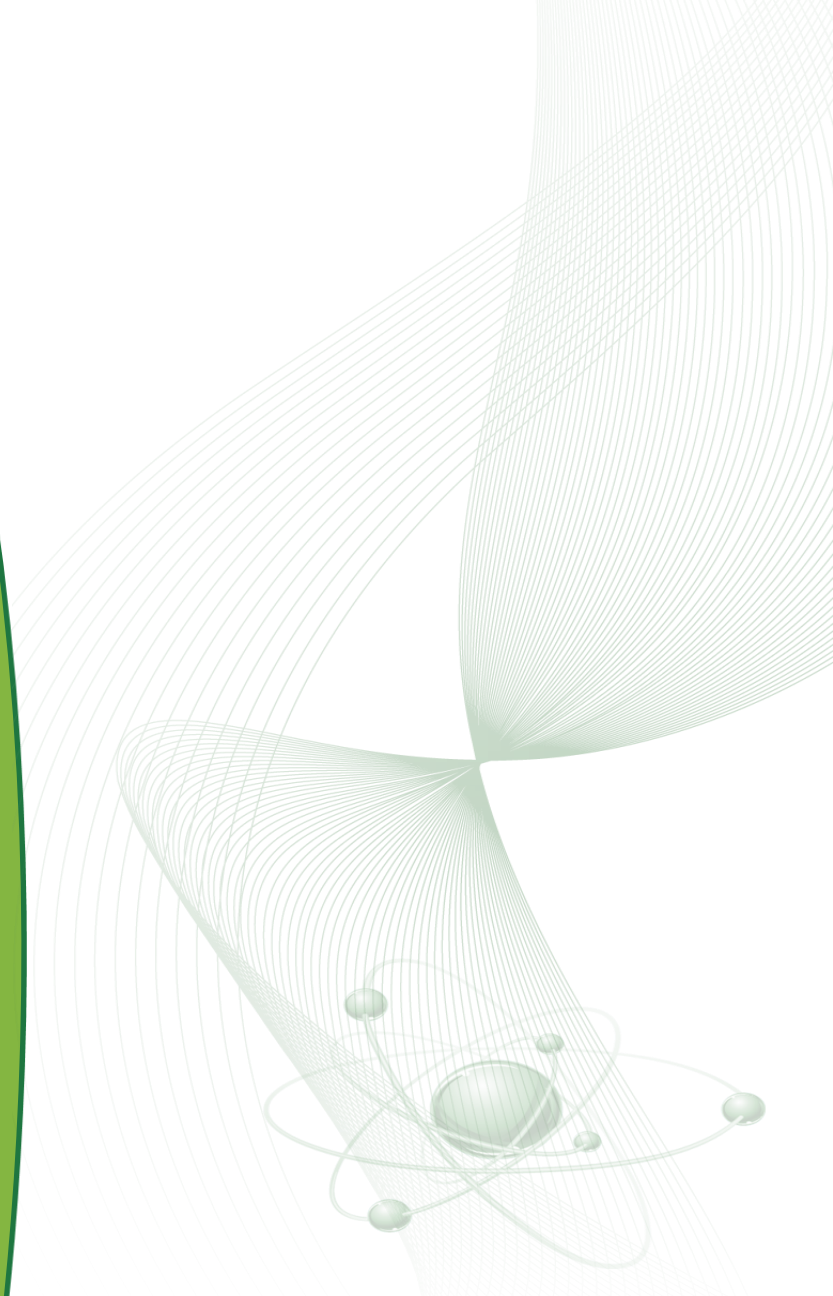
Li2IrO3 at 3.50 g/cm³

Source neutrons: 1.000 Å = 81.80 meV = 3956 m/s
 Source X-rays: 1.542 Å = 8.042 keV

1/e penetration depth (cm)		Scattering length density (10 ⁻⁶ /Å ²)		Scattering cross section (1/cm)		X-ray SLD (10 ⁻⁶ /Å ²)	
abs	abs+incoh	real	imag	coh	abs	real	imag
0.383	0.381	2.009	-0.013	0.102	2.611	24.021	-1.617
0.350	0.350	0.777		0.015			

Neutron transmission is 7.23% for 1 cm of sample (after absorption and incoherent scattering).
 Transmitted flux is 7.233e+6 n/cm²/s for a 1e8 n/cm²/s beam.

**Light Elements that are hard
to see with other techniques**



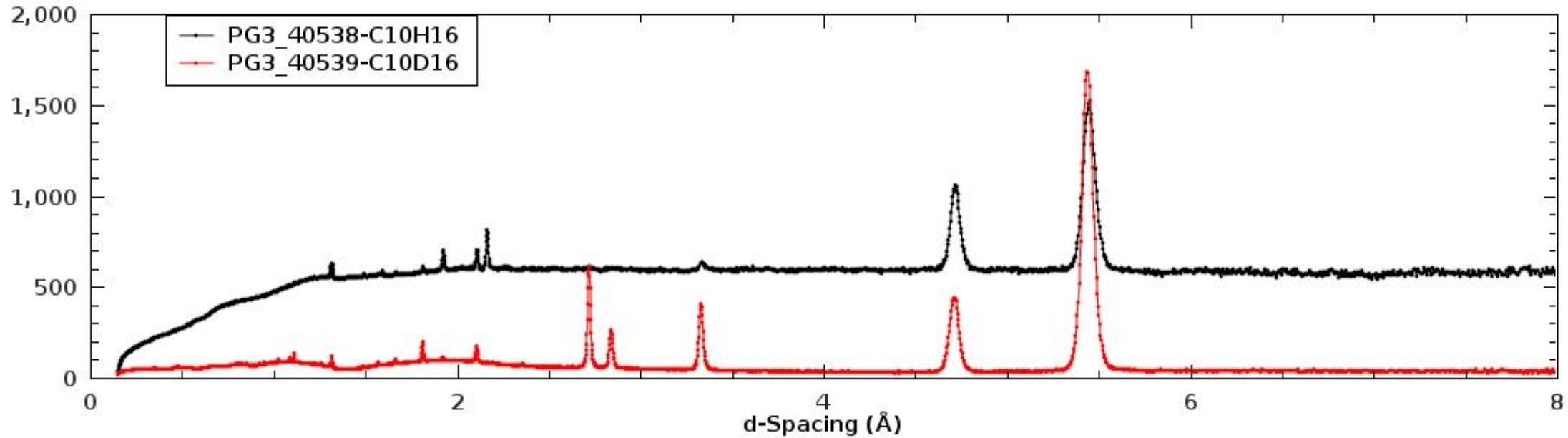
Hydrogen is special



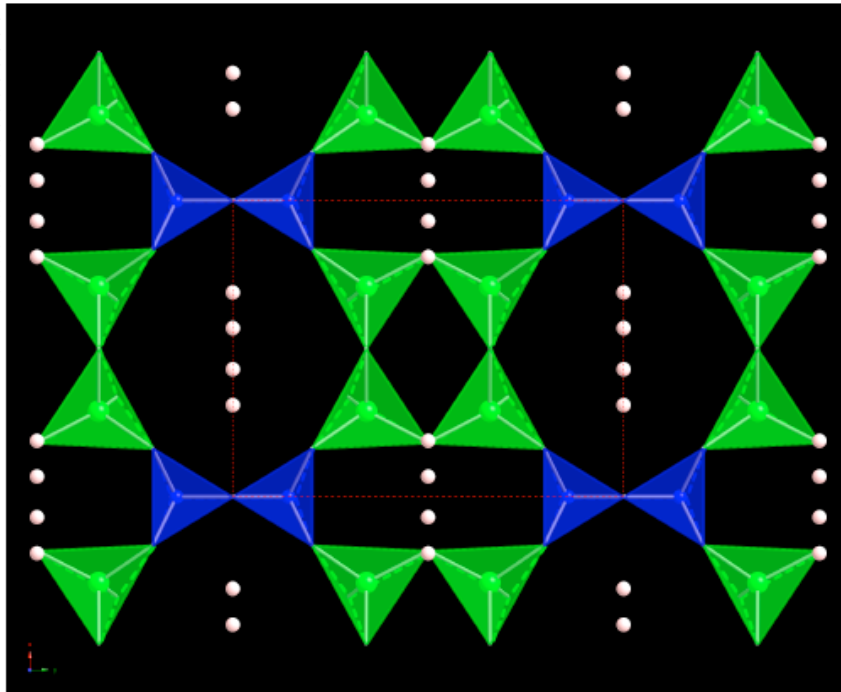
Neutron scattering lengths and cross sections							
Isotope	conc	Coh b	Inc b	Coh xs	Inc xs	Scatt xs	Abs xs
H	---	-3.7390	---	1.7568	80.26	82.02	0.3326
1H	99.985	-3.7406	25.274	1.7583	80.27	82.03	0.3326
2H	0.015	6.671	4.04	5.592	2.05	7.64	0.000519
3H	(12.32 a)	4.792	-1.04	2.89	0.14	3.03	0



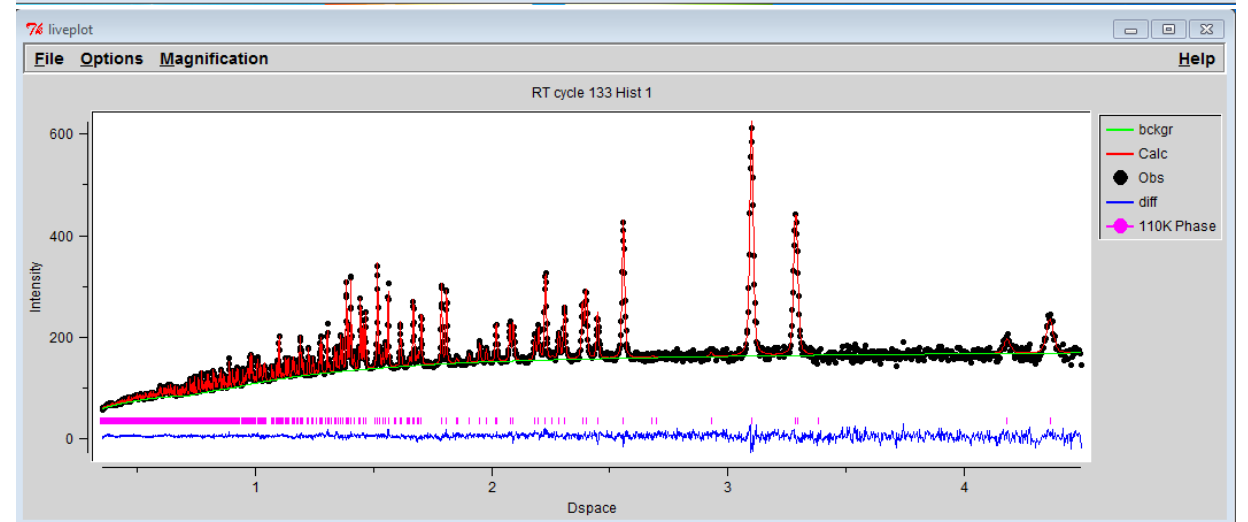
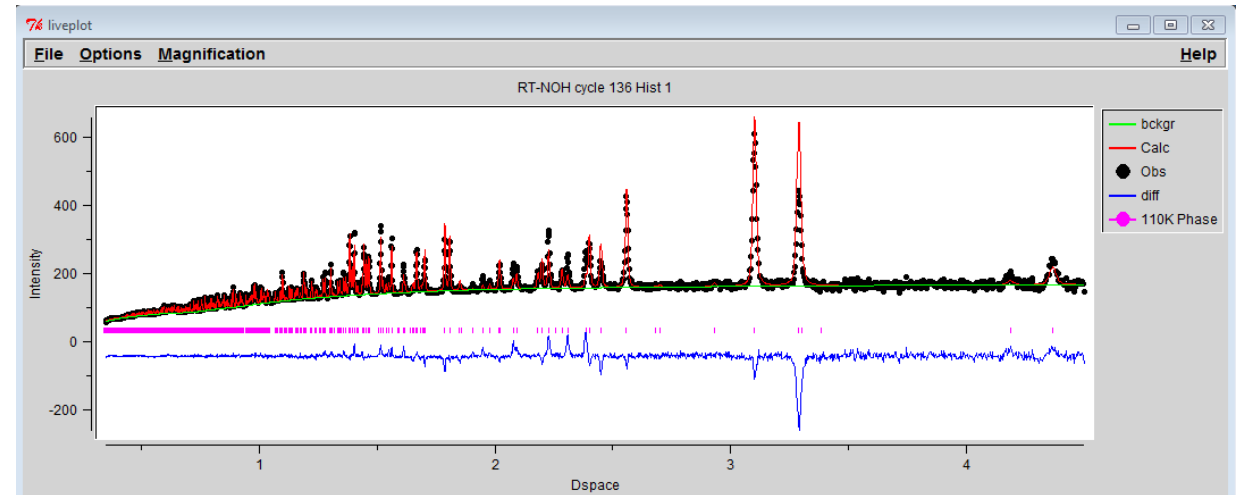
Adamantane



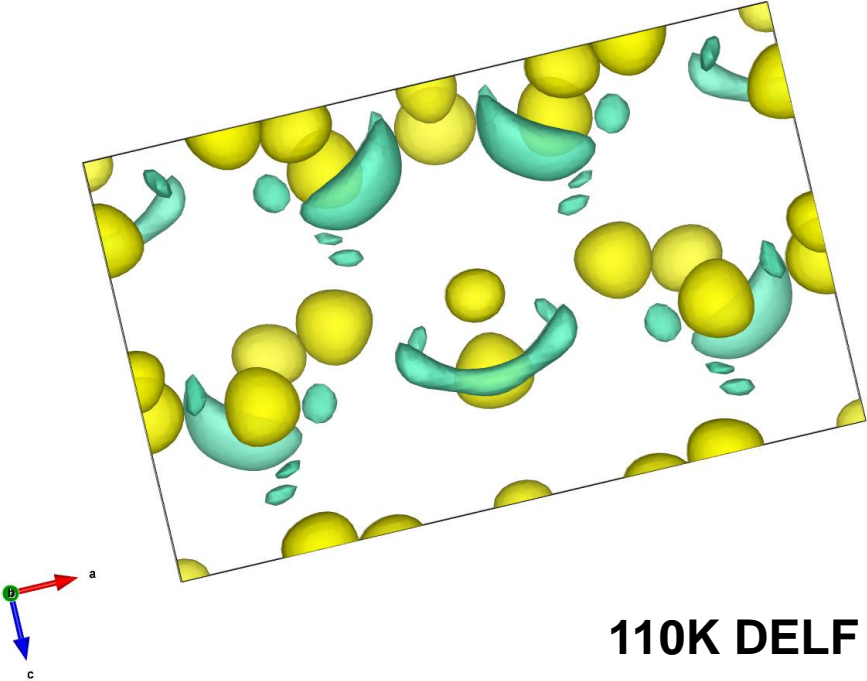
Crystal Structure of Hemimorphite ($\text{Zn}_4\text{Si}_2\text{O}_8 \cdot \text{H}_2\text{O}$)



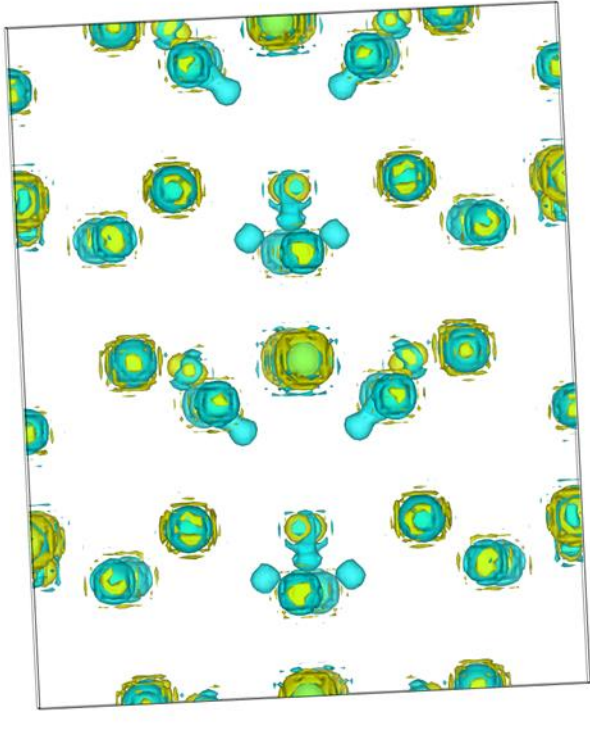
Structure of Hemimorphite ($\text{Zn}_4\text{Si}_2\text{O}_8 \cdot \text{H}_2\text{O}$), showing two large open channels. Green (Zn), blue (Si), white (H). Unit cell dimension shown ($a = 8.181 \text{ \AA}$, $b = 10.841 \text{ \AA}$).



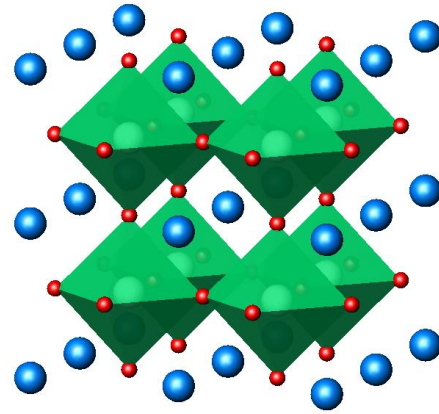
Difference Map from Powder Data



10K Fobs

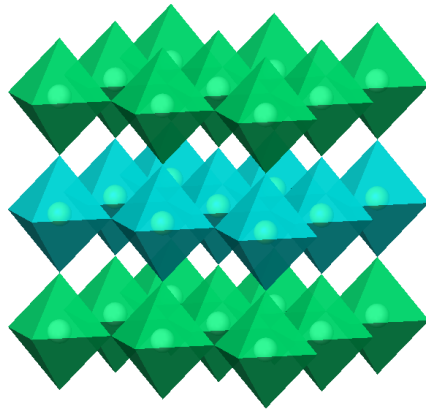


Ba₂CuWO₆: An Ordered Tetragonal Perovskite

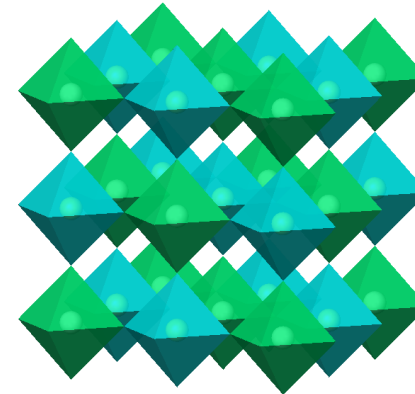


Simple cubic AMX₃
perovskite: $a = 3.8045$.

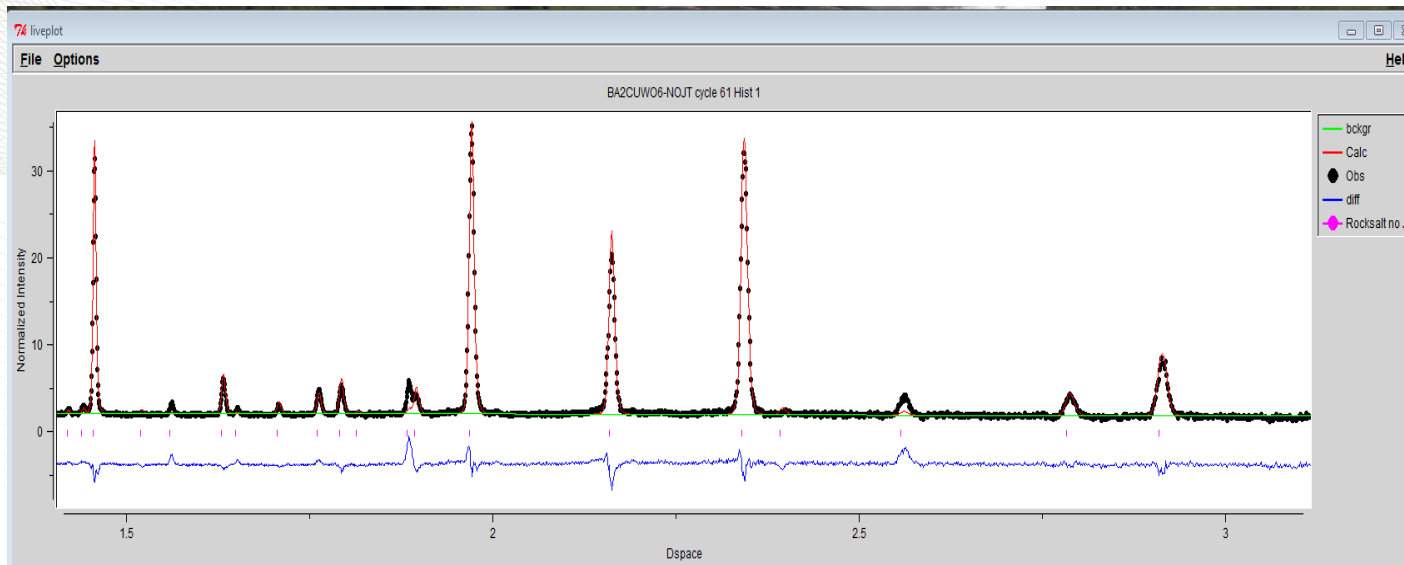
Double Perovskites A₂MM'O₆: Out of 3 possible orderings only 2 observed



Model #1: Ordered alternation of MO₆ and M'O₆ octahedra in one direction, leading to formation of layered perovskite.

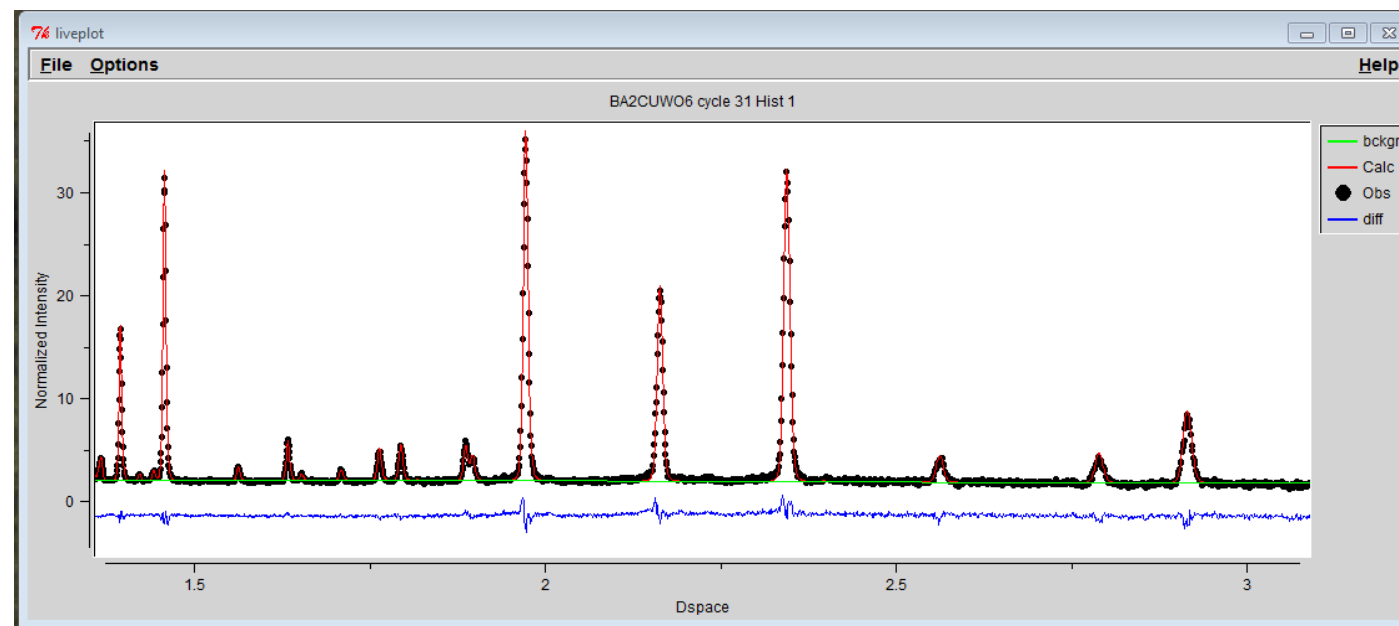


Model #2: Ordered alternation in the three directions of space, resulting in rock-salt ordered superstructure.

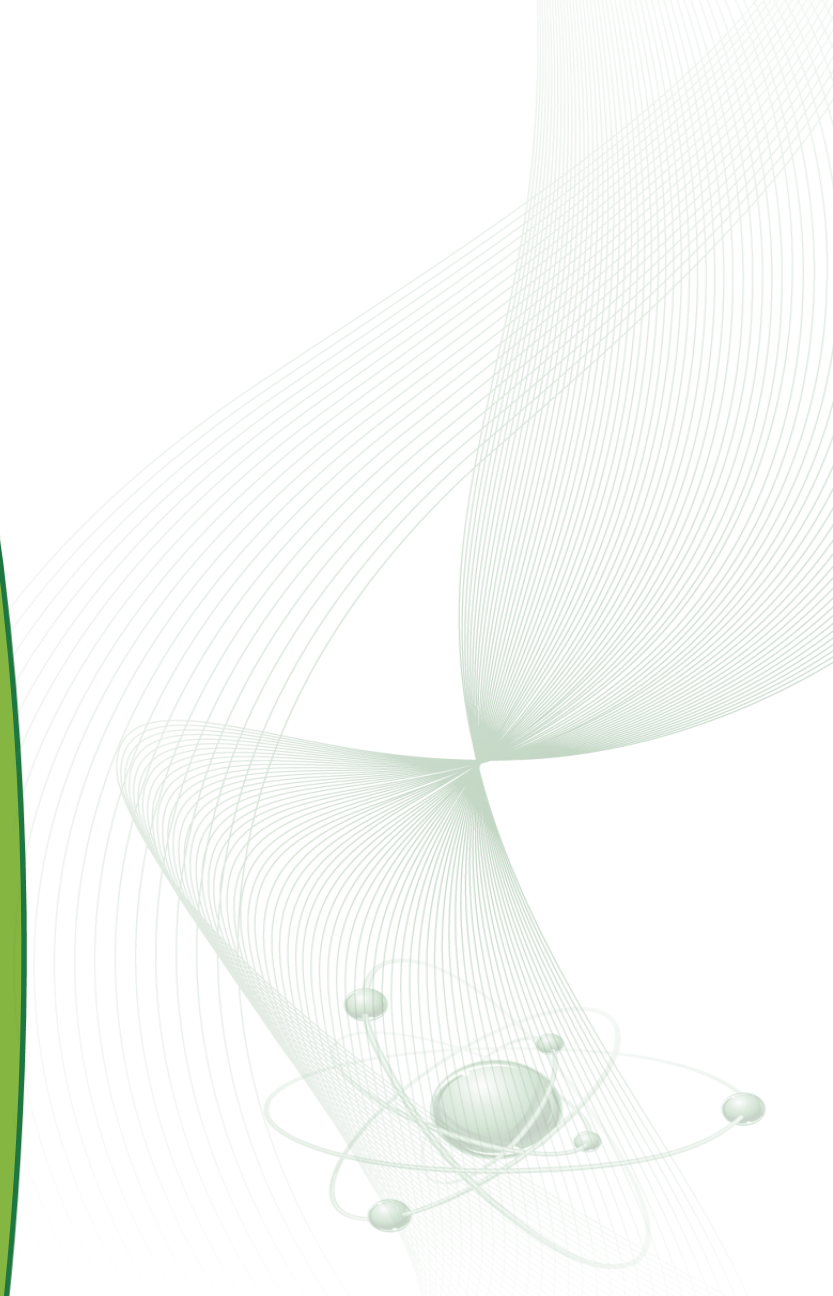


Recall Cu^{2+} electronic configuration $(t_{2g})^6(e_g)^3$: Jahn Teller Distortion?

So in fact CuO_6 octahedra are elongated along the c axis. The e_g orbital is split into



Elements that have similar Z.



LiNi_{0.5}Mn_{1.5}O₄ : Order Disorder

Shin D.W., Bridges C.A., Huq A., Paranthaman M.P., Manthiram A., "Role of cation ordering and surface-segregation in high-voltage spinel LiMn_{1.5}Ni_{0.5-x}M_xO₄ (M = Cr, Fe, and Ga) cathodes for lithium-ion batteries", *Chemistry of Materials*, 24, 19, 3720-3731 (2012)

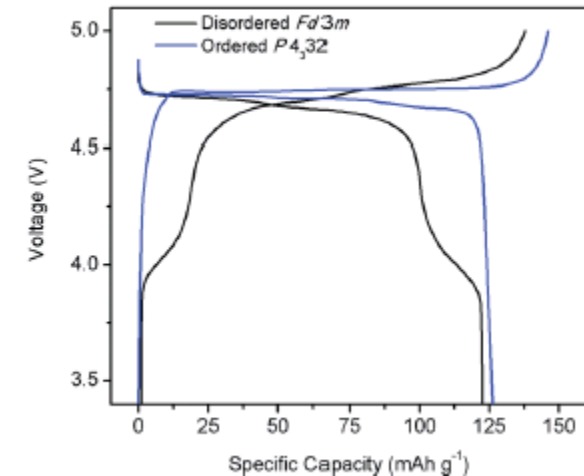
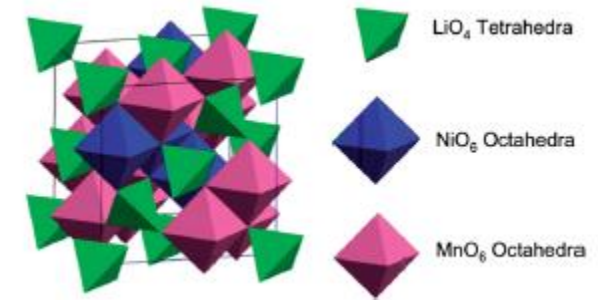
Kim J.H., Huq A., Chi M., Pieczonka N.P., Lee E., Bridges C.A., Tessema M.M., Manthiram A., Persson K.A., Powell B.R., "Integrated Nano-Domains of Disordered and Ordered Spinel Phases in LiNi_{0.5}Mn_{1.5}O₄ for Li-Ion Batteries", *Chemistry of Materials*, 26, 15, 4377-4386 (2014).

Liu J., Huq A., Moorhead-Rosenberg Z., Manthiram A., Page K., "Nanoscale Ni/Mn Ordering in the High Voltage Spinel Cathode LiNi_{0.5}Mn_{1.5}O₄", *Chemistry of Materials*, 28, 6817-6821 (2016).

GM R&D, Optimal CAE Inc., LBNL, University of Texas @ Austin, ORNL

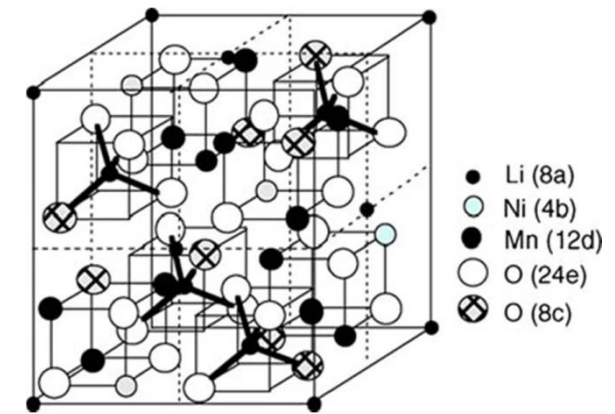
Motivation: ~4.7V with capacity ~135mA h/g

How does synthesis and doping effect the order disorder? What is the nature of this and how does it effect performance?

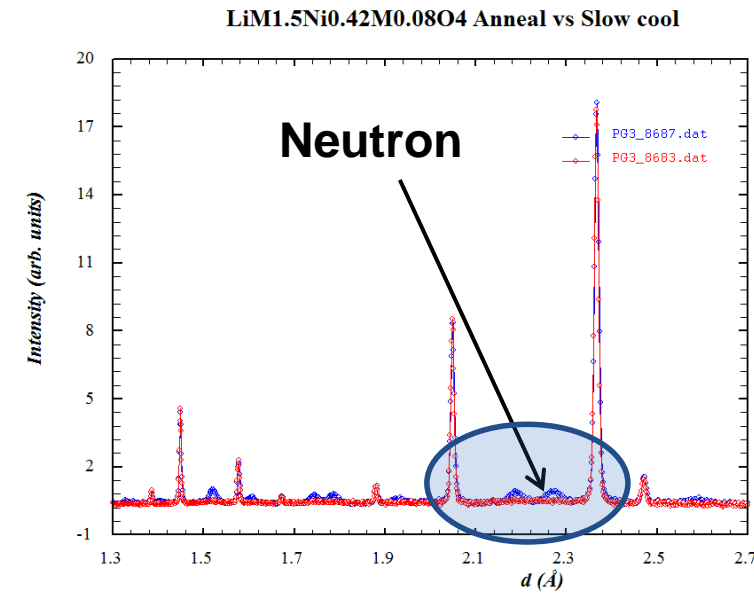
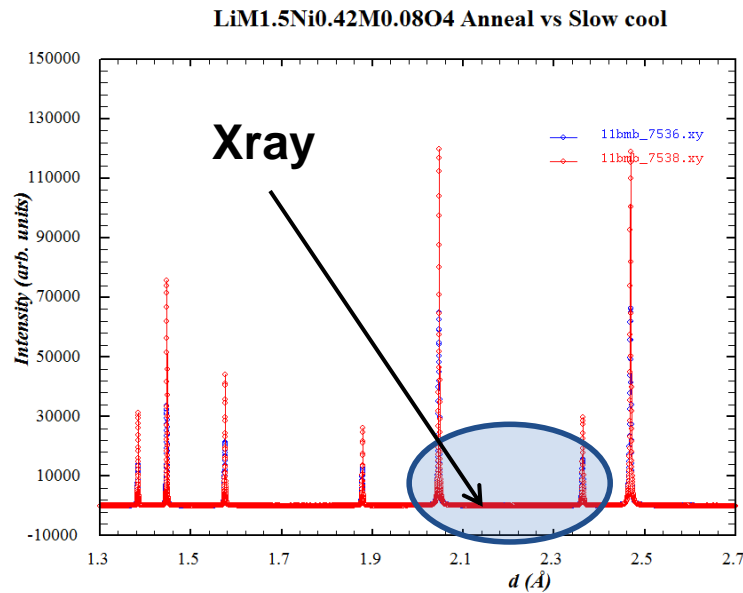


Spinel Cathode ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$)

In disordered F d -3 m Ni and Mn are disordered in the octahedral interstitials (16d site). The order between Ni and Mn (1:3 ratio) lowers the symmetry. Ordered Phase Space Group: $P4_332$.

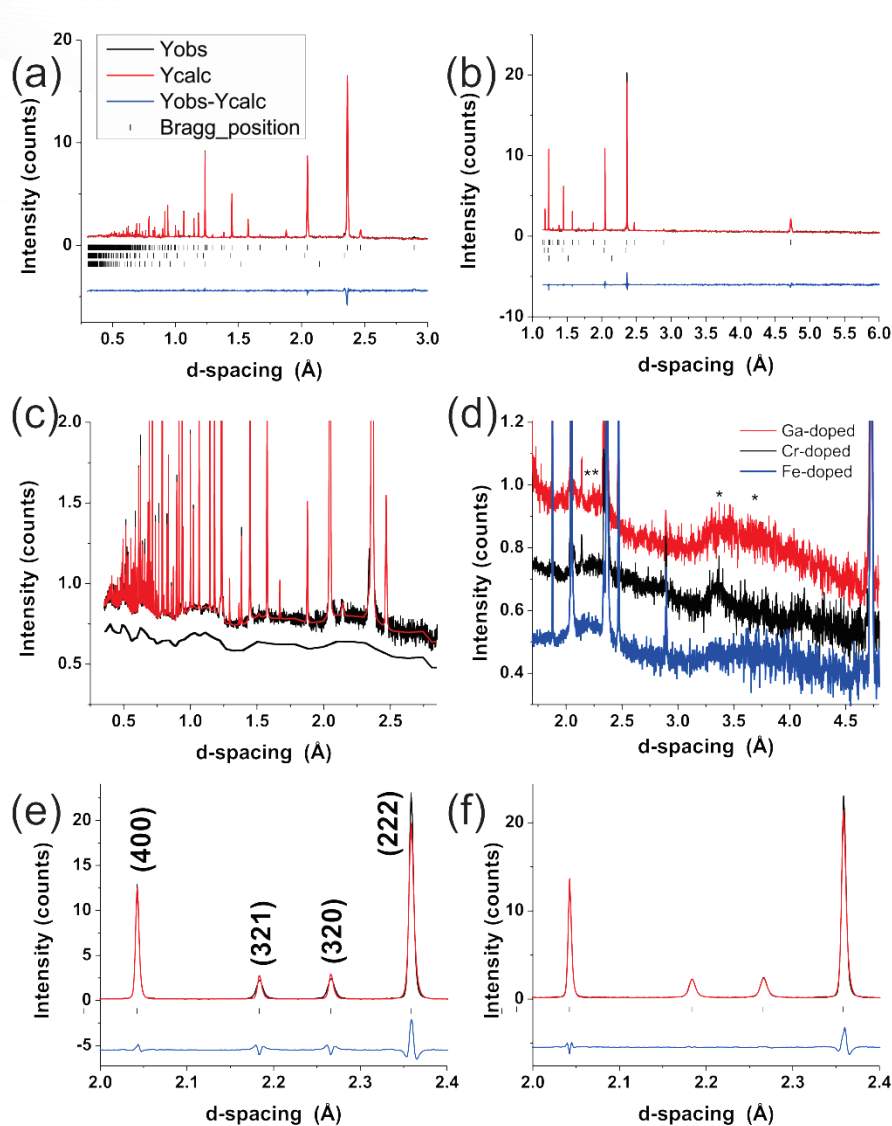


- The crystal structure can accommodate both ordered or disordered Ni and Mn distribution based on thermal history in synthesis process.
- Formation of rock salt secondary phase causes reduced energy density.



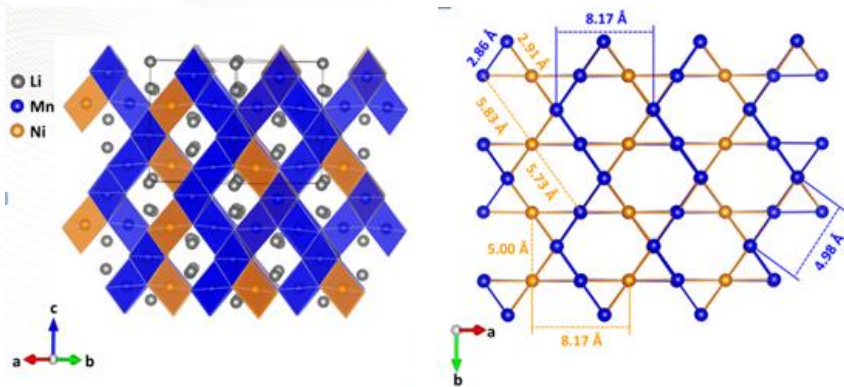
Anneal vs Slow Cool

Controlling the level of cation ordering by doping $\text{LiNi}_{0.5-x}\text{M}_x\text{Mn}_{1.5}\text{O}_4$ (M=Fe, Cr and Ga)

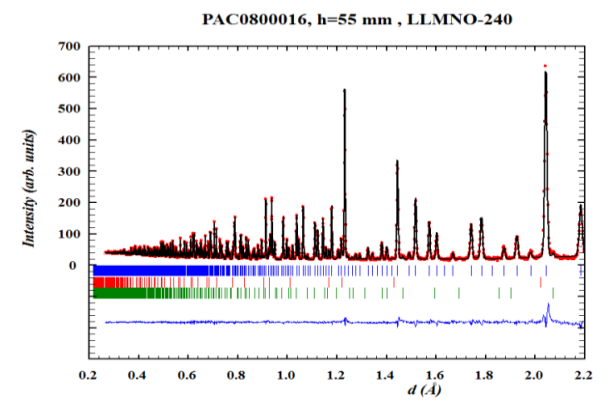
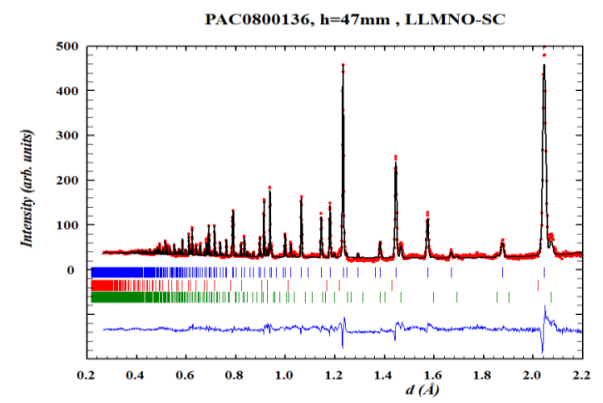
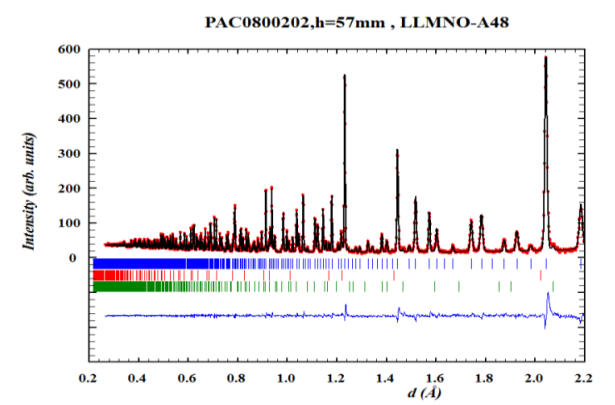
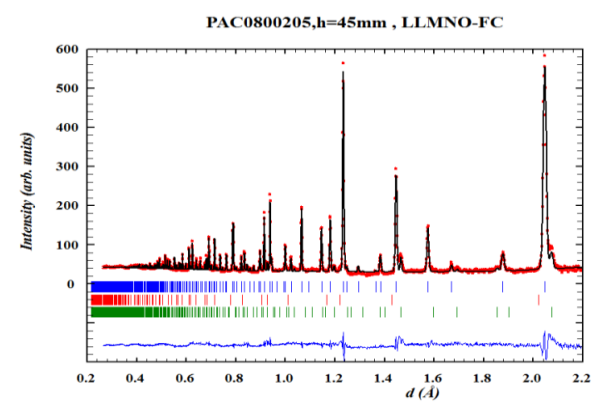
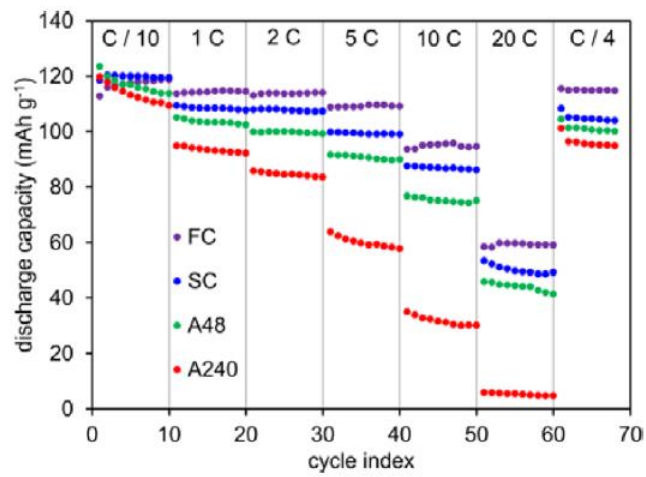


Annealing temperature and doping can be used to tune the level of cation ordering which effect the electrochemical performance of the cathode.

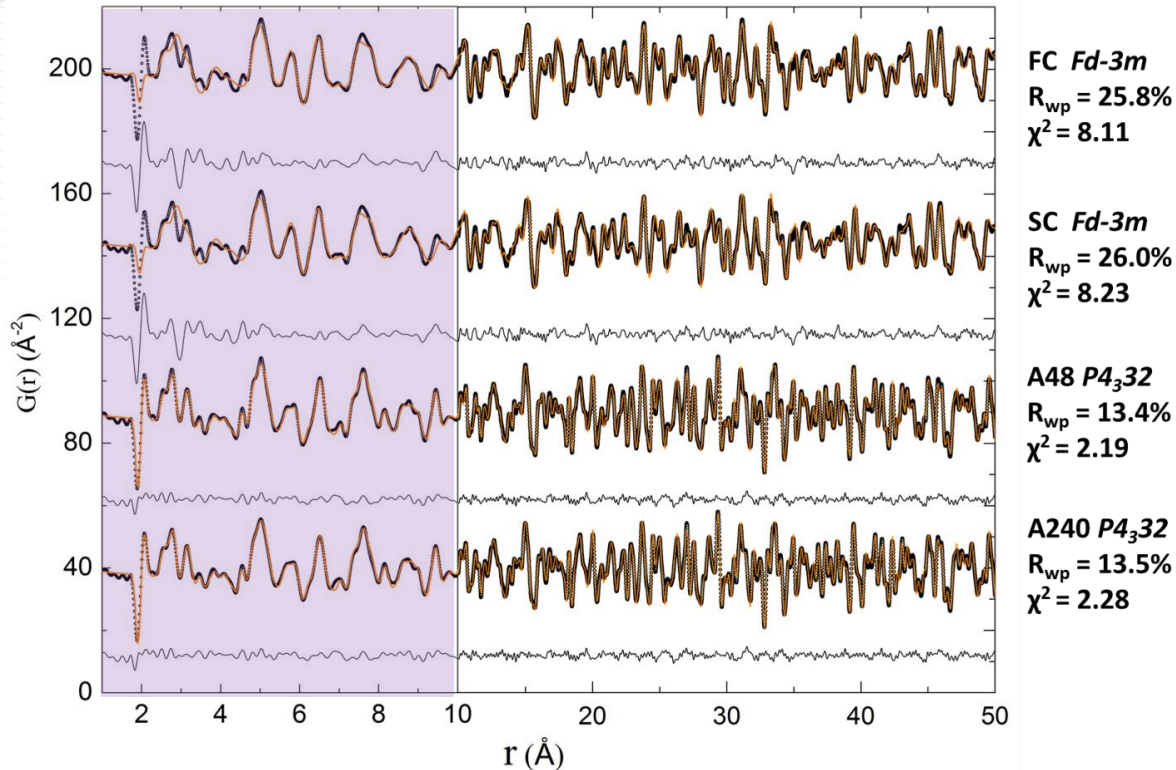
Ni/Mn order/disorder in the ordered and disordered



- Heat Treatments;**
- SC: Slow cooled 1.5°C/min from 900°C (8h)
 - FC: Fast cooled 5°C/min from 900°C (8h)
 - A48: Annealed for 48h at 700°C
 - A240: Annealed for 240h at 700°C



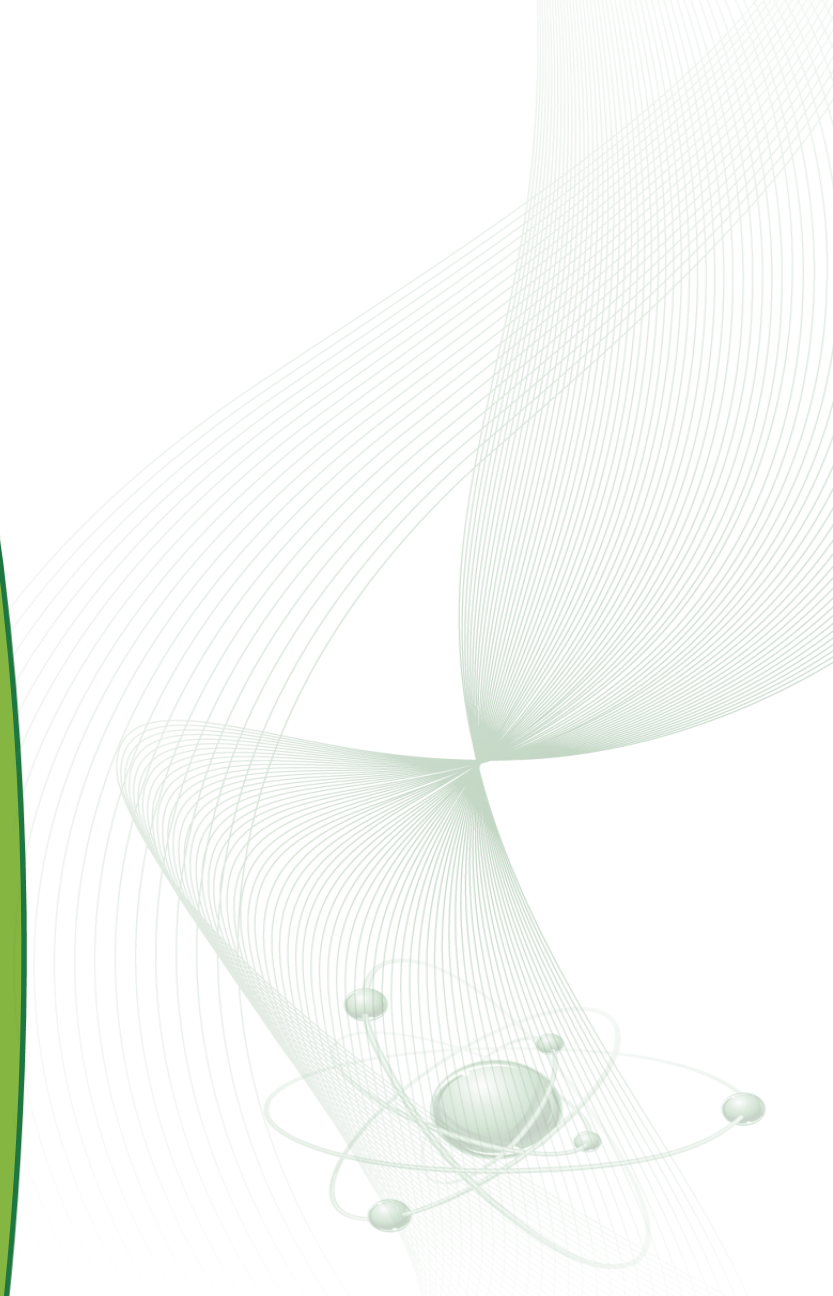
Ni/Mn order/disorder in the ordered and disordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$



- Ni/Mn are **locally well ordered** in both ordered and disordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$
- Ni/Mn are partially ordered up to 16 Å (two unit cells) in the disordered phase
- Ni/Mn are long range disordered in the disordered phase .

1. Mn^{3+} is not critical to enable high rate capability, as the conductivity enhancement from Mn^{3+} carriers in the fully lithiated spinel is far less significant than the increased conductivity from the generation of Ni^{3+} carriers.
2. A slightly ordered spinel, such as A48, which does not contain any initial Mn^{3+} carriers, is still capable of high rate capability because it may be able to form a kinetic solid solution at the two-phase boundary more easily than a very ordered spinel, such as A240.
3. Level of local ordering does not drive performance but rather Ni/Mn domain size/boundaries may instead be more important.

Very often life is not so simple and one has to use both X-rays and Neutrons to get to the right picture

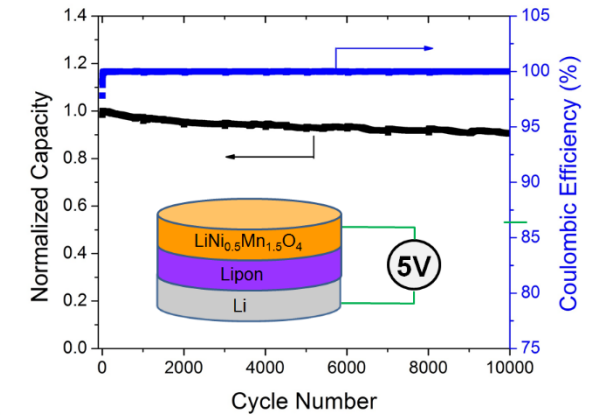
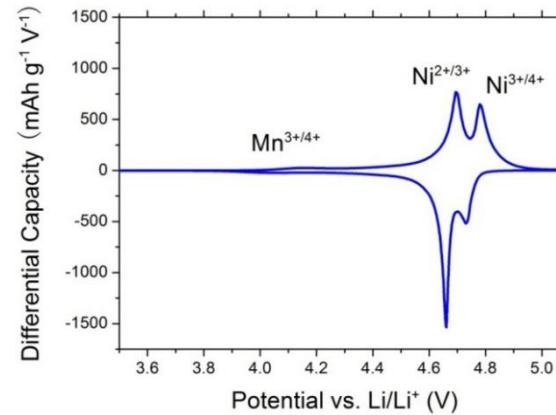
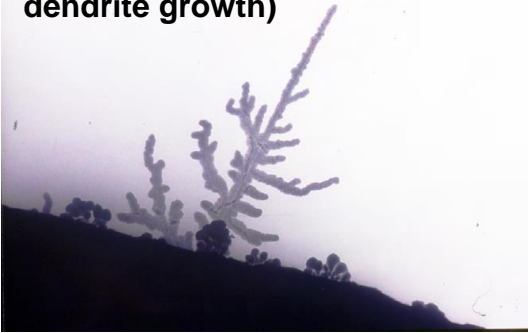


$\text{Li}_{7-x}\text{La}_3\text{Zr}_{2-z}\text{Ta}_z\text{O}_{12}$: Solid Electrolyte

- Thompson T., Wolfenstine J., Allen J.L., Johannes M., Huq A., David I.N., Sakamoto J., "Tetragonal vs. cubic phase stability in Al - free Ta doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO)", *Journal of Materials Chemistry A*, 2, 13431-13436, (2014).
- Thompson T., Sharafi A., Huq A., Allen J. L., Wolfenstine J., Sakamoto J., "A Tale of Two Sites: On Defining the Carrier Concentration in Garnet-Based Ionic Conductors for Advanced Li Batteries", *Advanced Energy Materials*, (2015).
- Mukhopadhyay S., Thompson T., Sakamoto J., Huq A., Wolfenstine J., Allen J. L., Bernstein N., Stewart D. A., Johannes M. D., "Structure and stoichiometry in supervalent doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ", *Chemistry of Materials*, (2015).

University of Michigan, Army Research Laboratory, Naval Research Laboratory, ORNL

Courtesy of S. Whittingham (Li dendrite growth)



Li, Juchuan, et.al. *Adv. Energy Mat.* 5 [4] 1401408

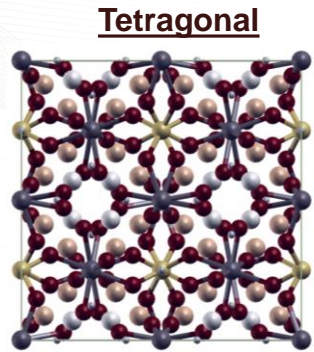
Motivation: Higher voltage cathode use to increase power/energy density is thwarted

Poor Safety, Capacity Fade, Limited Cycle life

SEI formation and dissolution of TM from cathode

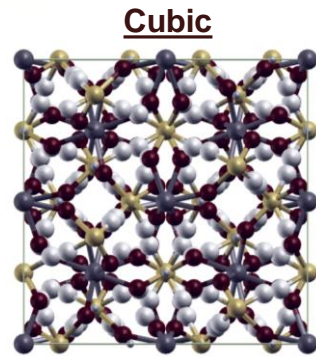
Possible Solution: Solid Electrolyte

Doping in Li or Zr site for performance



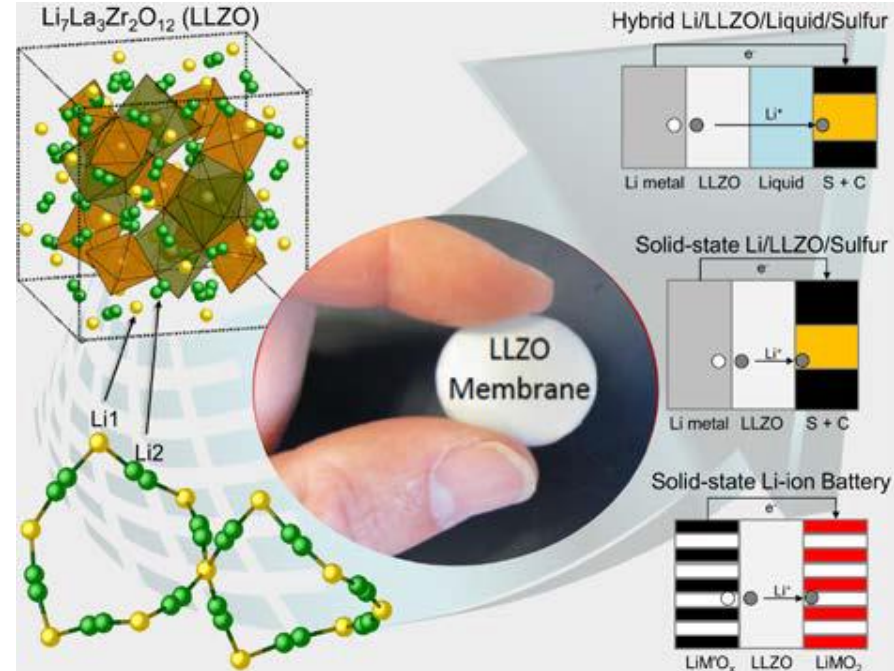
- Li₁ = tetrahedral (1)
- Li₂ = octahedral (2)
- Li₃ = octahedral (4)

$$\sigma = 10^{-6} \text{ S/cm}$$



- Li₁ = tetrahedral (3)
- Li₂ = octahedral (12)

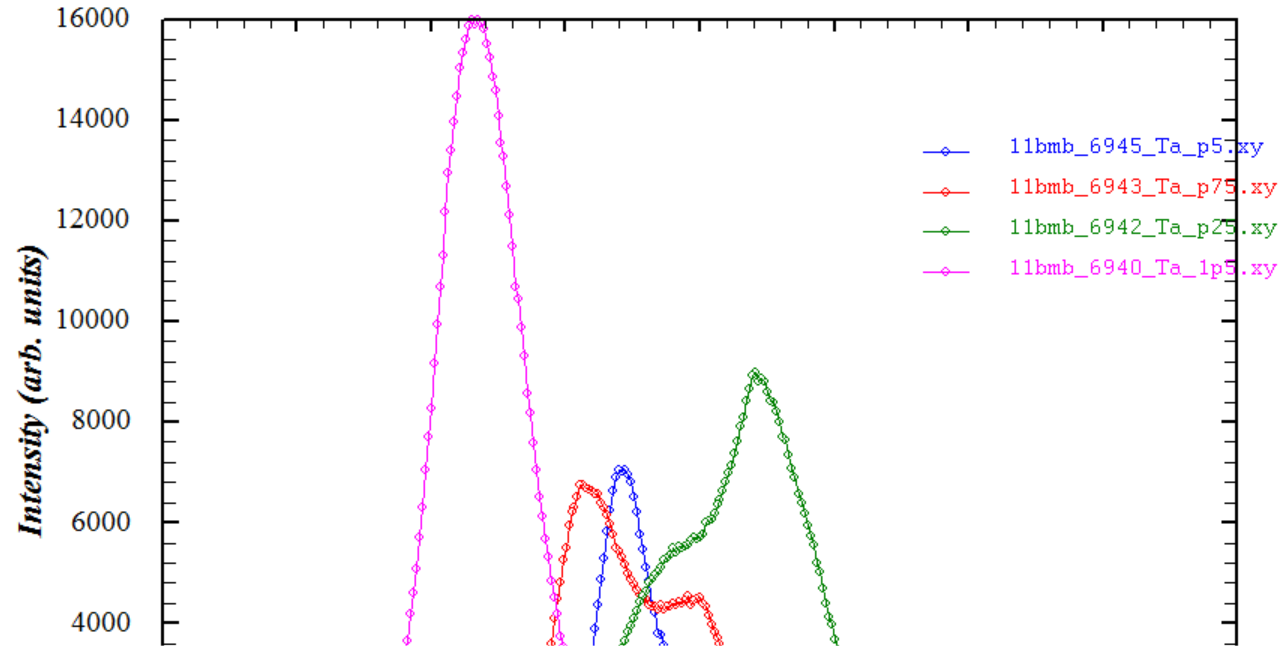
$$\sigma = 10^{-3} \text{ S/cm}$$



- **High Li⁺ Ionic Conductivity** → 0.4 mS/cm at 298K is hard to reproduce.
- **Stable against lithium**
- **Synthesized/processed in air**
- **Low grain boundary resistance**
- **Challenges:**
 - densification
 - stabilizing cubic phase: Need to add Li vacancy

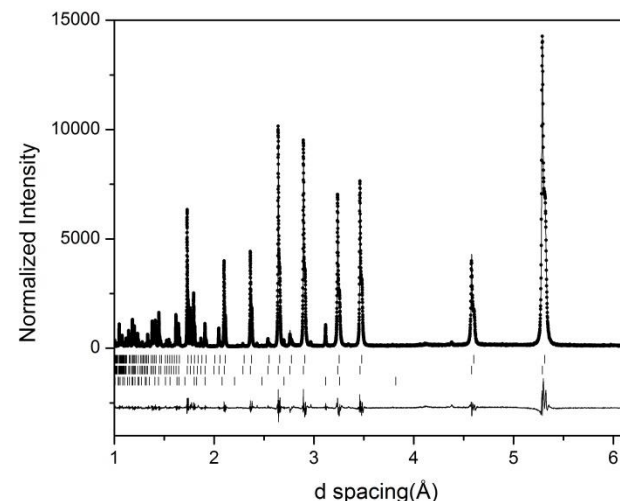
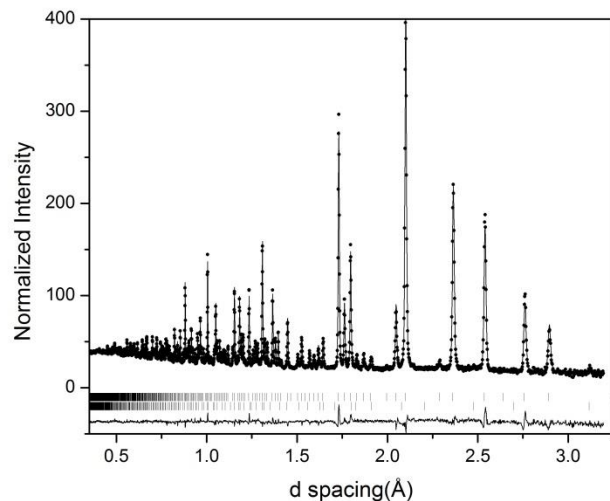
Ta doping in Zr site: What happens to the structure?

LLZO High res Synchrotron : 11BM-B 300K



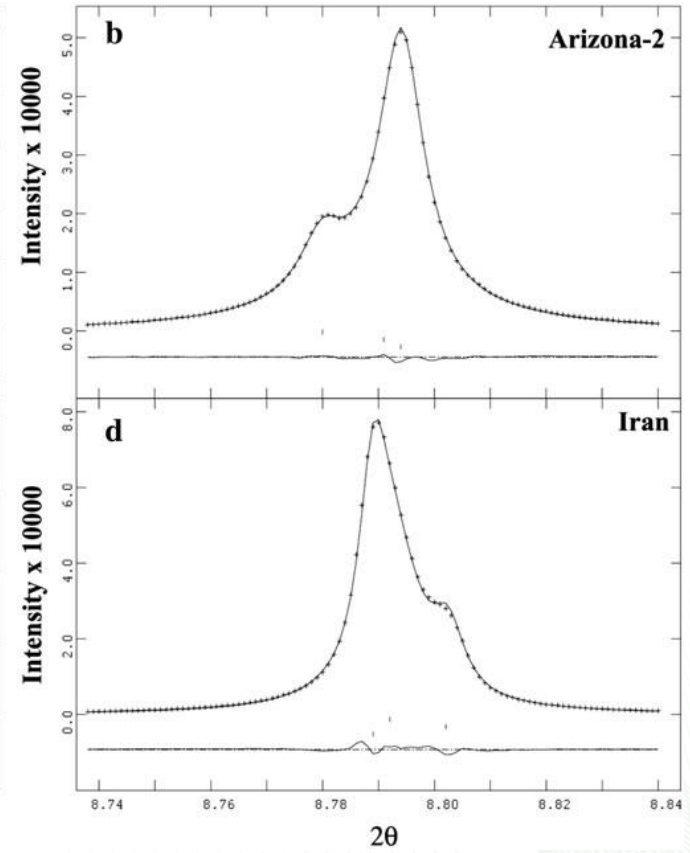
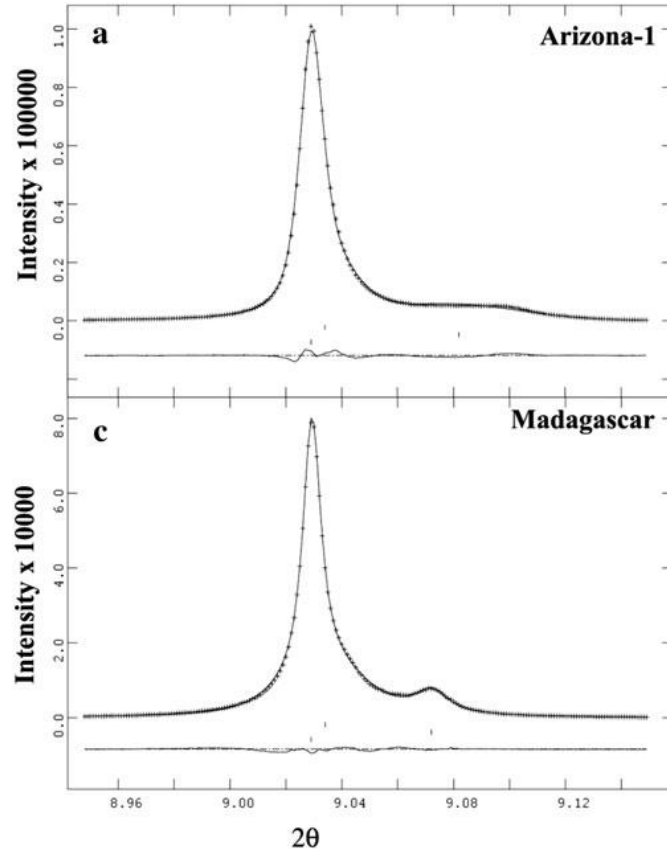
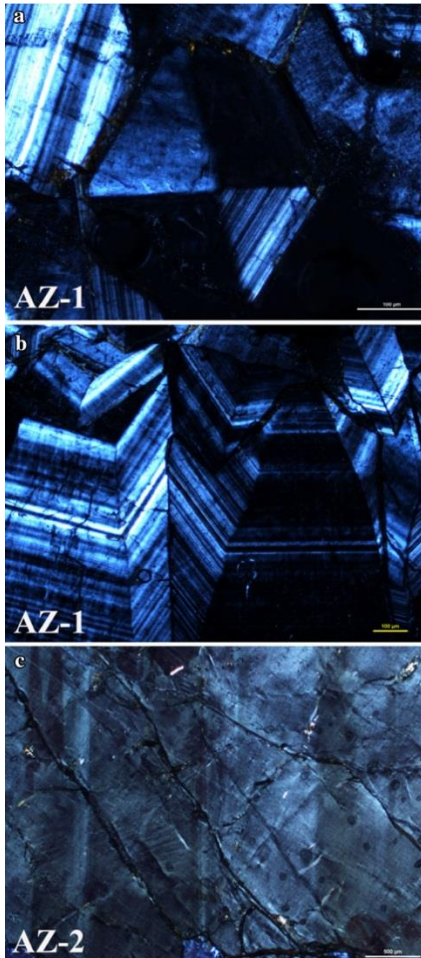
	Li	La	Zr	Ta	O
Neutron (b)	-1.9	8.24	7.16	6.91	5.8
X-ray (Z)	3	57	40	73	8

High Resolution Diffraction : Be careful what you ask for 😊

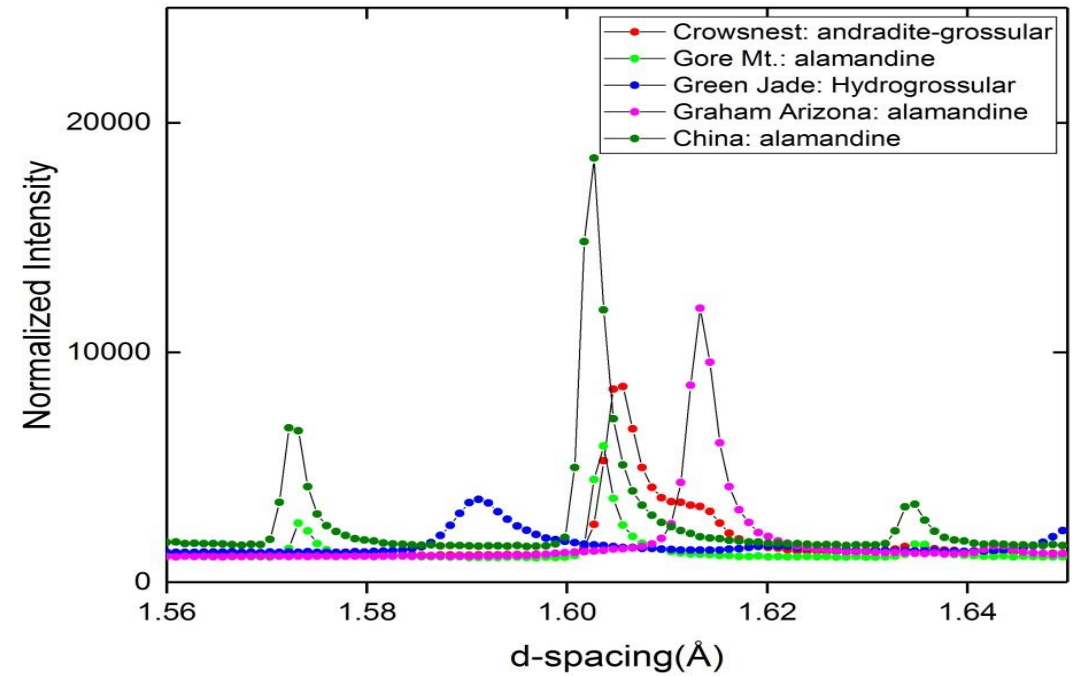
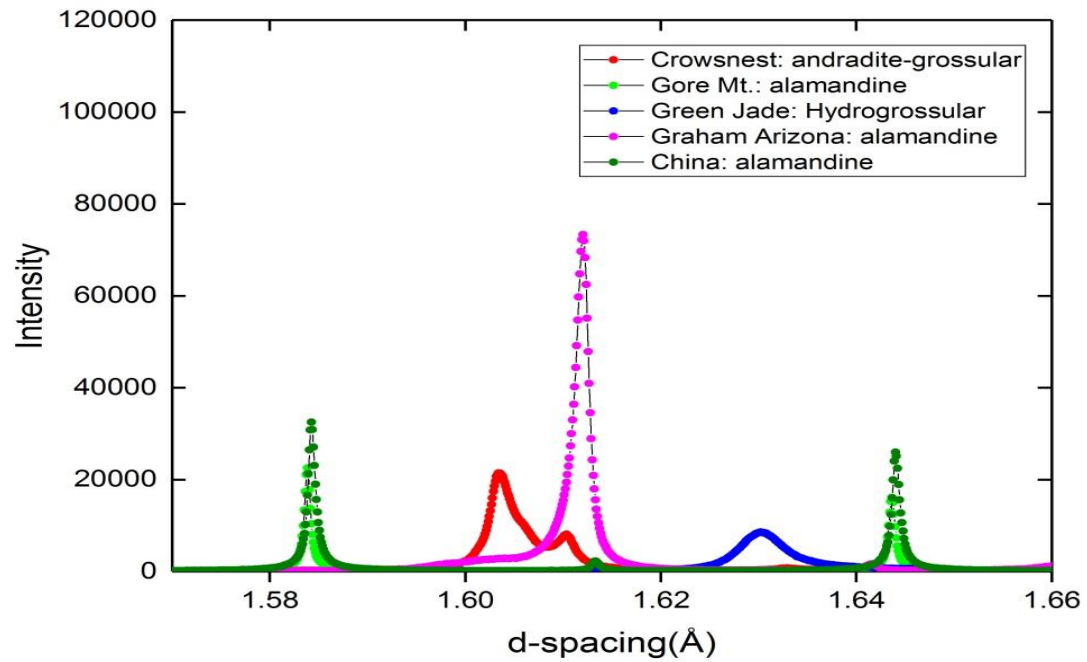


Nominal	Measured		Neutron		Synchrotron			Synchrotron Wt %		
Ta	Ta	Li	a	c	a	a'	c	cubic I	cubic II	pyrochlore
0.25	0.2500	6.9863	12.9181	13.0503	13.0090		13.0577			
0.5	0.5112	5.4645	12.9305		13.0131	12.9529		0.4623	0.5245	0.0132
0.75	0.7701	5.4900	12.9086		12.9912	12.9310		0.5293	0.4526	0.0180
1.5	1.5762	4.4082	12.8343		12.8677					

Garnets in Nature (Numerous work by Antao et. Al.)



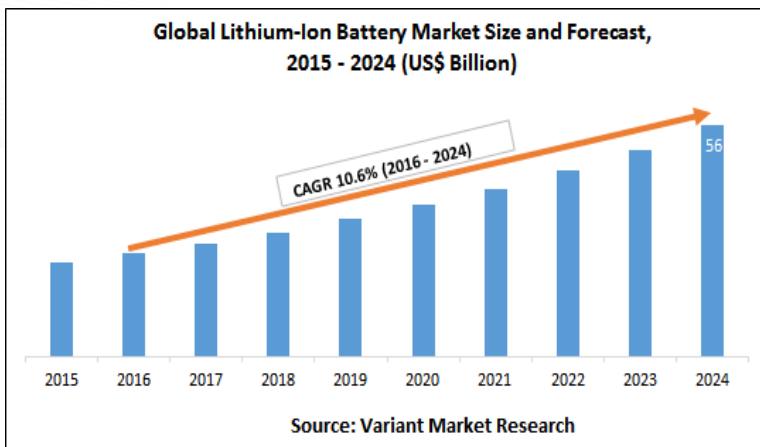
Natural Garnets X vs N



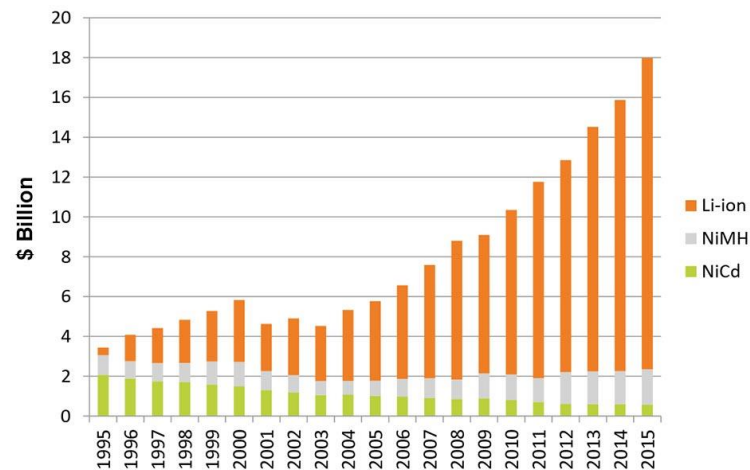
In situ studies

- **Li-ion Battery**
- **Solid Oxide Fuel Cell material**
- **Sample Synthesis**

Some Facts on LIB

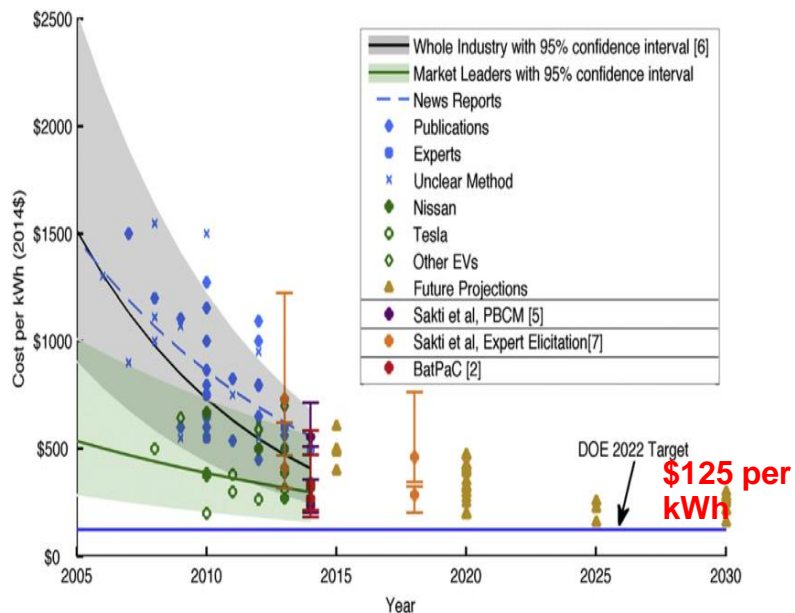


<https://www.variantmarketresearch.com/report-categories/semiconductor-electronics/lithium-ion-battery-market>

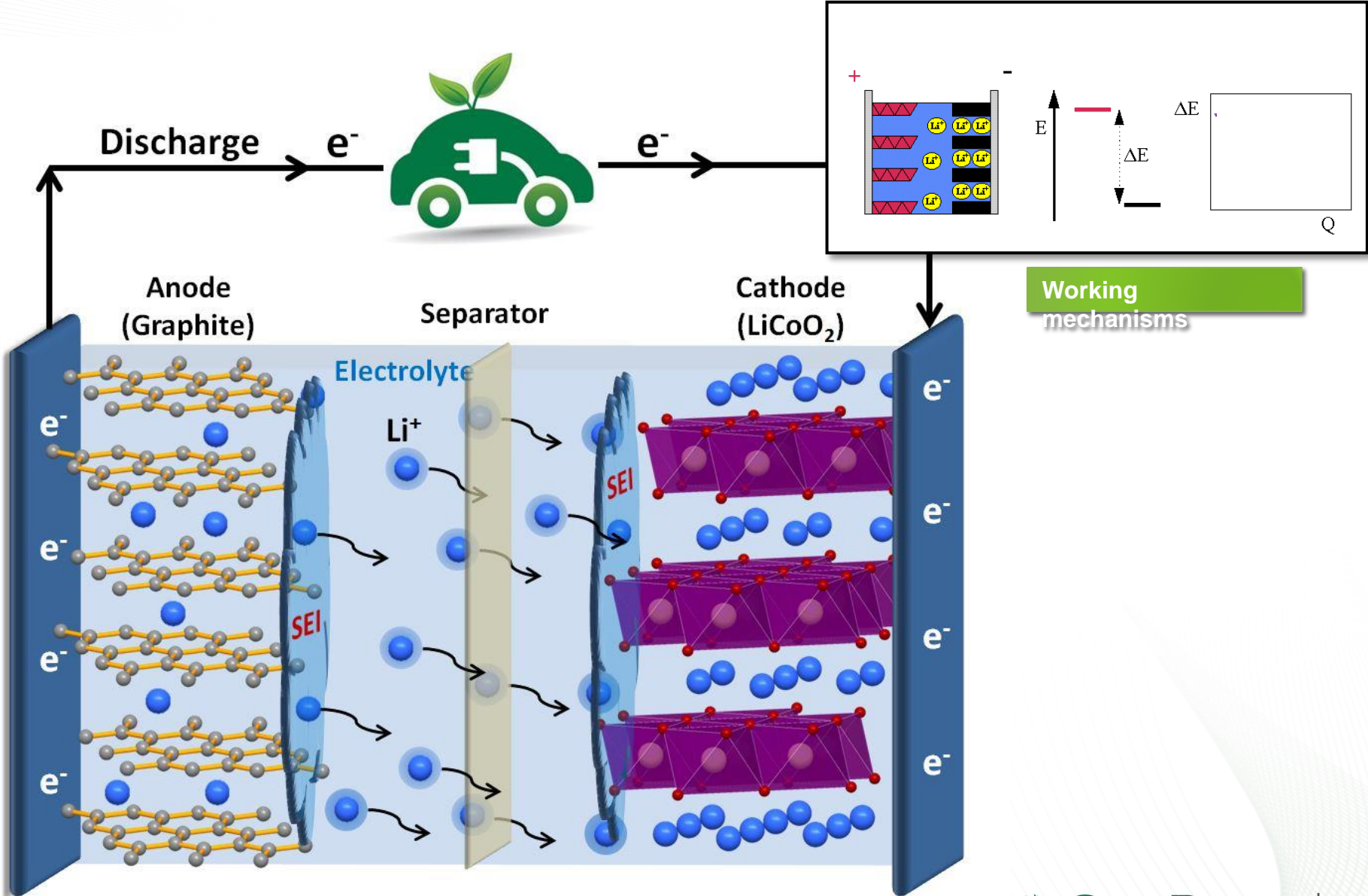


Search word: Lithium Battery

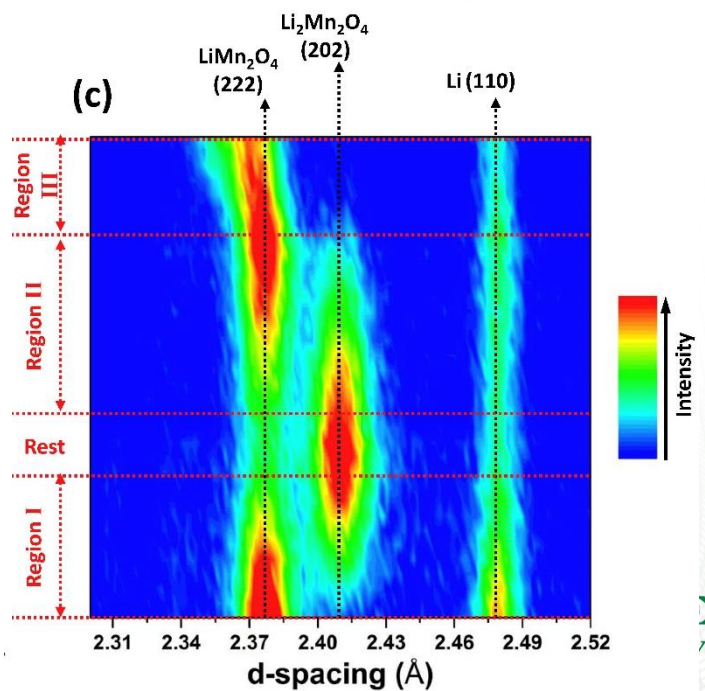
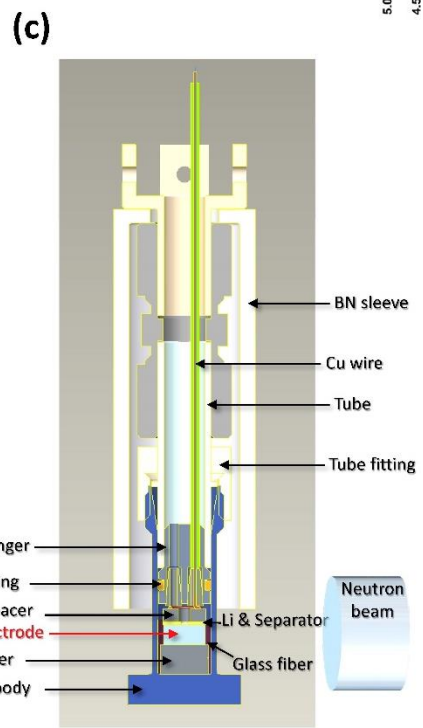
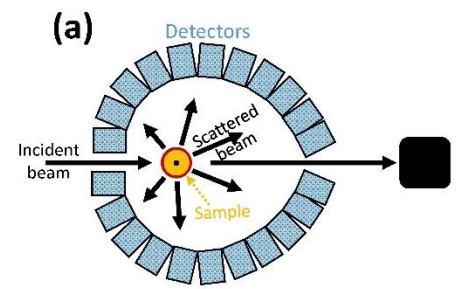
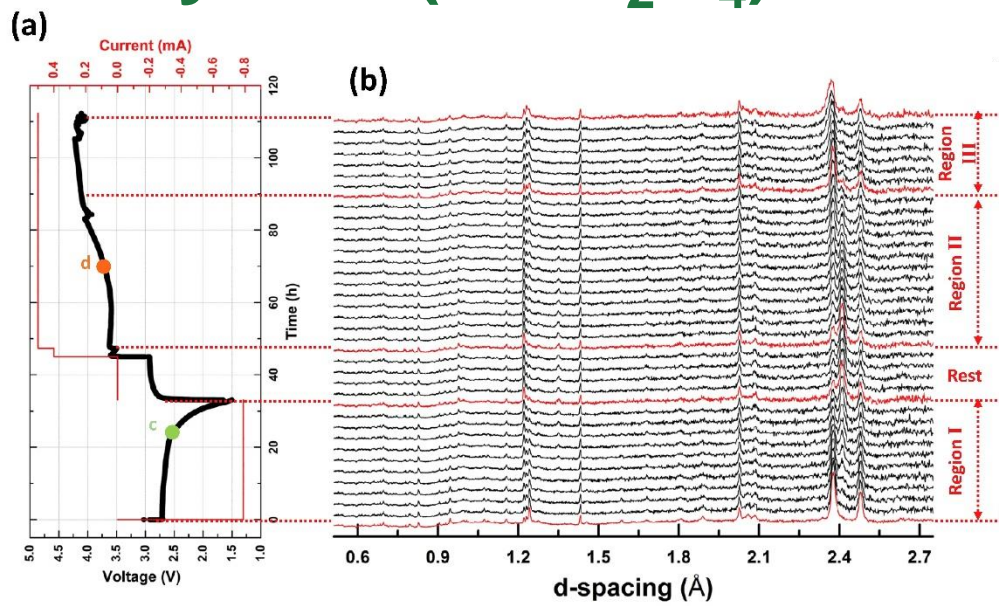
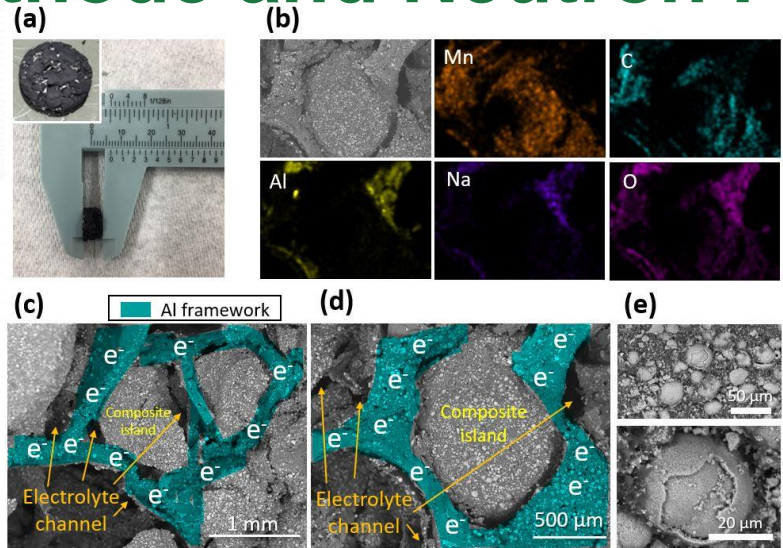
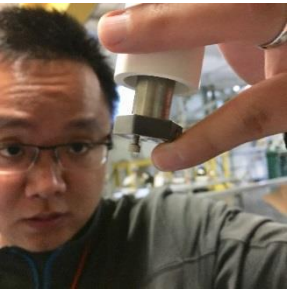
WOS	# of papers	# citations	h-index
1970-1980	144	1630	20
1981-1990	437	6157	42
1991-2000	3616	190,985	181
2001-2005	5806	287,895	208
2006-2010	9863	514,097	269
2011-2018	58589	??	??



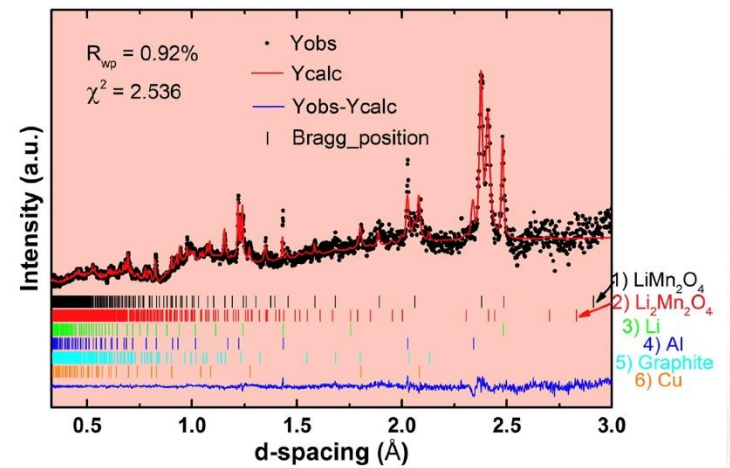
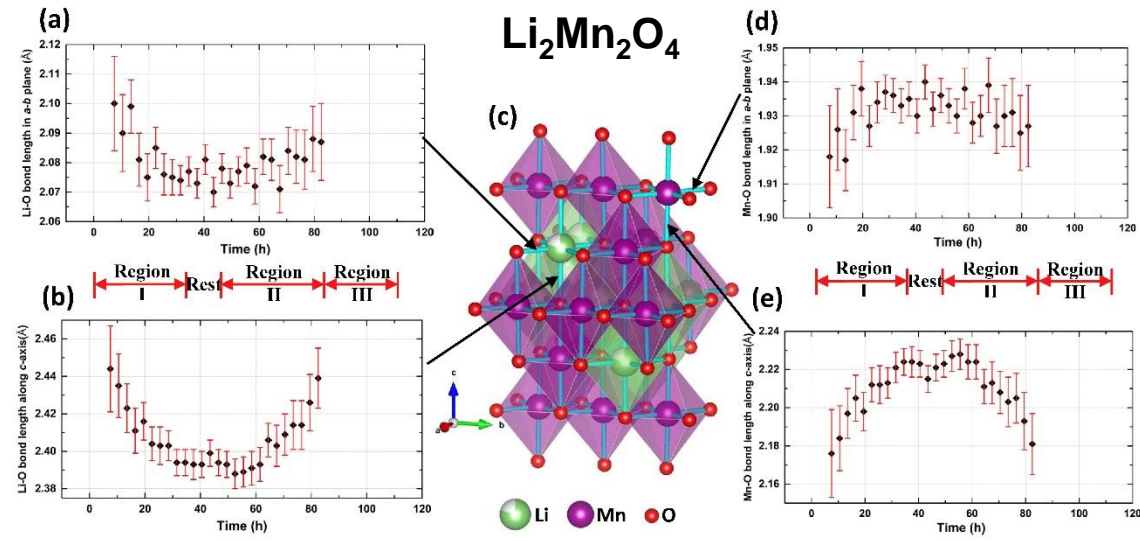
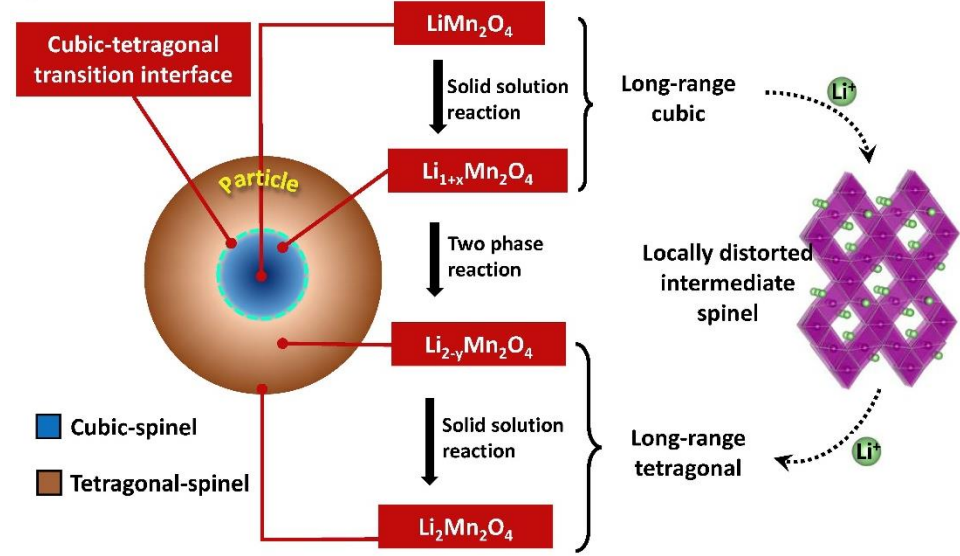
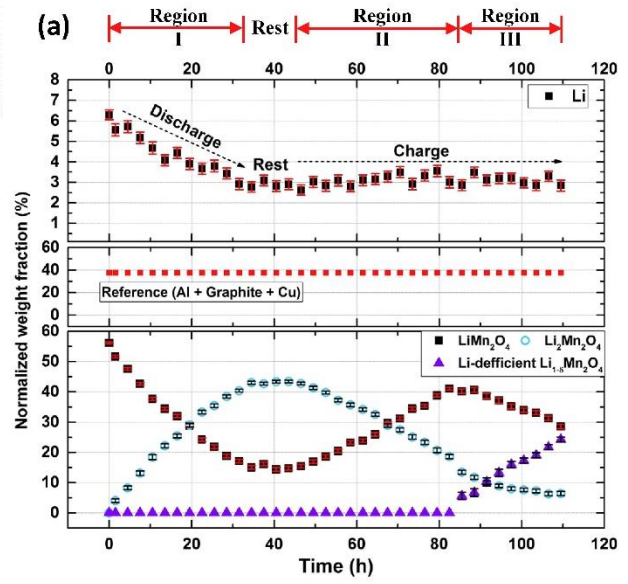
What is LIB



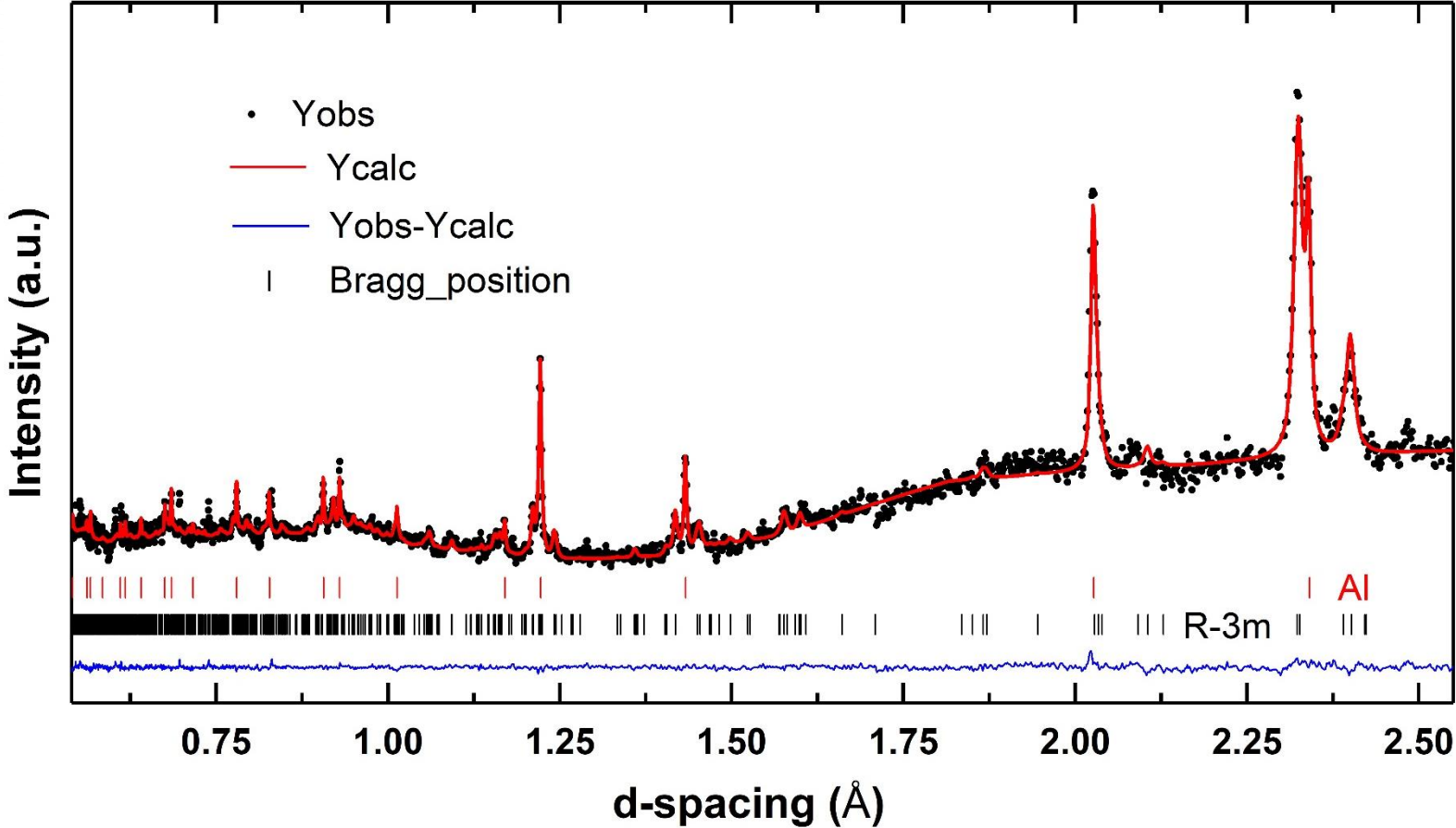
Thick cathode and Neutron Friendly Cell (LiMn_2O_4)



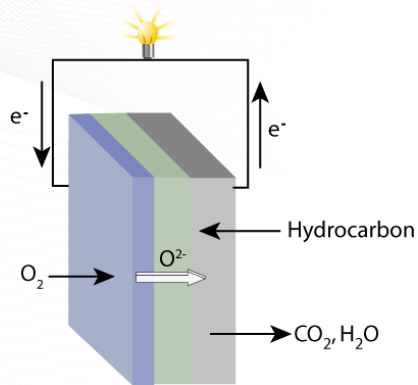
Metastable $\text{Li}_{1+\delta}\text{Mn}_2\text{O}_4$ ($0 \leq \delta \leq 1$) spinel formation



Actively working on improving data quality



Understanding Structure and Function in Solid Oxide Fuel Cell (SOFC)

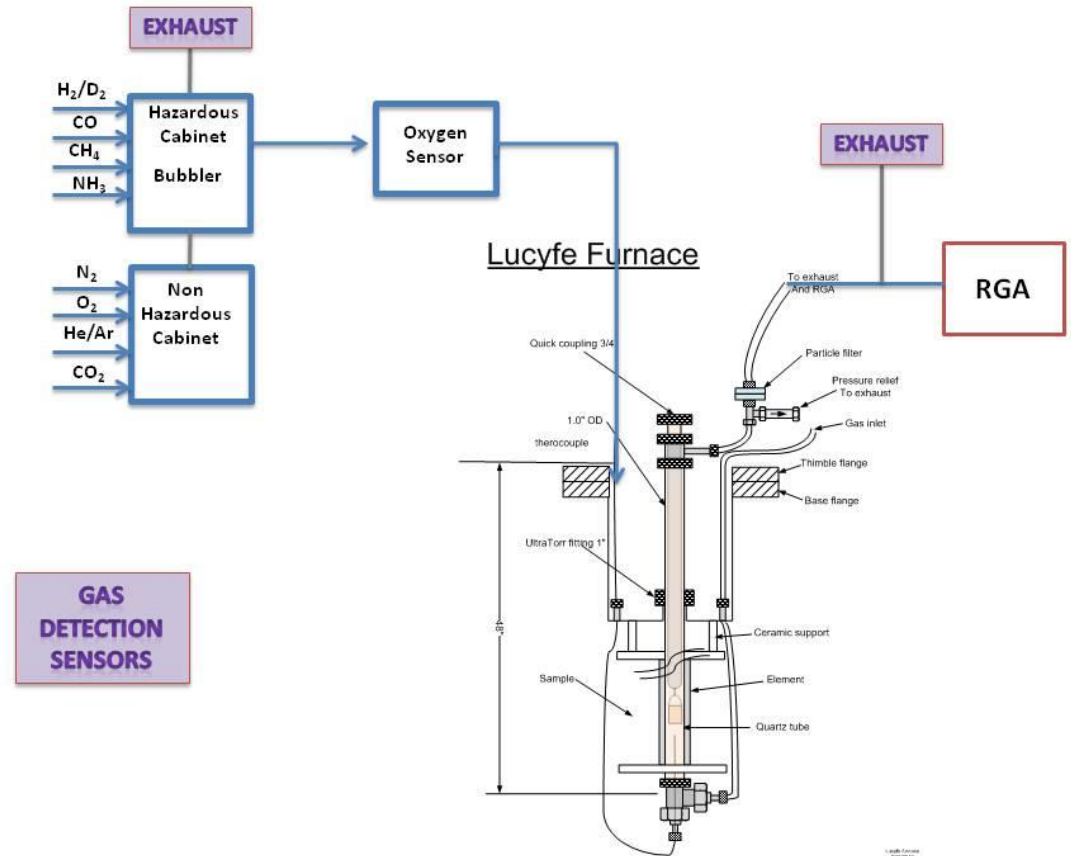


- - Cathode - Porous, 2-phase composite
- - Electrolyte - Dense, single phase
- - Anode - Porous, Multi-phase composite

Challenge

A basic understanding of the structure-function relationship that describes the influence of crystal structure and composition on oxygen ion transport is needed to fully optimize the performance of these materials.

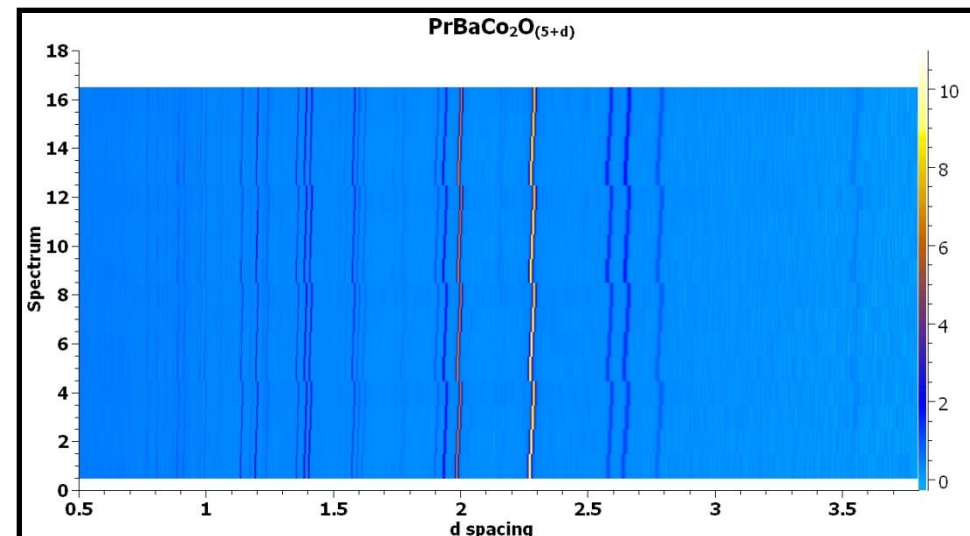
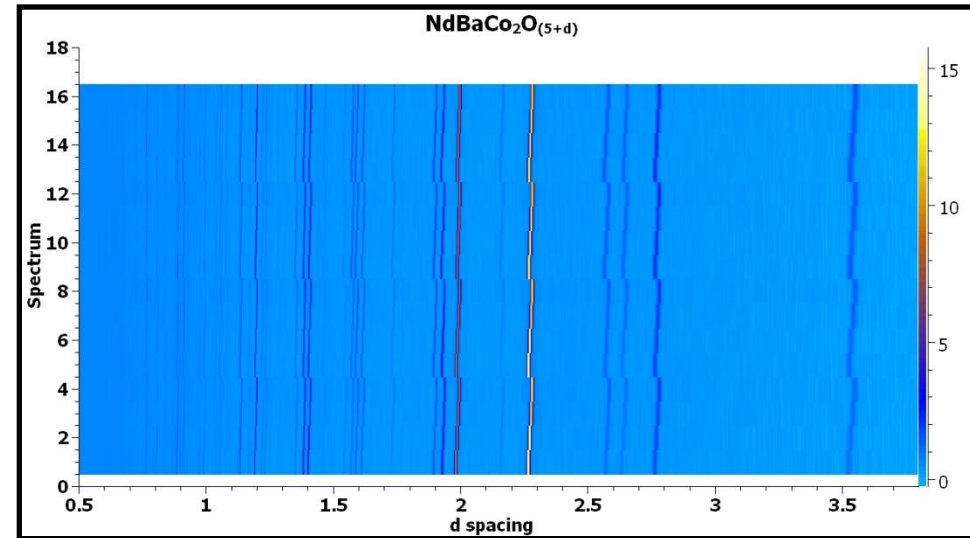
This valuable structural information must be obtained under operational condition.



An integrated sample environment that includes a high temperature furnace, a gas flow insert, a pO_2 sensor and Residual Gas Analyzer (RGA) make experiments possible under operational condition.

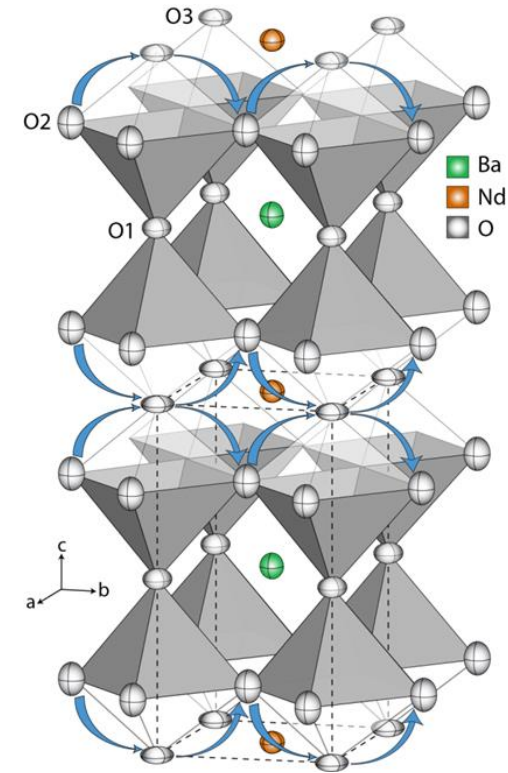
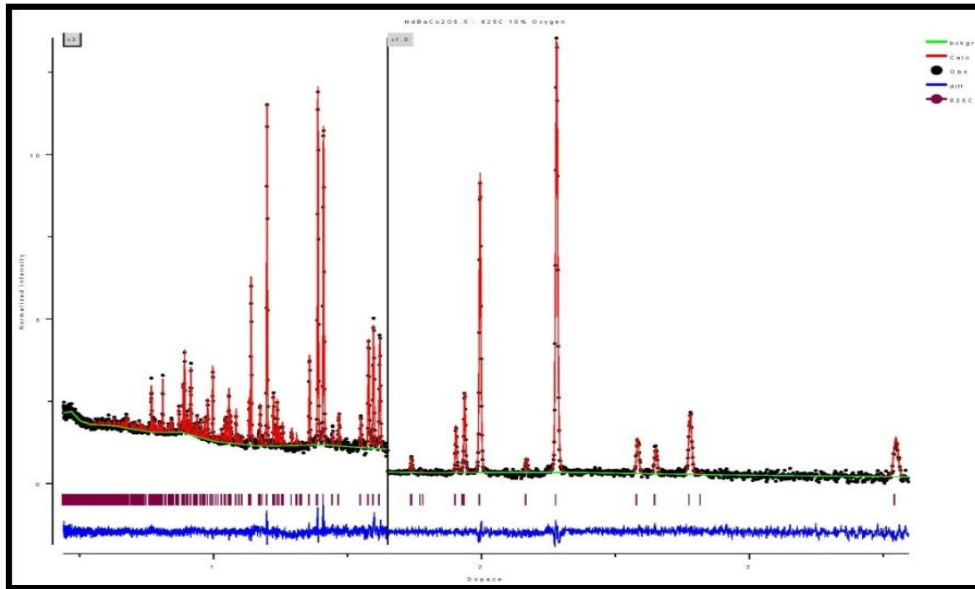
REBaCo₂O_{5±δ} : cathode materials for SOFC

- Samples of (Nd and Pr)BaCo₂O_{5±δ} were measured @ four different pO₂ and four different temperature at each pO₂
- Equilibrium state was achieved by measuring the lattice parameter. Once the lattice parameter stopped changing, longer data was collected.
- Temperature of the sample was calibrated using a standard powder under identical condition.



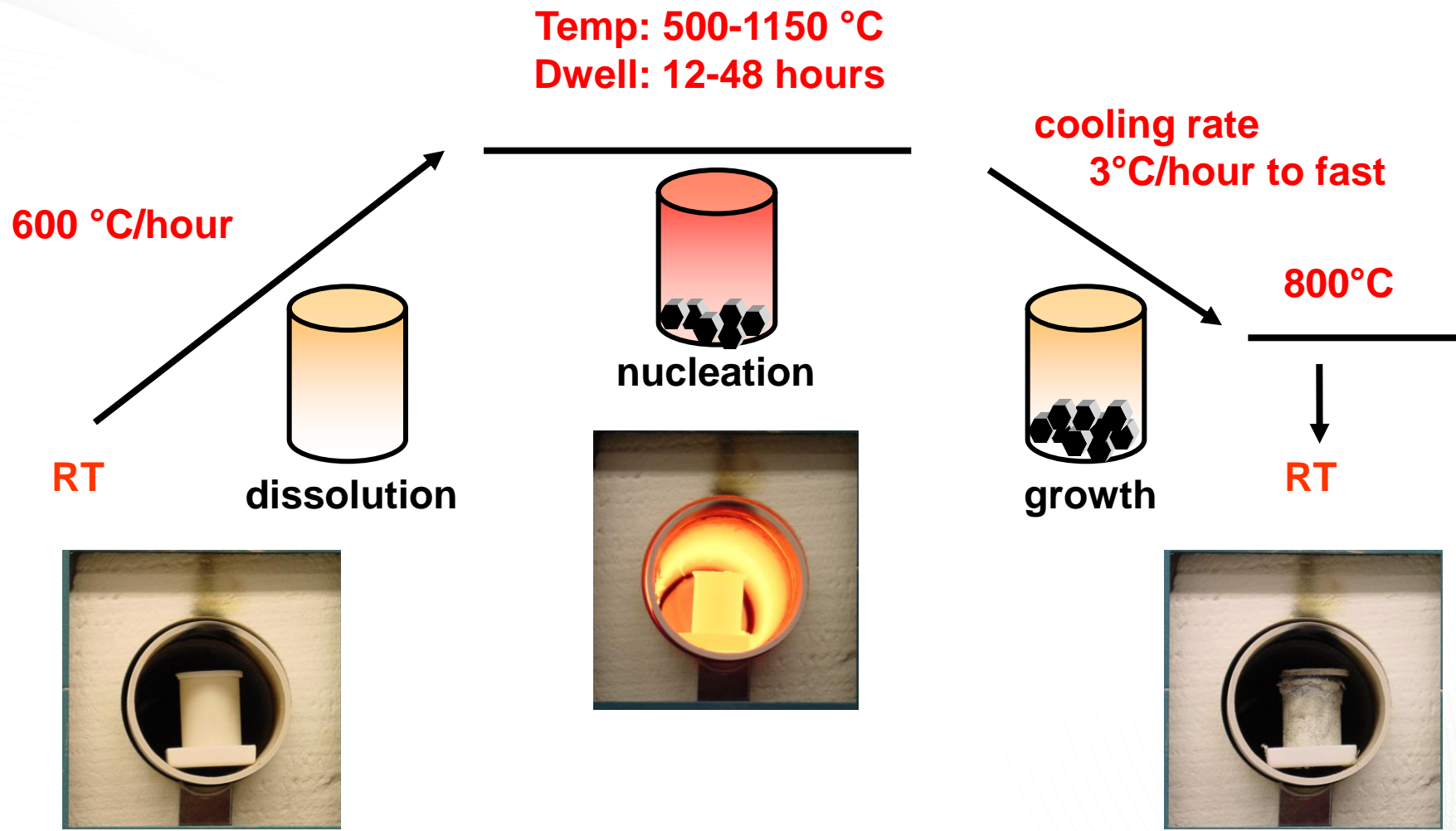
Neutrons show Oxygen migration pathway in $\text{NdBaCo}_2\text{O}_{5\pm\delta}$

R.A. Cox-Galhotra, A. Huq, J.P. Hodges, J.H. Kim, C. Yu, X. Wang, A. J. Jacobson, S. McIntosh, "Visualizing oxygen anion transport pathways in $\text{NdBaCo}_2\text{O}_{5+d}$ by in situ neutron diffraction", *J. of Mater. Chem. A* 1, 3091 (2013)

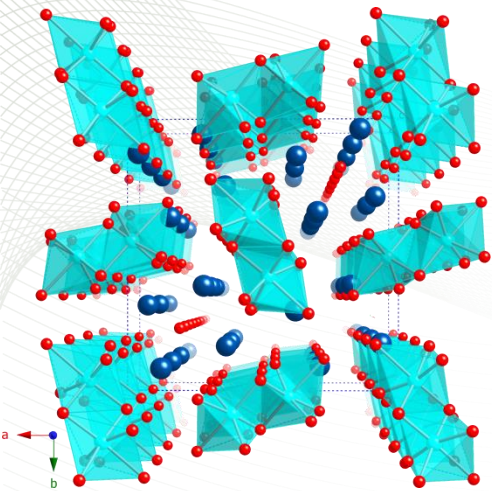


- High Q data allows refinement of anisotropic thermal parameters and oxygen vacancy. Combined with near neighbor distances, it allows us to directly visualize the oxygen diffusion pathway.
- The structure is Tetragonal and not Orthorhombic as previously suggested in these $p\text{O}_2$ values.
- O3 site exhibits the largest vacancy and anisotropic motion. Motion of O2 is also very anisotropic which can hop to the near neighbor in the vacancy rich NdO plane. Fully Occupied O1 site has very small displacement and hence limited motion.

Open Crucible Flux Crystal Growth

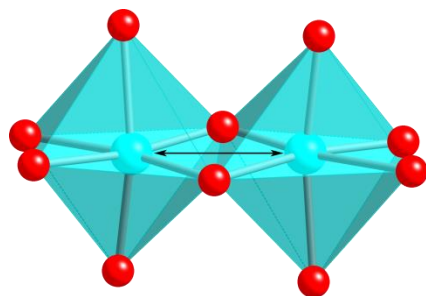


Synthesis of $\text{La}_4\text{Mo}_2\text{O}_{11}$ using flux growth at POWGEN



$\text{La}_4\text{Mo}_2\text{O}_{11}$
 Space Group: $P 4_2/n$
 $a=13.0036 \text{ \AA}$
 $c=5.6573 \text{ \AA}$

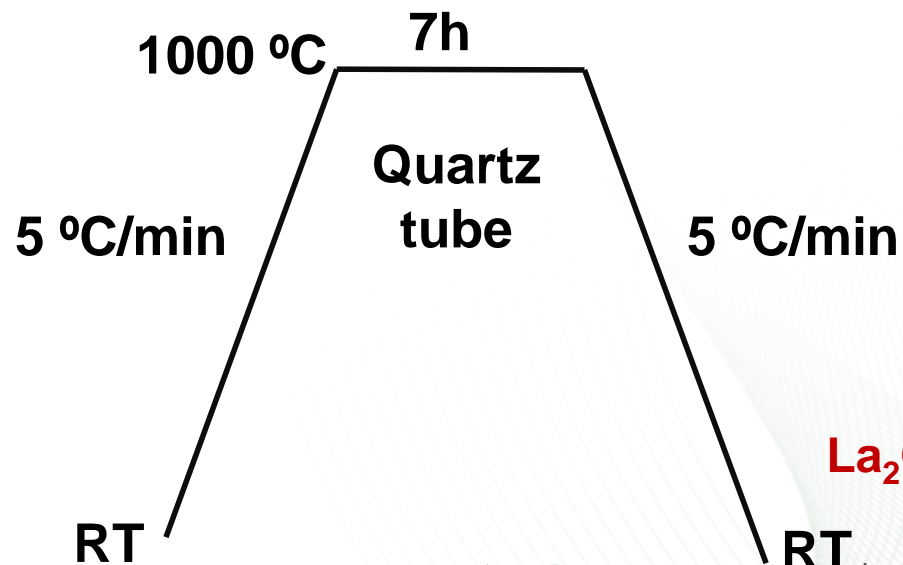
Two distorted MoO_6 octahedra are edge shared with each other to form isolated Mo_2O_{12} clusters.



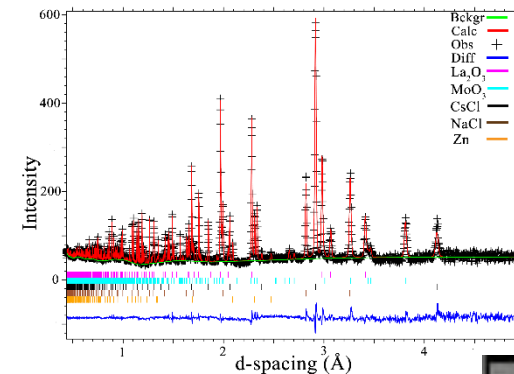
Two distorted MoO_6 octahedra are edge shared with each other to form isolated Mo_2O_{12} clusters.



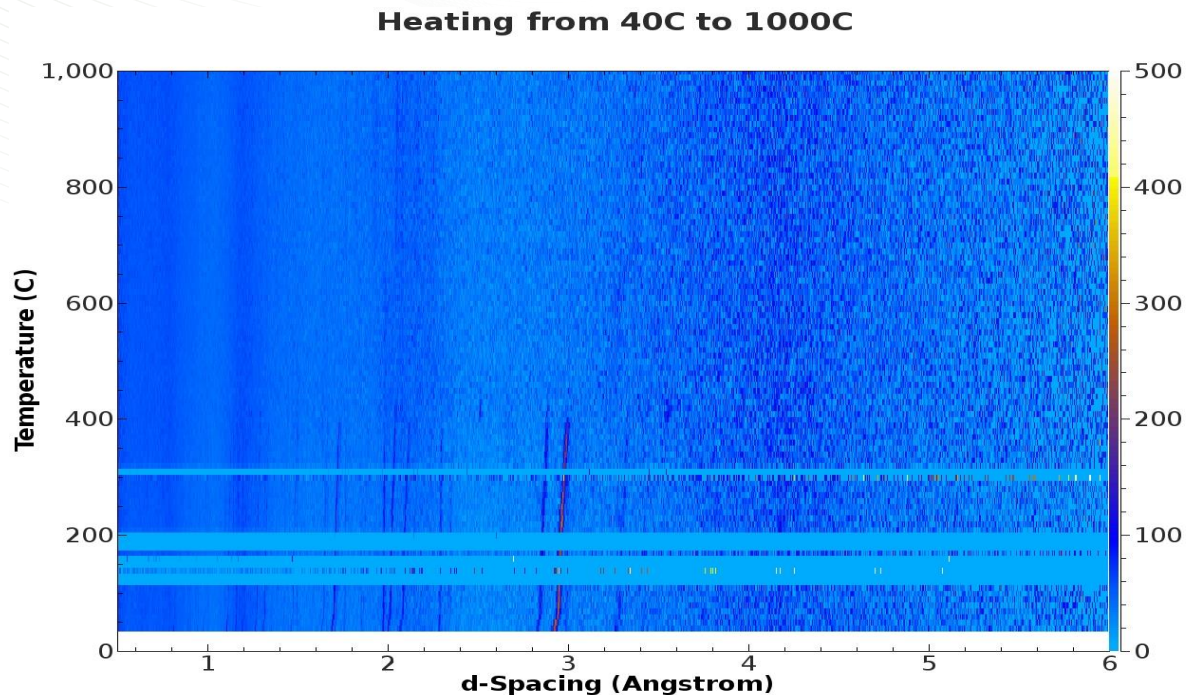
1:2 reagent to flux ratio



$\text{La}_2\text{O}_3 + \text{MoO}_3 = 0.3\text{g}$



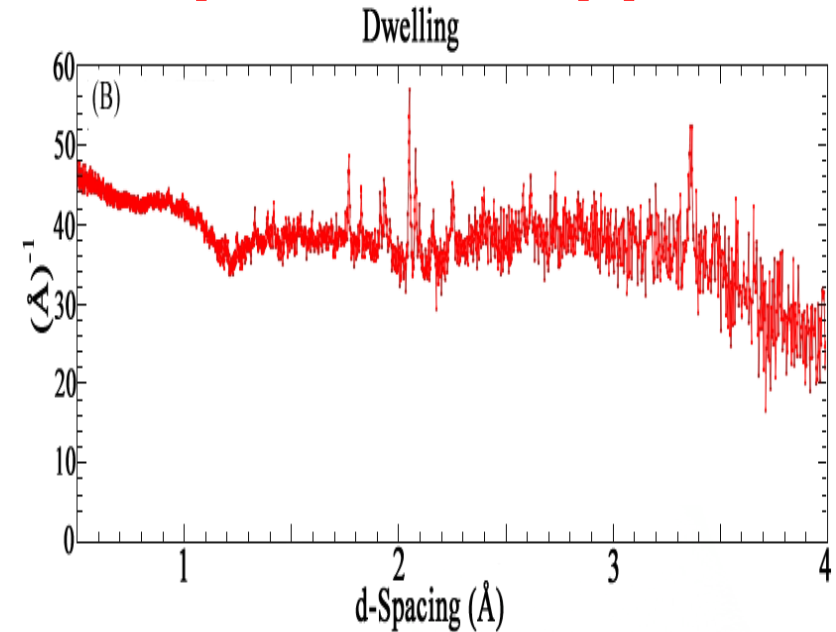
Heating the sample and continuously collecting Data (Event mode)



2D-plot of the heating of $\text{La}_4\text{Mo}_2\text{O}_{11}$

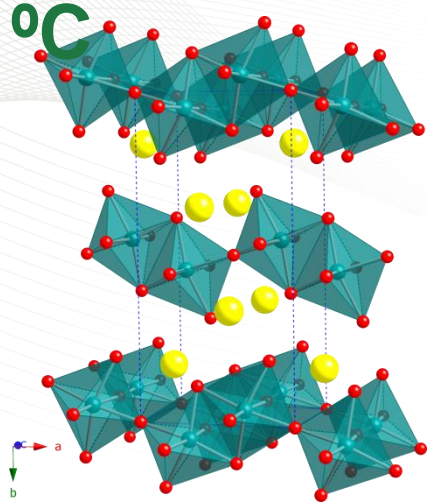
At roughly 450 °C starting materials melted. No diffraction peaks were observed afterwards.

Dwelling at 1000 °C : Peaks grow in – not the expected product With time, peaks disappear

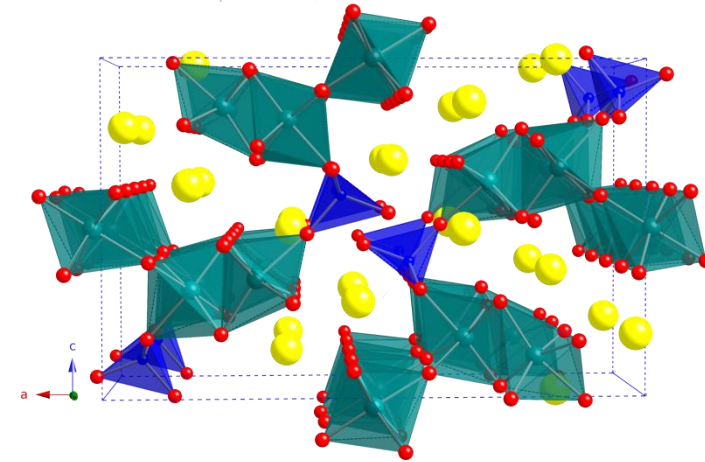


- Diffraction peaks can be observed in the dwelling at 1000 °C, which are not the final products. These peaks disappear on cooling.
- Lab experiments were subsequently carried out to isolate the phase(s) formed during the dwelling period.

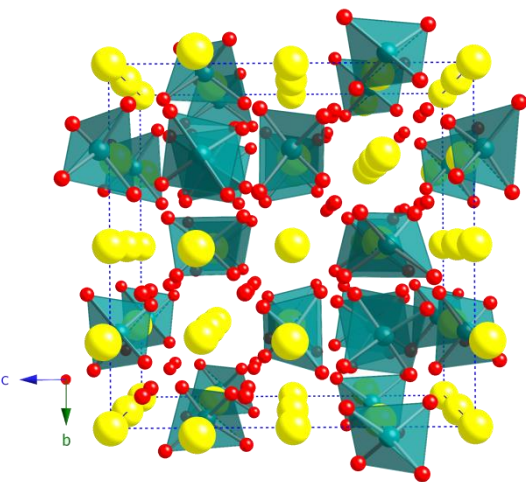
Laboratory Experiments – Quenched Reactions at 1000



$\text{La}_2\text{Mo}_2\text{O}_7$ (Mo^{4+}) – Black powder

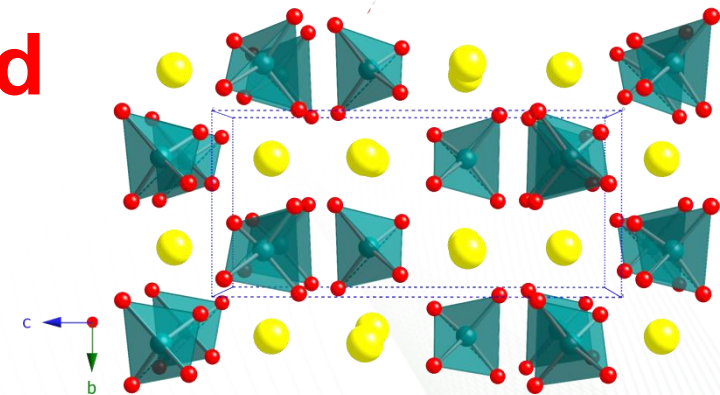


$\text{La}_3\text{Mo}_4\text{SiO}_{14}$ ($\text{Mo}^{4.5+}$) – Black rods



$\text{La}_5\text{Mo}_3\text{O}_{16}$ ($\text{Mo}^{5.6+}$) – Black cubes

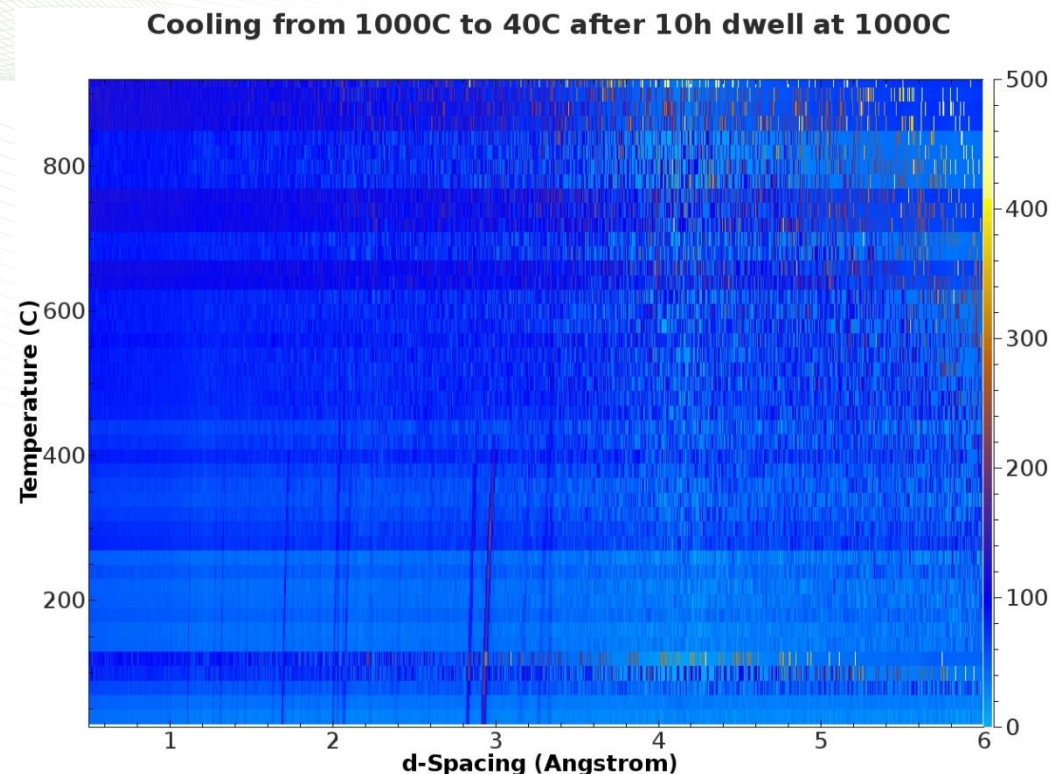
Note: None of the phases are the expected phase, $\text{La}_4\text{Mo}_2\text{O}_{11}$



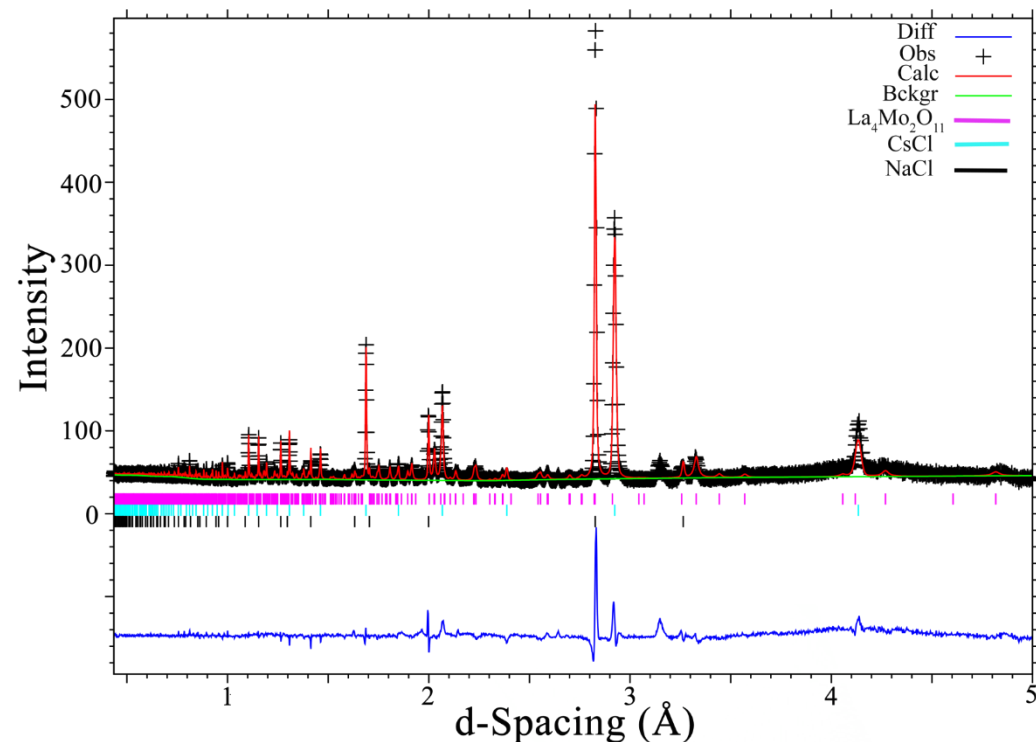
$\text{La}_{0.5}\text{Na}_{0.5}\text{MoO}_4$ (Mo^{6+}) – Gray bars



Cooling to form $\text{La}_4\text{Mo}_2\text{O}_{11}$



Roughly around 450 °C, diffraction peaks start to appear. These match the final product, $\text{La}_4\text{Mo}_2\text{O}_{11}$, and the flux, NaCl/CsCl.

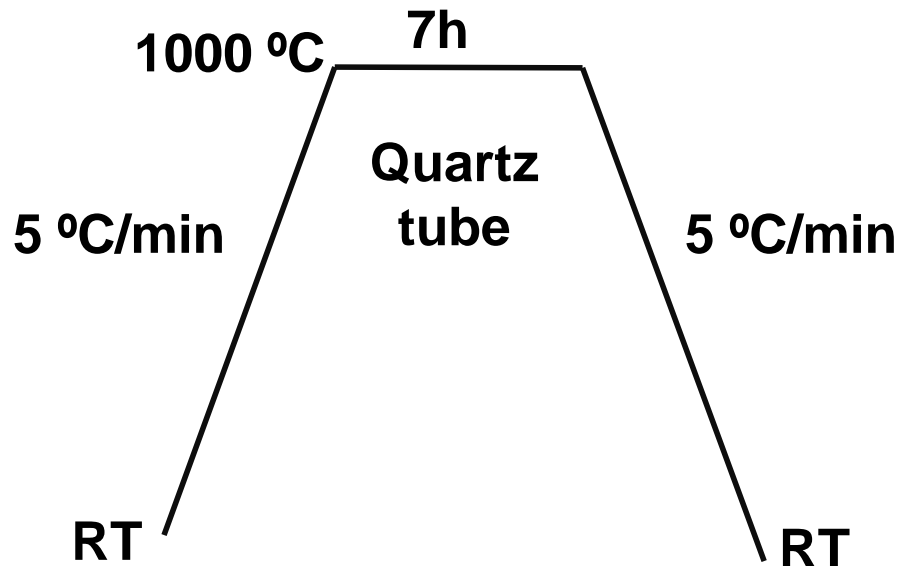


Neutron diffraction data of the end product, $\text{La}_4\text{Mo}_2\text{O}_{11}$, along with NaCl/CsCl flux. RT data at end of experiment – some impurity?

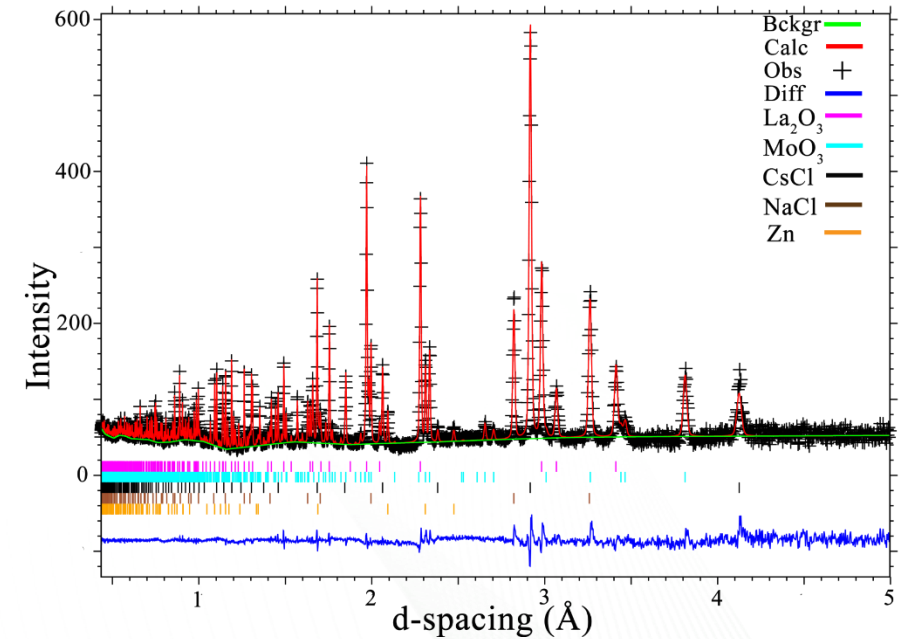
Neutron Studies at POWGEN with More Starting Materials



2:1 reagent to flux ratio

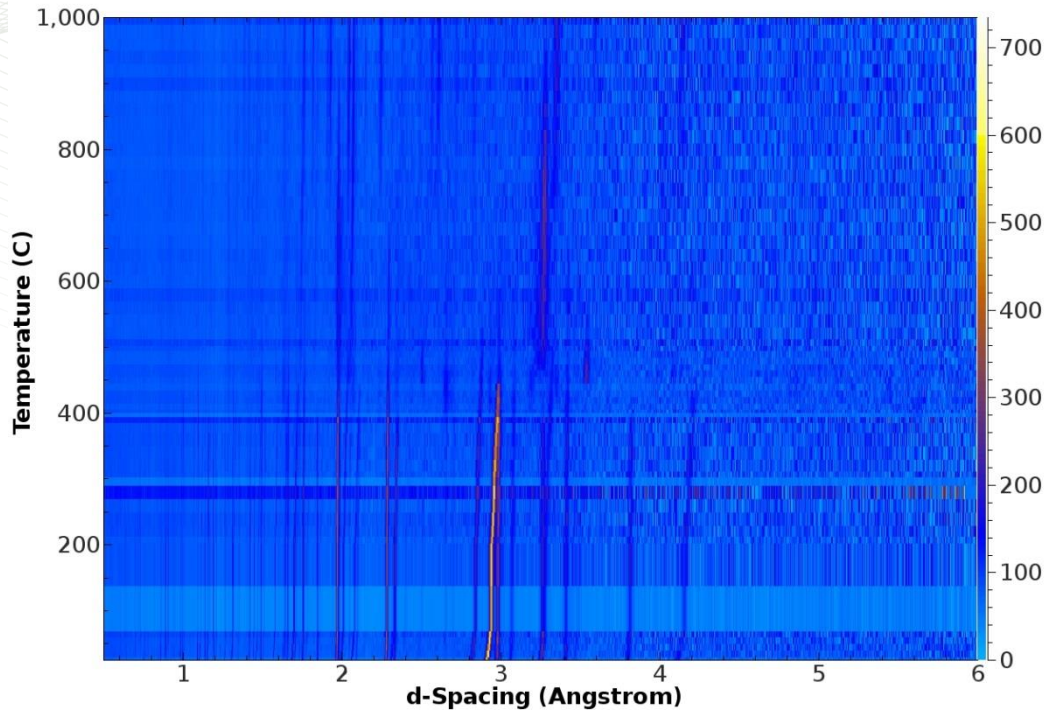


$\text{La}_2\text{O}_3 + \text{MoO}_3 = 1\text{g}$



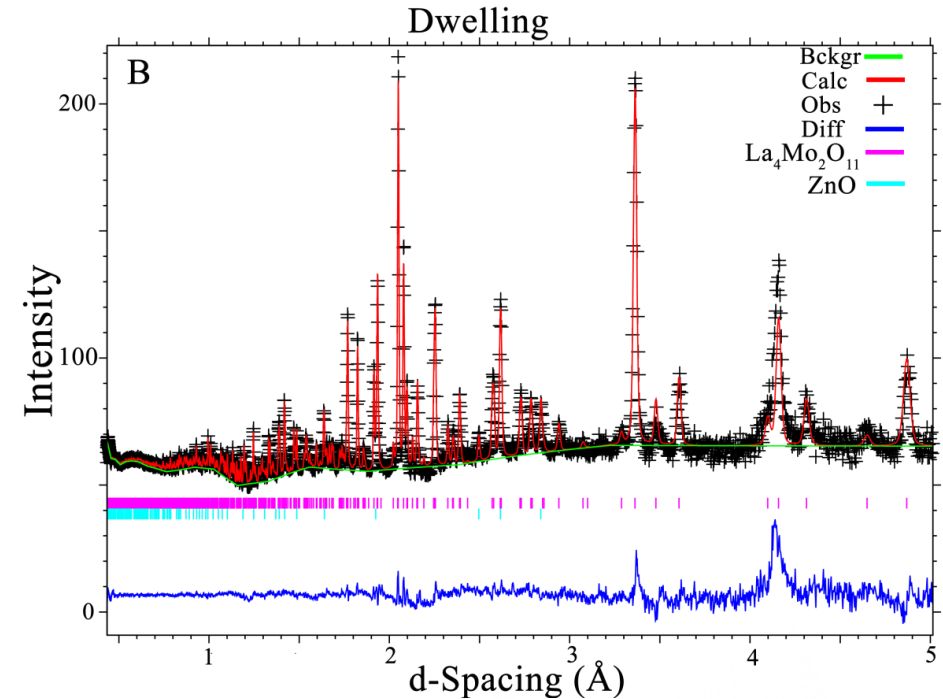
Heating to 1000C

Heating from RT to 1000C



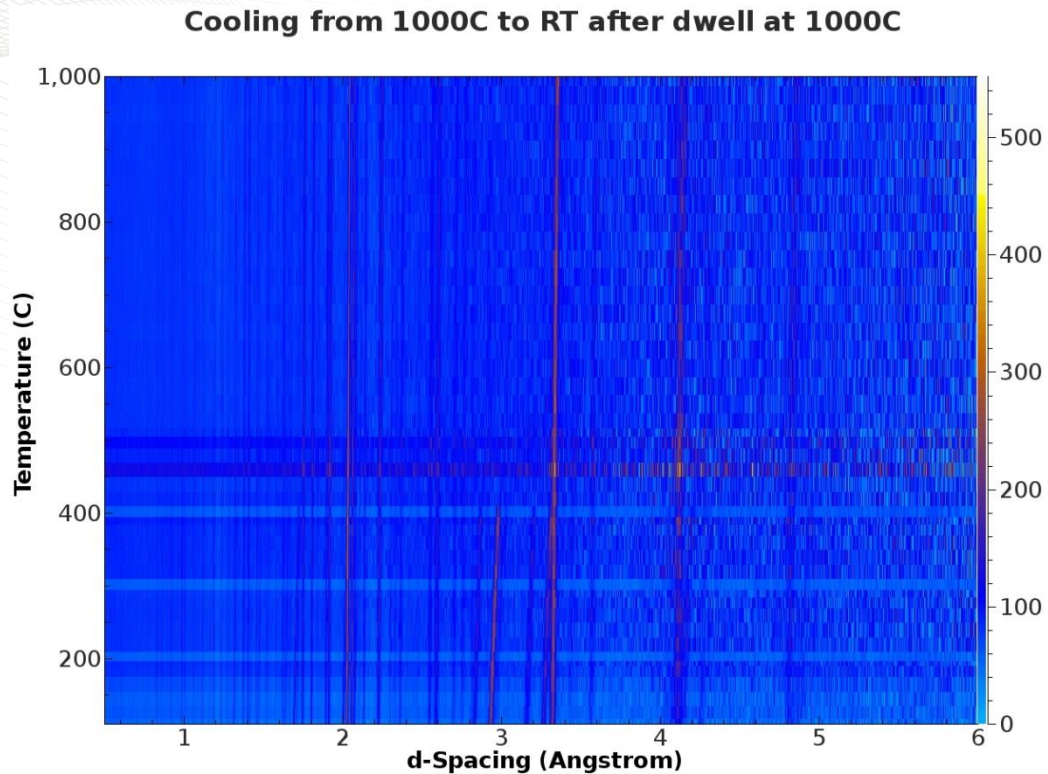
Very different from the last set of data. At roughly around 400 °C, starting materials starts to disappear, but new phase(s) form afterwards.

Dwelling at 1000 °C Peaks grow in – This time the target phase

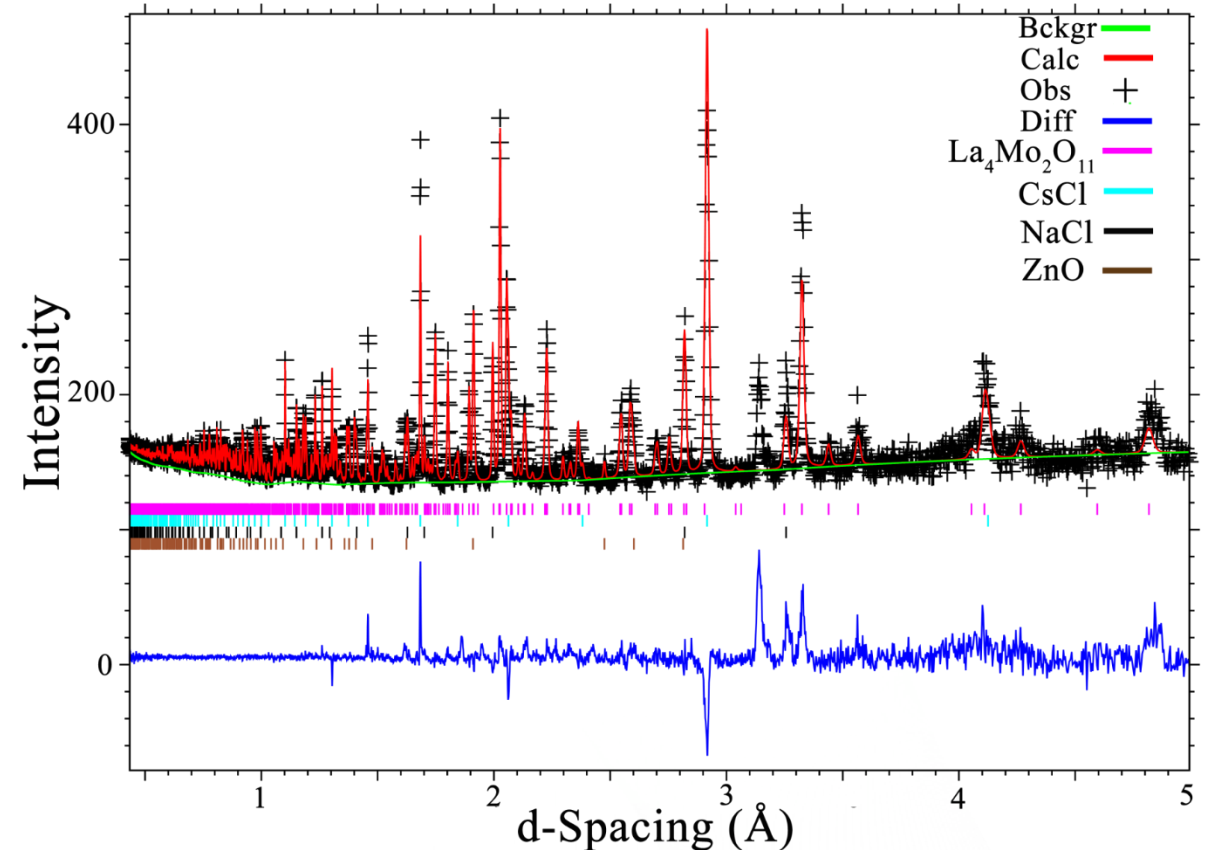


- Diffraction peaks can be observed in the dwelling at 1000 °C, which are final products.
- Lab quenching experiments also confirmed this result.

Cooling from 1000C to RT

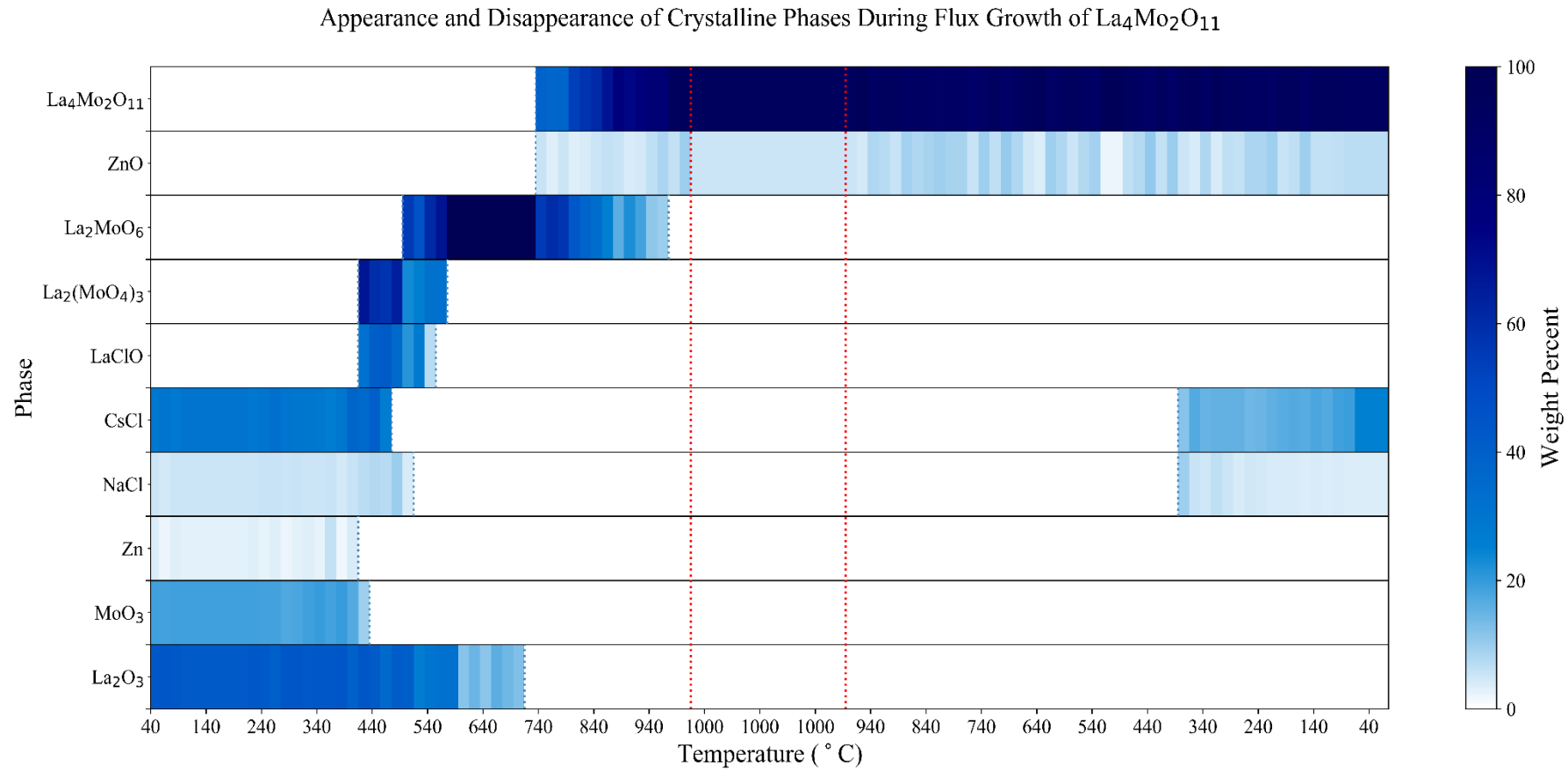


La₄Mo₂O₁₁ and ZnO observed at 1000 °C continued remain in the cooling period.



Neutron diffraction data of the end product, La₄Mo₂O₁₁ and ZnO, along with NaCl/CsCl flux. RT data at end of experiment – same impurity? peak observed in the last experiment.

Appearance and Disappearance of Crystalline Phases During Flux of $\text{La}_4\text{Mo}_2\text{O}_{11}$



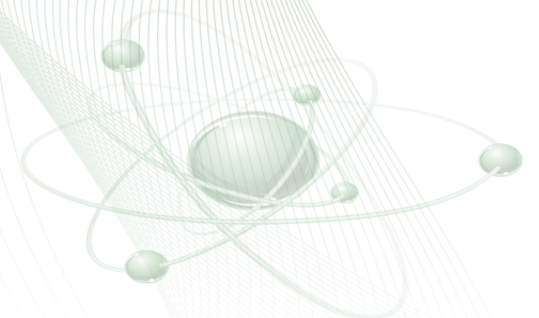
Magnetism using Powder Diffraction



- Neutrons have a **MAGNETIC** moment
- + determine microscopic magnetic structure
 - + study magnetic fluctuations

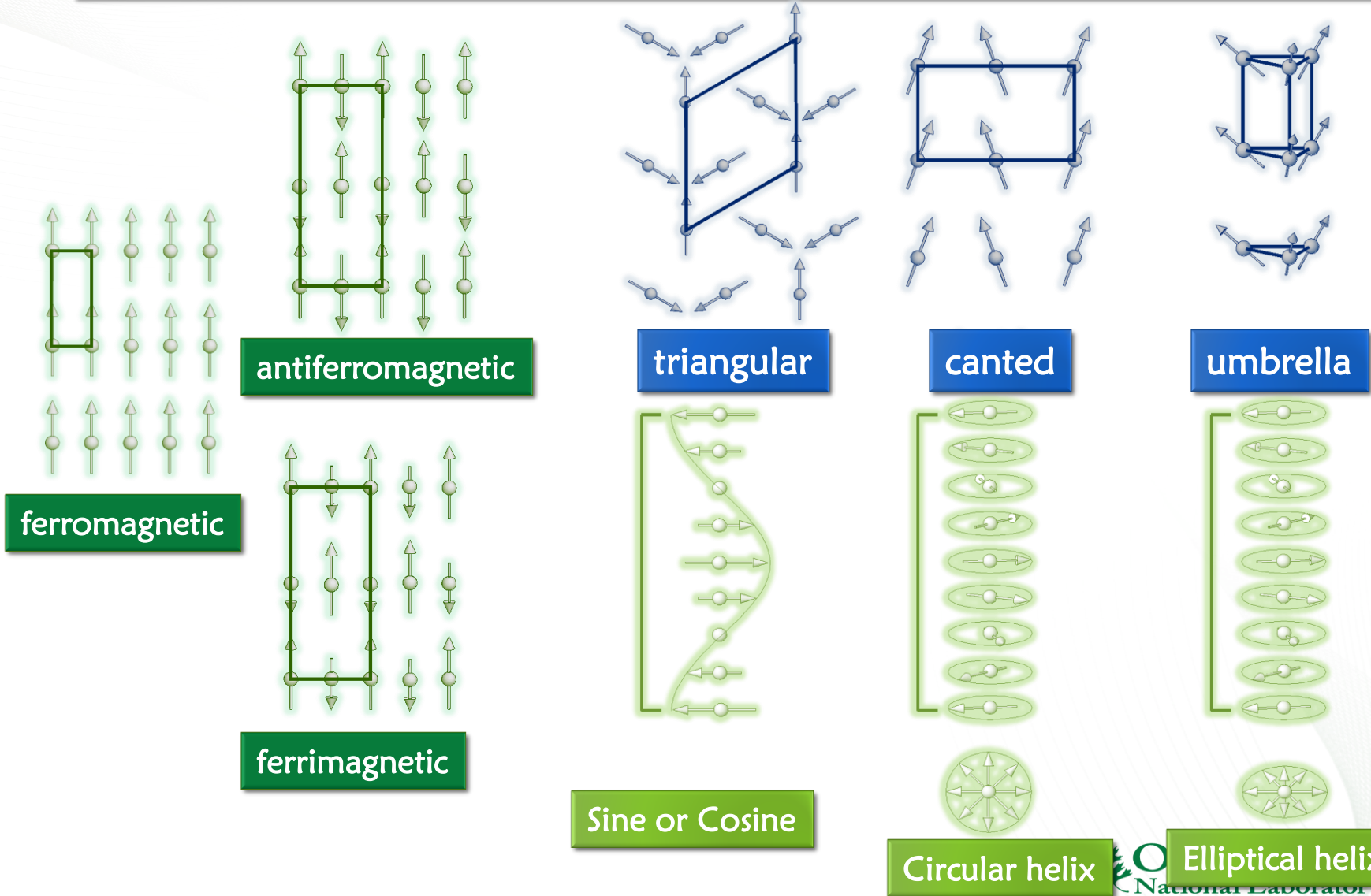


- Neutrons have **SPIN**
- + can be formed into polarized neutron beams



Magnetic structures

MAGNETISM → originates from orbital and spin motions of unpaired electrons and their interactions



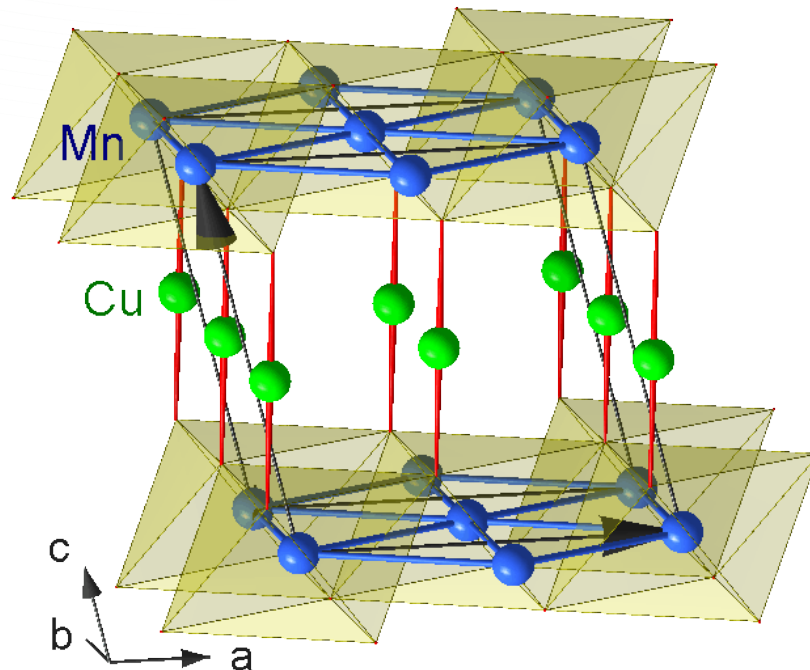
Magnetoelastic effect in the Triangular Lattice System CuMnO_2

F. Damay *et al.*, PRB 80, 094410 (2009)
V. O. Garlea *et al.*, PRB 83, 172407 (2011)

Monoclinic: $C2/m$

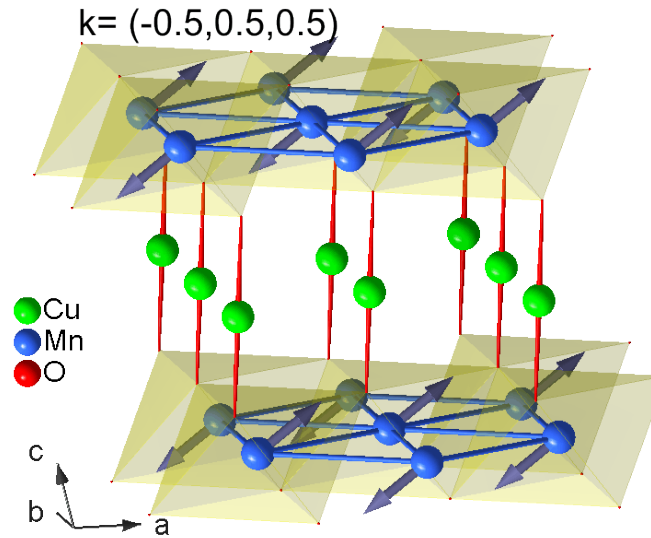
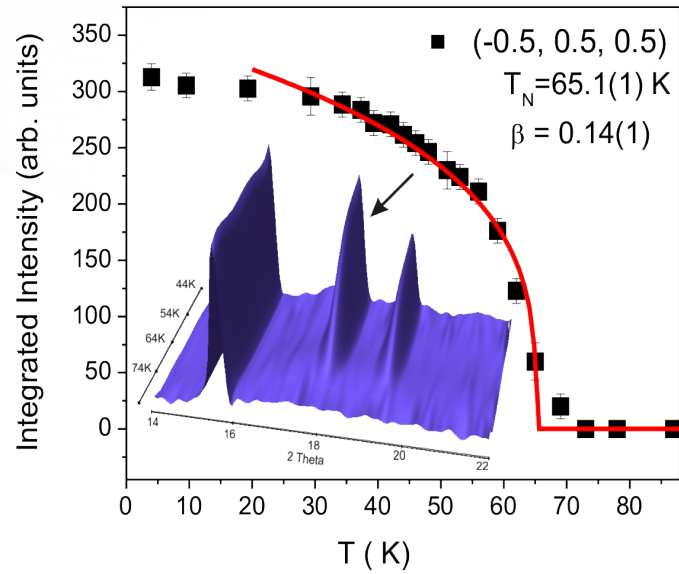
Jahn-Teller distortion of Mn^{3+}O_6
($3d^4$)

Ferro-orbital ordering $d_{3x^2-z^2}$

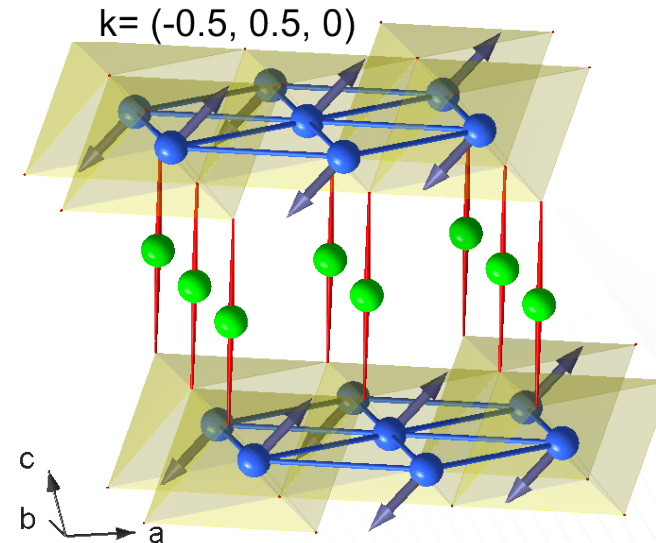
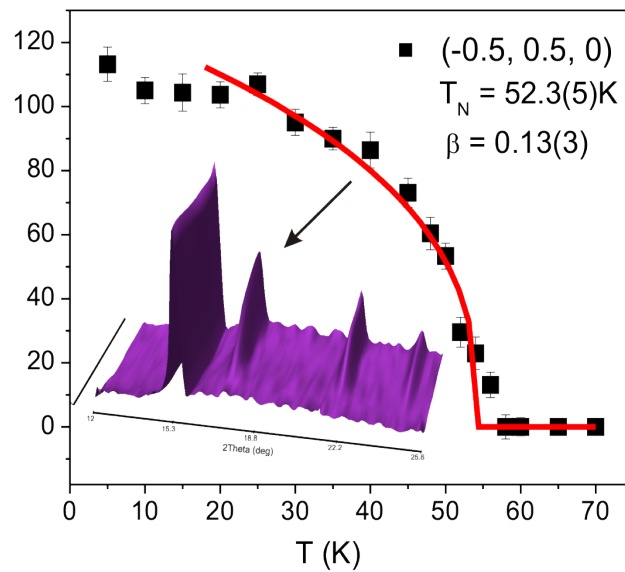


Cu(Mn_{1-x}Cu_x)O₂ : Tuning of Magnetism by chemical substitution

CuMnO₂



Cu(Mn_{0.93}Cu_{0.07})O₂



Thank You Questions?

