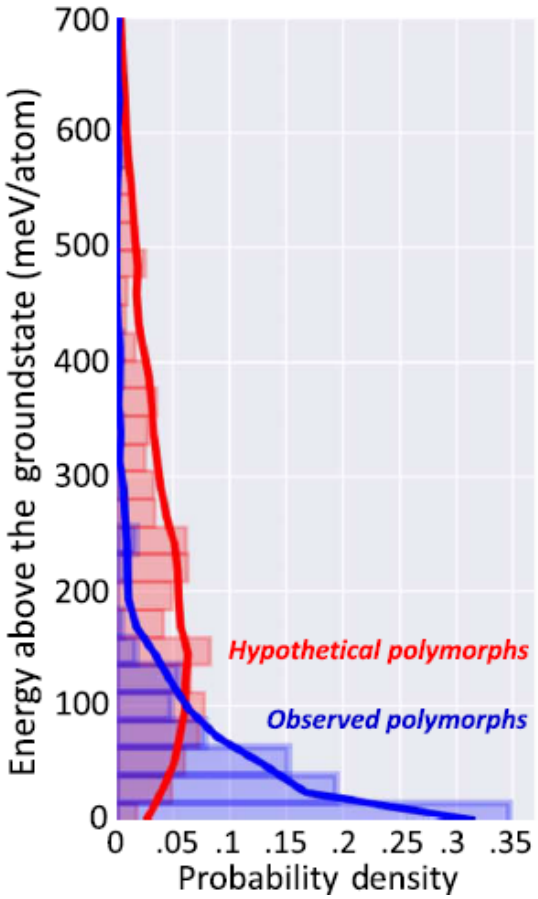
CNGMD
Incorporating Metastability

2015-2019

Center for Next Generation Materials by Design

a DOE Office of Science Energy Frontier Research Center • *www.cngmd-efrc.org*

Evaluating the synthesizability of metastable materials beyond the DFT convex hull



MATERIALS SCIENCE & ENGINEERING
UNIVERSITY OF MICHIGAN

Wenhao Sun

Dow Early Career Professor

University of Michigan

Materials Science and Engineering

AI-Guided Discovery of Metastable Materials

NATIONAL ACADEMIES Sciences Engineering Medicine

nature

Google DeepMind

AI tool GNoME finds 2.2 million new crystals, including 380,000 stable materials that could power future technologies

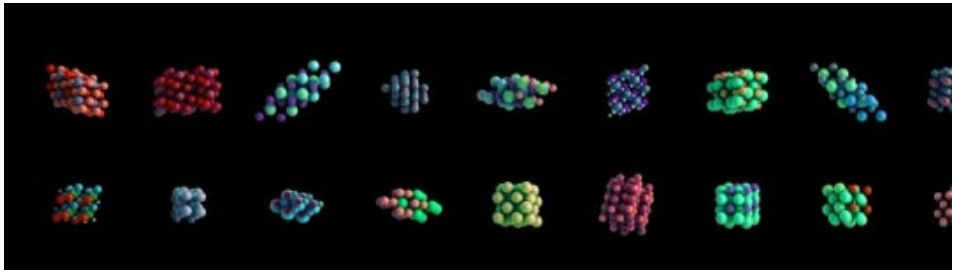
Merchant, Amil, et al. "Scaling deep learning for materials discovery." *Nature* (2023)

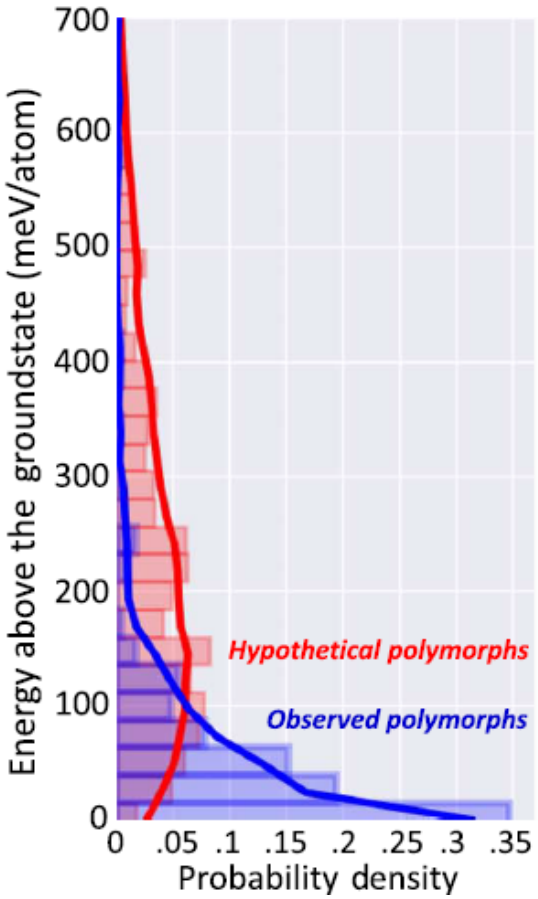
nature

Microsoft | Research

Much like an image diffusion model generates pictures from a text prompt … MatterGen generates proposed structures by adjusting the positions, elements, and periodic lattice from a random structure.

Zeni, Claudio, et al. "A generative model for inorganic materials design." *Nature* (2025)





AI-Guided Discovery of Metastable Materials

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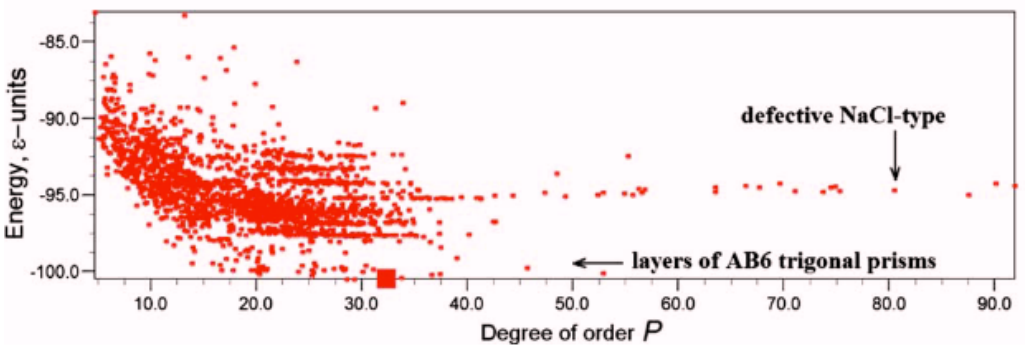
THE JOURNAL OF CHEMICAL PHYSICS **130**, 104504 (2009)

How to quantify energy landscapes of solids

Artem R. Oganov[1,2,a)] and Mario Valle[3]



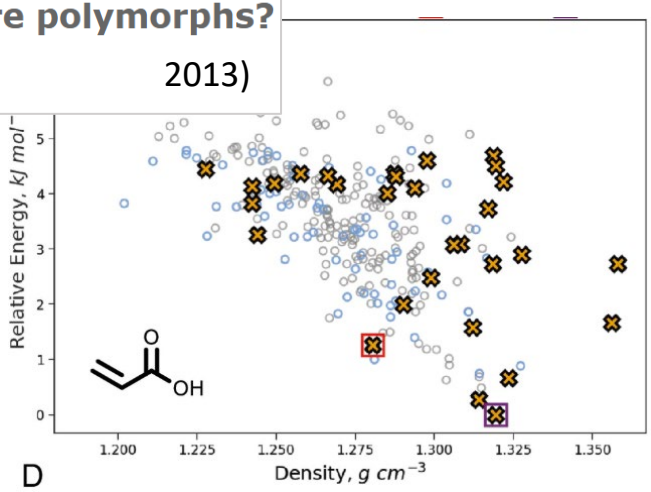
Why don't we find more polymorphs?

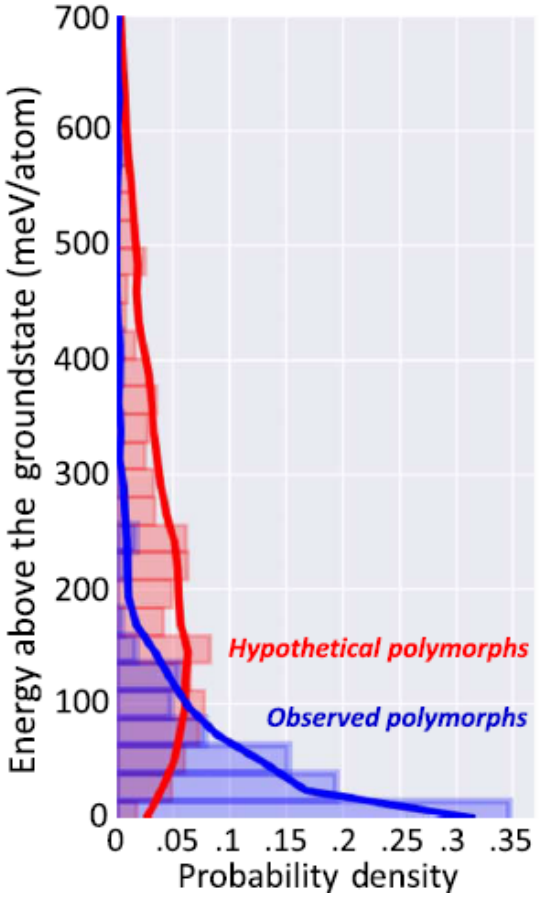
Sarah L. Price*

2013)

Acta Cryst B
STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Butler, Day, *PNAS* (2023)





*W. Sun, *et al.*, *Science Advances* (2016)

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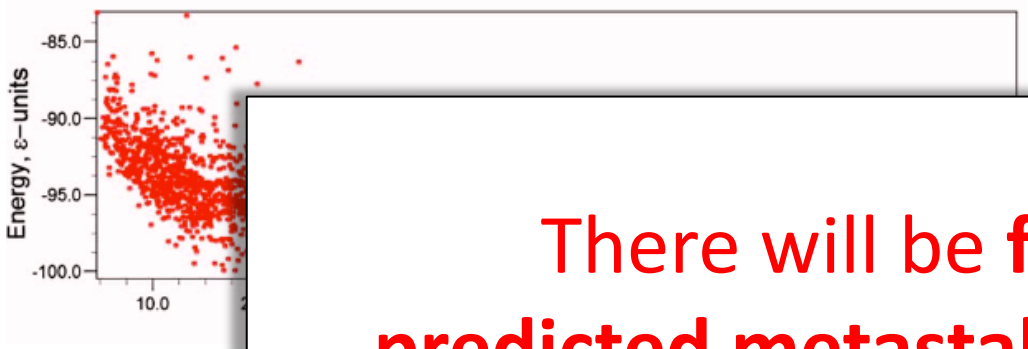


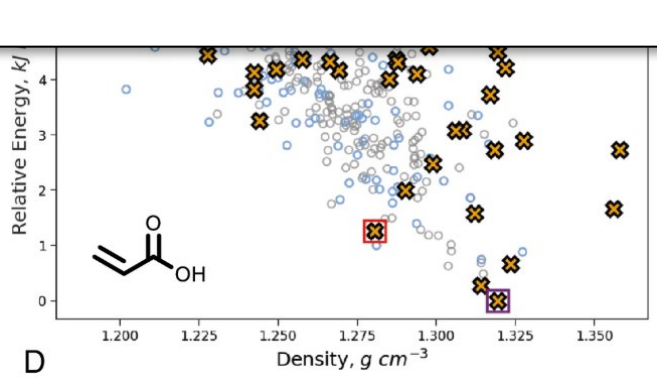
Why don't w

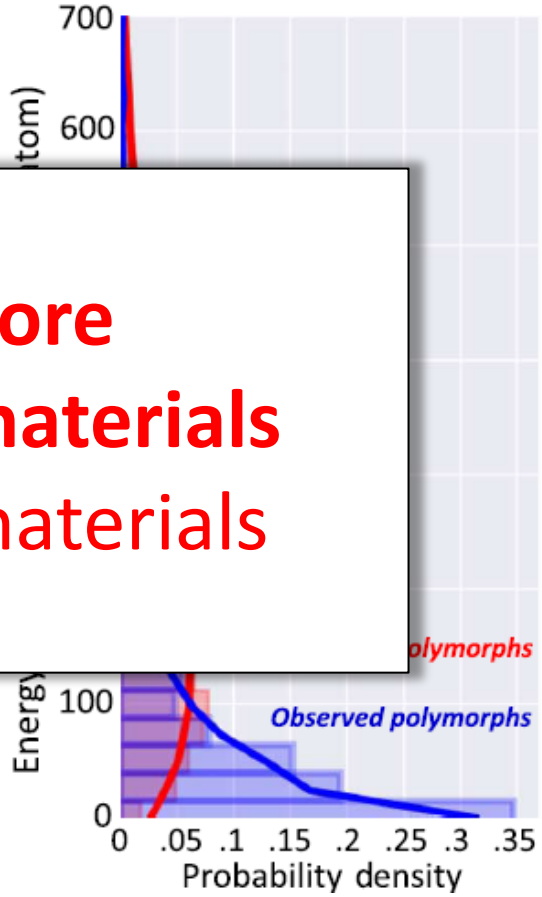
Sarah L. Price*

Acta Cryst B STRUCTUR CRYSTAL ENGINEERING MATERIALS

Butler, Day, *PNAS* (2023)

There will be **far more**
predicted metastable materials
than predicted stable materials





*W. Sun, *et al.*, *Science Advances* (2016)

AI-Guided Discovery of Metastable Materials

NATIONAL ACADEMIES Sciences Engineering Medicine

The Overprediction Problem

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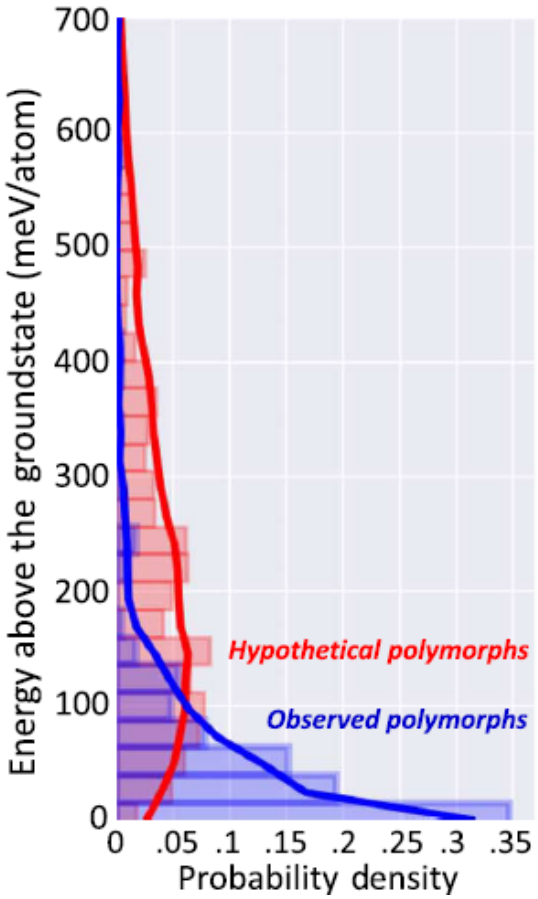

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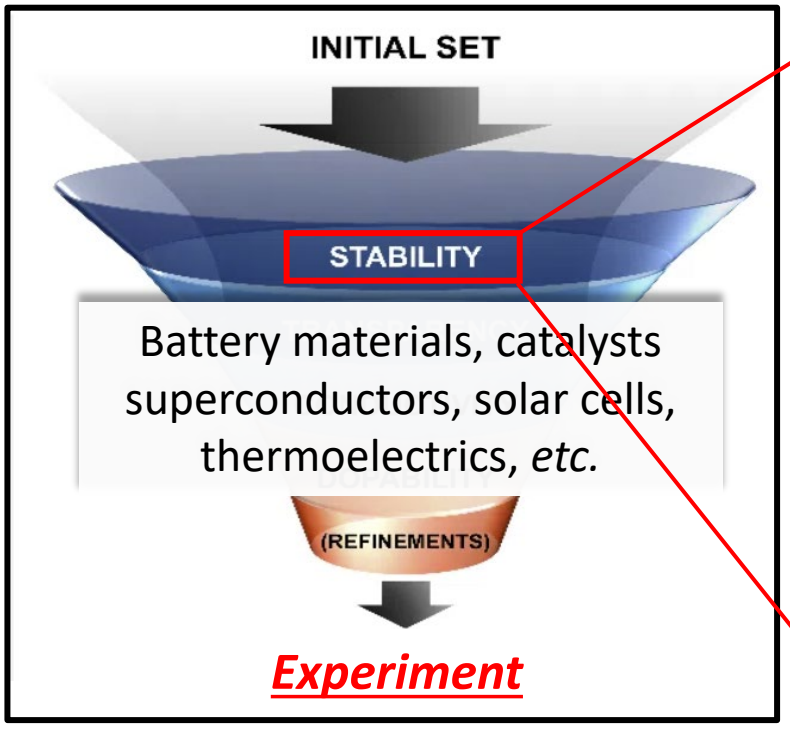
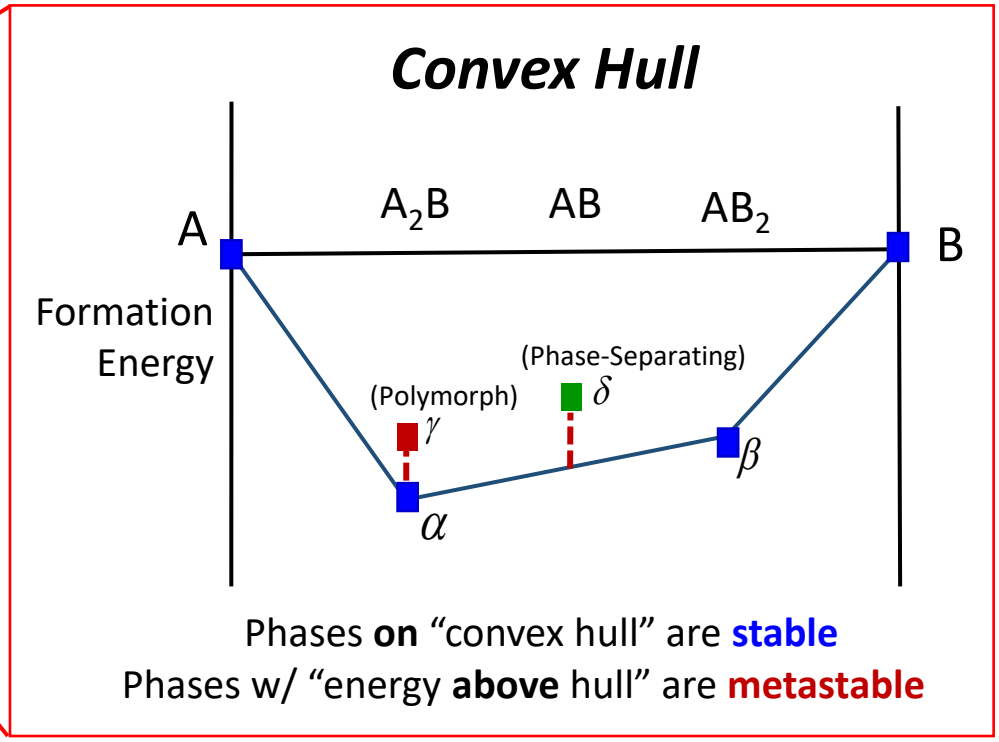




We know that:

Most materials we encounter are stable.

Metastable materials exist and can be useful (Diamond C, Anatase TiO_2, $YBa_2Cu_3O_{7-x}$)

90% of known metastable materials have $\Delta E_{hull} < 70$ meV/atom *W. Sun, *et al.*, *Science Advances* (2016)

100% of known metastable materials have ΔE_{hull} < 'Amorphous limit' *M. Aykol *et al.*, *Science Advances* (2018)

The Synthesizability Assumption

Stable materials ($\Delta E_{hull} = 0$) are synthesizable

Metastable material close to the hull ($\Delta E_{hull} < 70$ meV/atom) are probably synthesizable

Highly metastable materials are risky to pursue experimentally

RESEARCH ARTICLE | MATERIALS SCIENCE

Science Advances

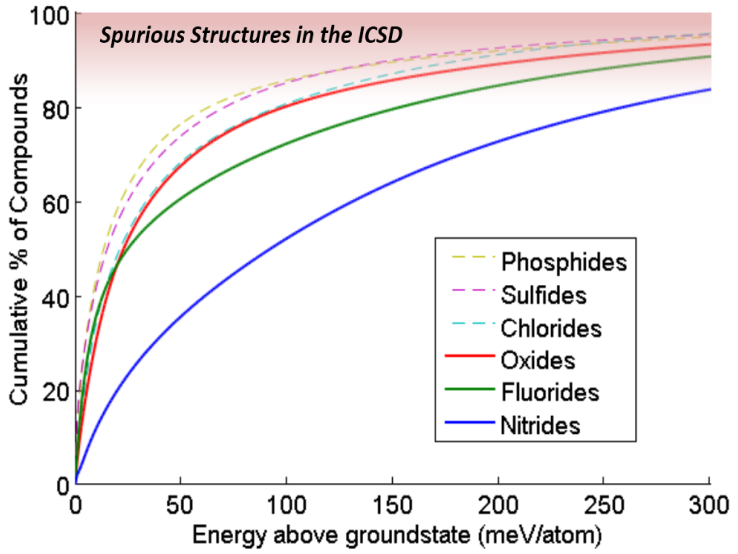
The thermodynamic scale of inorganic crystalline metastability

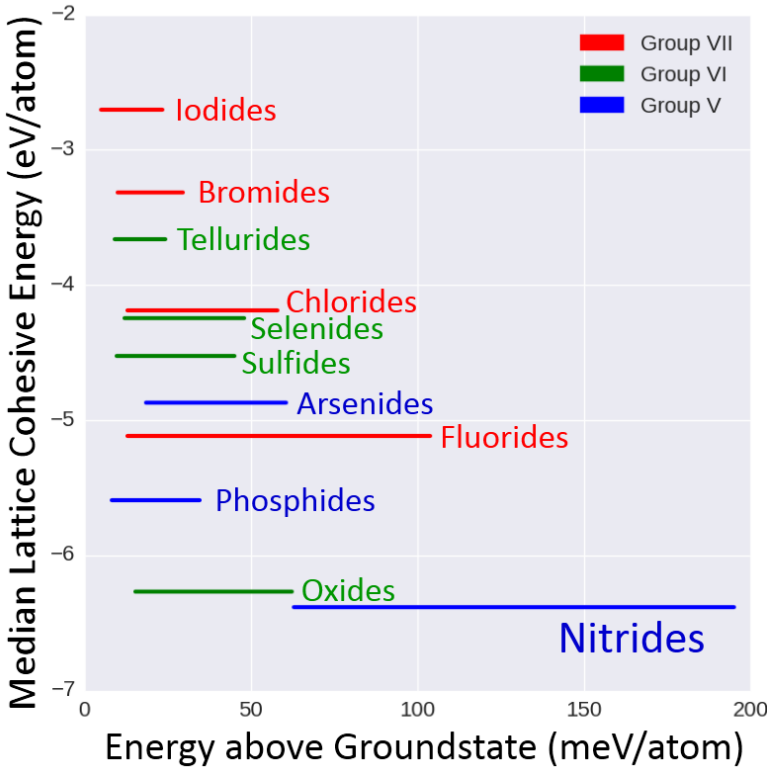
WENHAO SUN, STEPHEN T. DACEK, [...], AND GERBRAND CEDER +6 authors Authors Info & Affiliations

SCIENCE ADVANCES · 18 Nov 2016 · Vol 2, Issue 11 · DOI: 10.1126/sciadv.1600225

Abstract

The space of metastable materials offers promising new design opportunities for next-generation technological materials, such as complex oxides, semiconductors, pharmaceuticals, steels, and beyond. Although metastable phases are ubiquitous in both nature and technology, only a heuristic understanding of their underlying thermodynamics exists. We report a large-scale data-mining study of the Materials Project, a high-throughput database of density functional theory–calculated energetics of Inorganic Crystal Structure Database structures, to explicitly quantify the thermodynamic scale of metastability for 29,902 observed inorganic crystalline phases. We reveal the influence of chemistry and composition on the accessible thermodynamic range of crystalline metastability for polymorphic and phase-separating compounds, yielding new physical insights that can guide the design of novel metastable materials. We further assert that not all low-energy metastable compounds can necessarily be synthesized, and propose a principle of 'remnant metastability'—that observable metastable crystalline phases are generally remnants of thermodynamic conditions where they were once the lowest free-energy phase.





RESEARCH ARTICLE | MATERIALS SCIENCE

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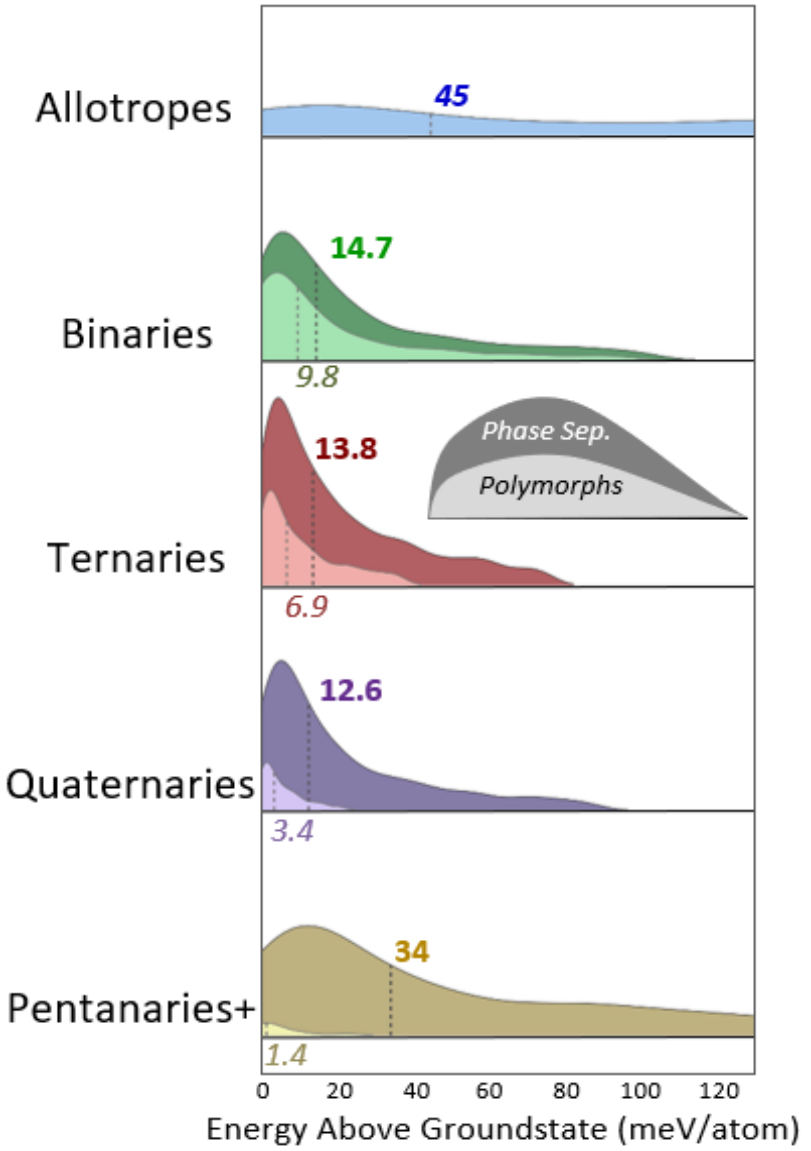
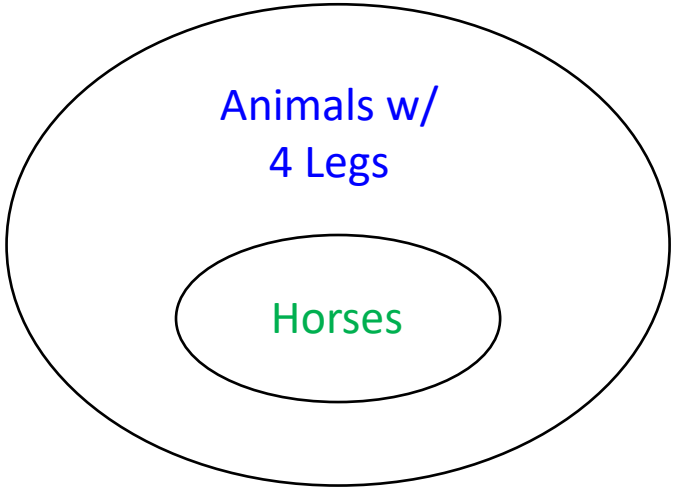


The statistics of metastability depend on **Chemistry** and **Composition**

Synthesizability assumption

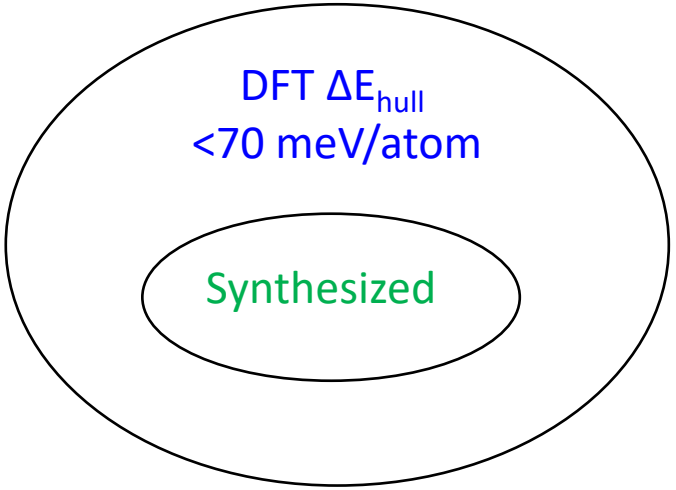
~~**Metastable** material close to the hull (ΔE_{hull} < 70 meV/atom) are probably synthesizable~~

Classic Logical Fallacy: If P, then Q. But if Q, not necessarily P.



Horses have 4 legs

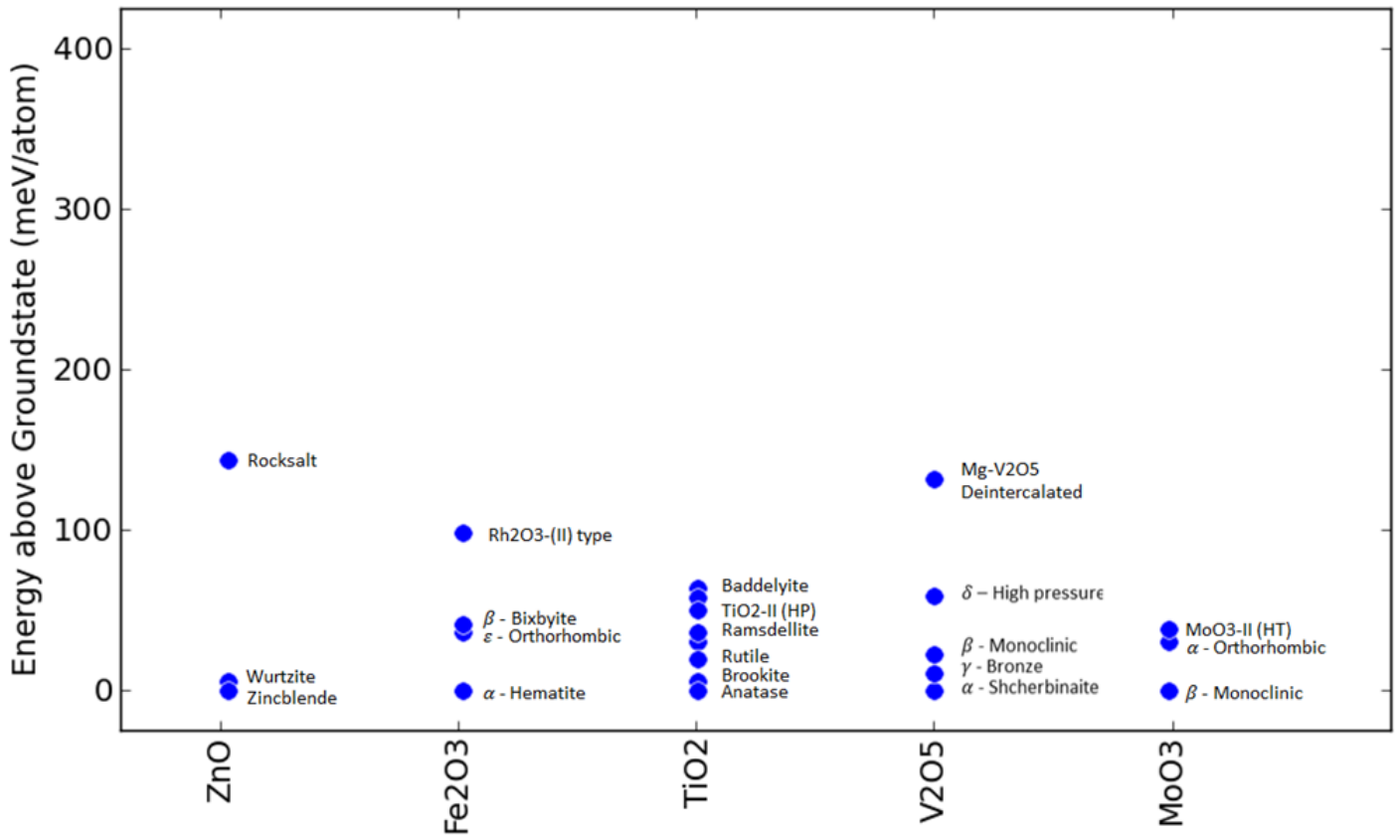
An animal with 4 legs doesn't imply a horse



Synthesized metastable materials have ΔE_{hull} < 70 meV/atom

But ΔE_{hull} < 70 meV/atom doesn't imply synthesizability

Is “low” energy above hull a sufficient condition for synthesizability?



Blue – Observed binary oxide polymorphs

W. Sun et al., *Science Advances* (2016)

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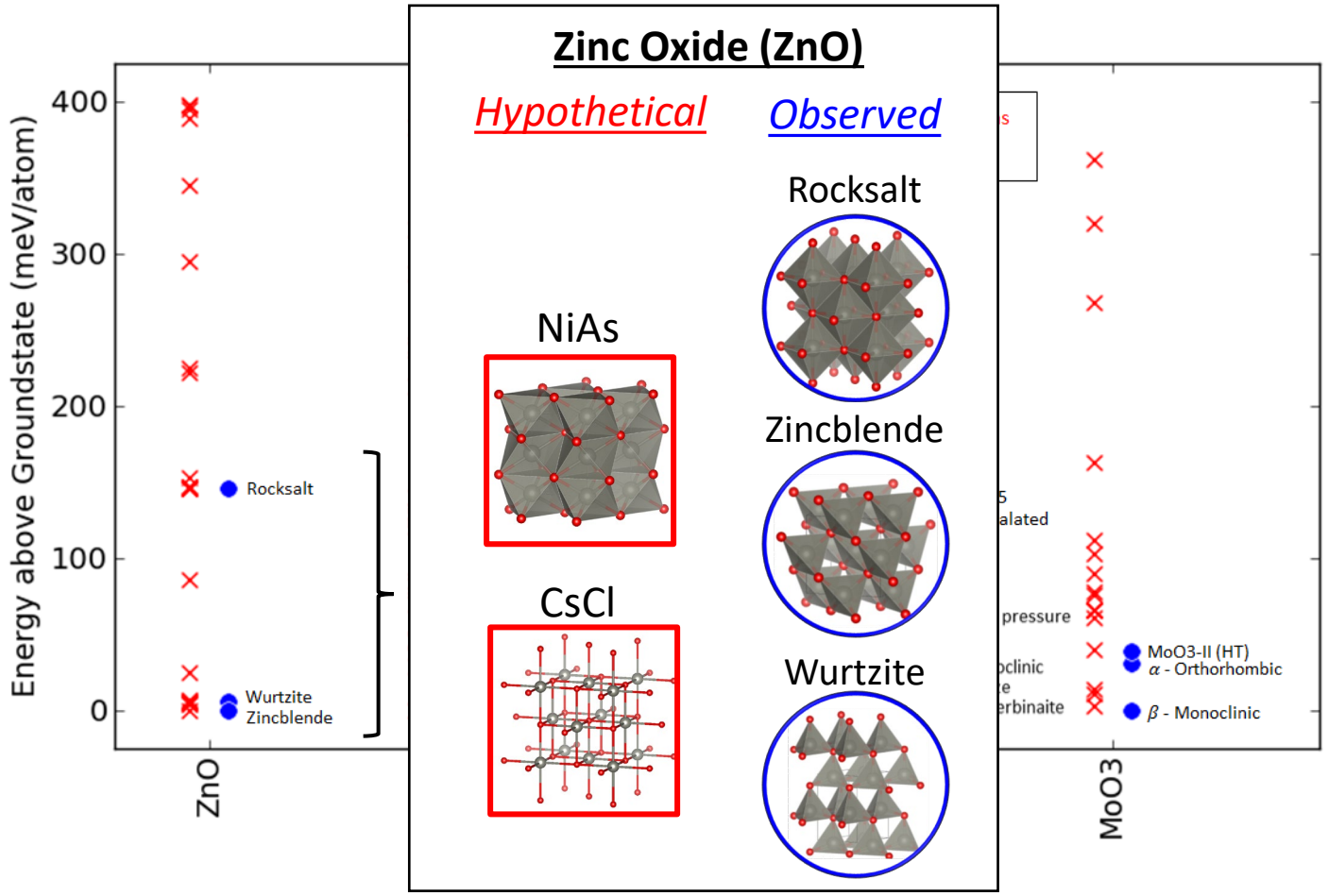


Blue – Observed binary oxide polymorphs

Red - Unobserved, hypothetical materials based off ionically-substituted crystal-structures.

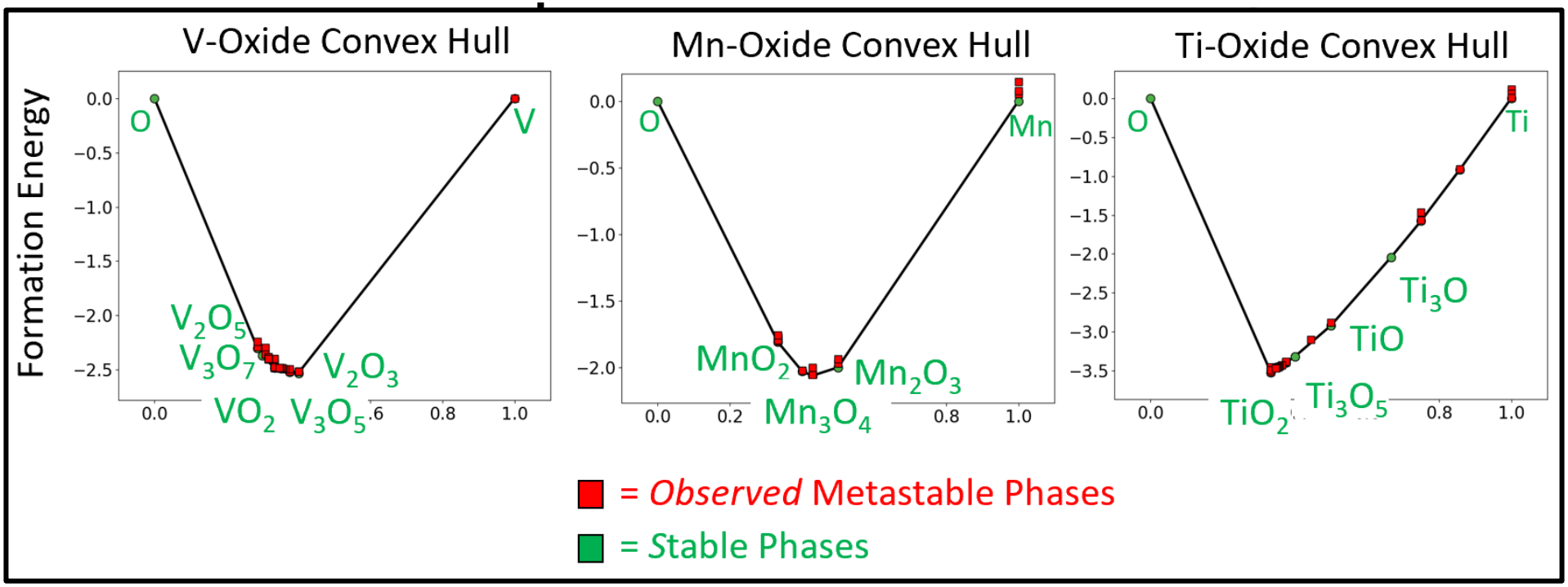
Not all predicted low-energy metastable phases may be synthesizable

W. Sun et al., *Science Advances* (2016)

The thermodynamic scale of metastability **(*Crystal structure*)**

is *much smaller* than

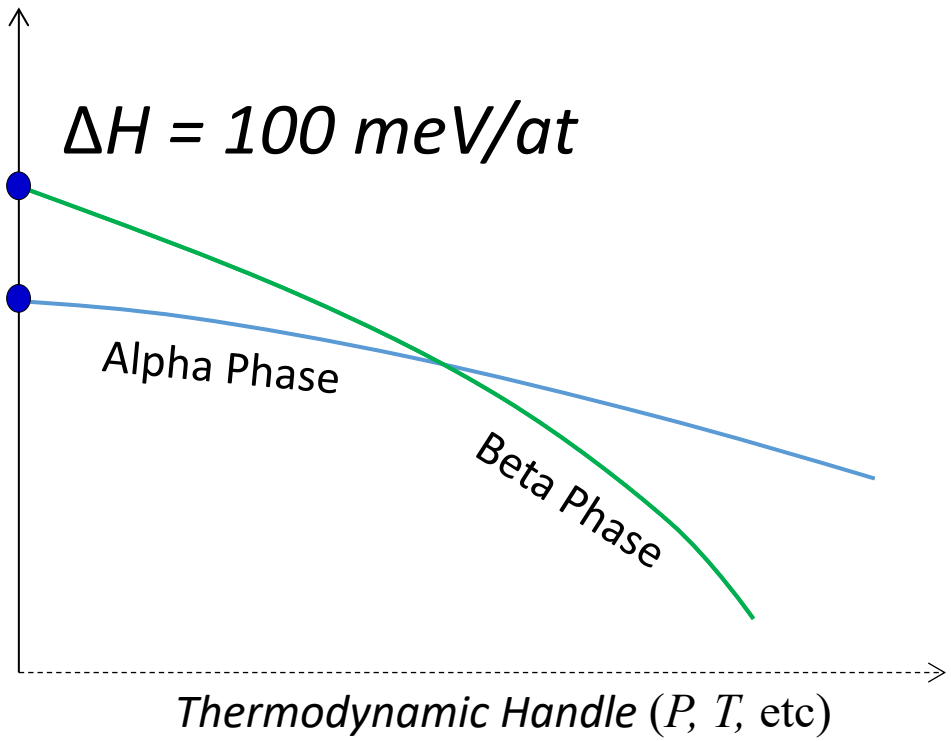
the energy scale of formation energies **(*Chemical bonds*)**



Phases **on** "convex hull" are **stable**

Phases w/ "energy **above** hull" are **metastable**

What's so special about ΔH_{hull}~100 meV/atom?



$\Delta G = \Delta H - T\Delta S = 0$

$\Delta H = T\Delta S$

$T \sim 1000$ K

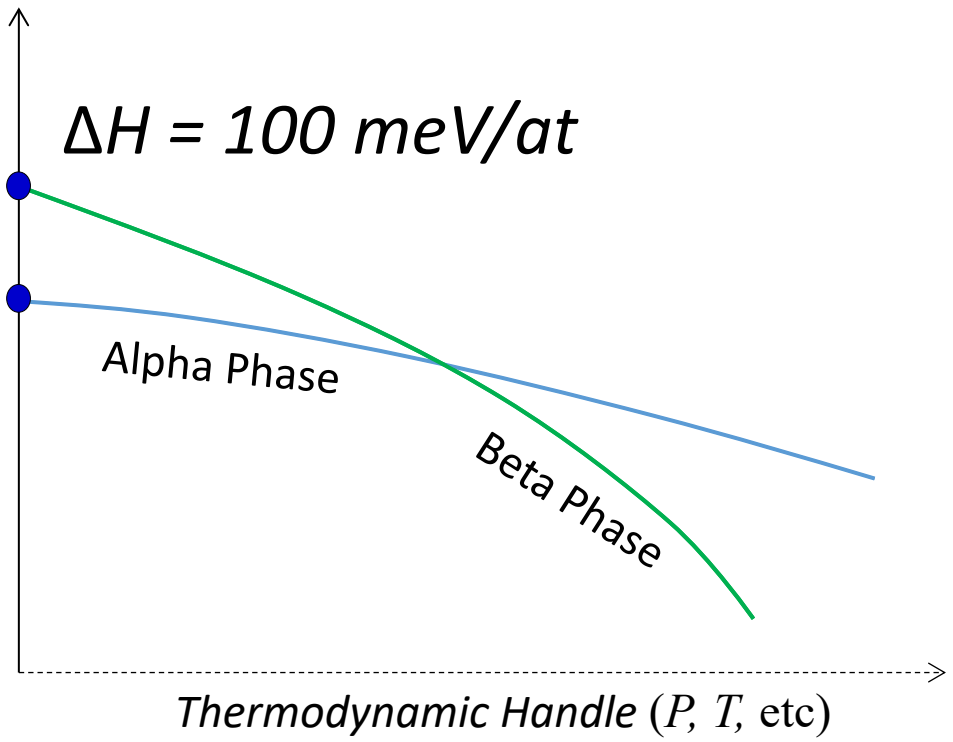
$\Delta S \sim 8.314$ J/K

$T\Delta S = 8$ kJ/mol

~ 100 meV/atom

***Temperature*-Driven** Phase Transition

What's so special about ΔH_{hull}~100 meV/atom?



$\Delta G = \Delta H - T\Delta S = 0$

$\Delta H = P\Delta V$

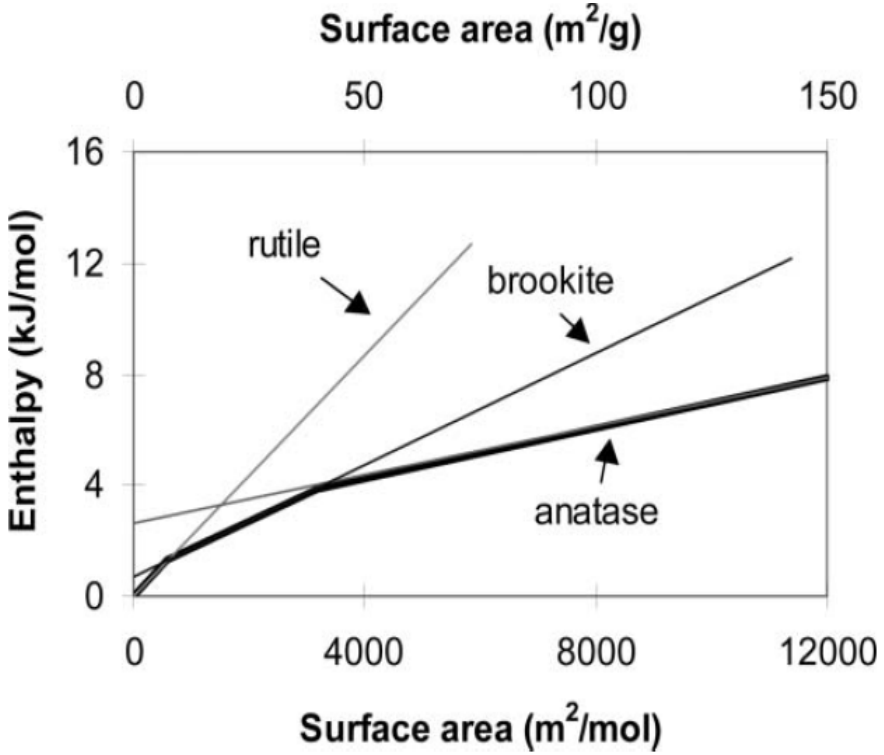
$P \sim 10$ GPa

$\Delta V \sim 2$ Å^3/atom

$P\Delta V =$ **~100 meV/atom**

***Pressure*-Driven** Phase Transition

What's so special about ΔH_{hull}~100 meV/atom?



Ranade *et al*, *PNAS* (2002).

$$E_{Total} = E_{Bulk} + \gamma A$$

A ~ 10,000 m^2/mol

$\Delta\gamma$ ~ 1 J/m^2

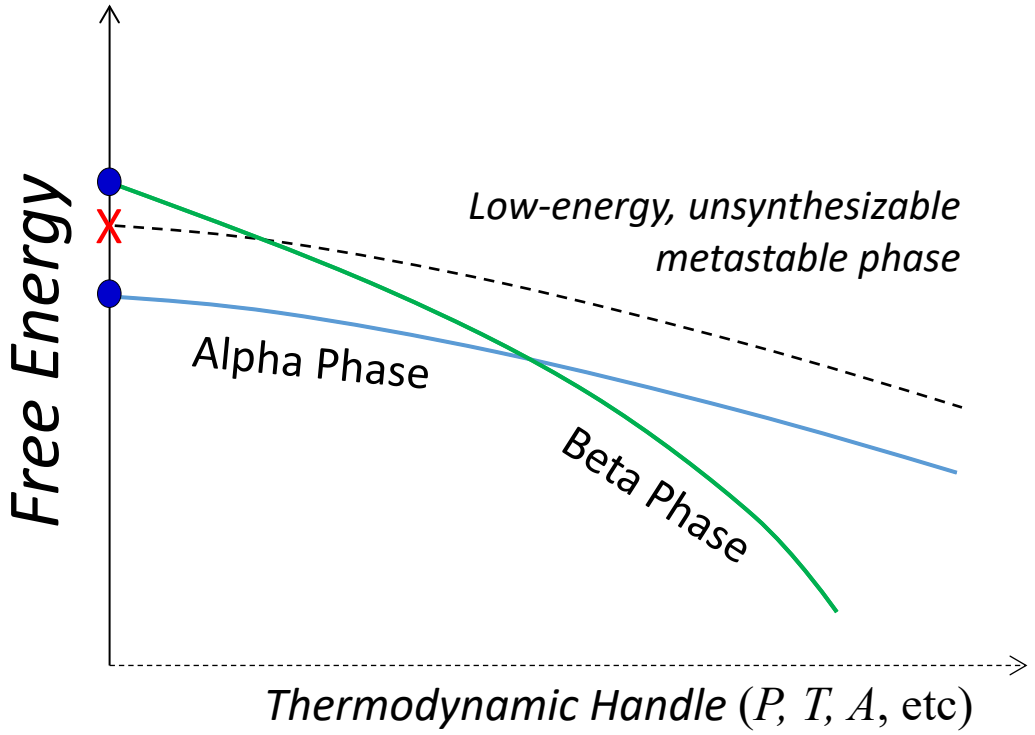
A$\Delta\gamma$ = **~100 meV/atom**

***Size*-Driven** Phase Transition

The **'strength' of thermodynamic handles** (TΔS, PΔV, A$\delta\gamma$, *etc*) is roughly 100 meV/atom = **the enthalpy scale of metastability**

“Remnant” Metastability Hypothesis

Observed metastable phases are generally remnants of thermodynamic conditions where they were once the lowest free-energy phase.



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NATIONAL ACADEMIES Sciences Engineering Medicine

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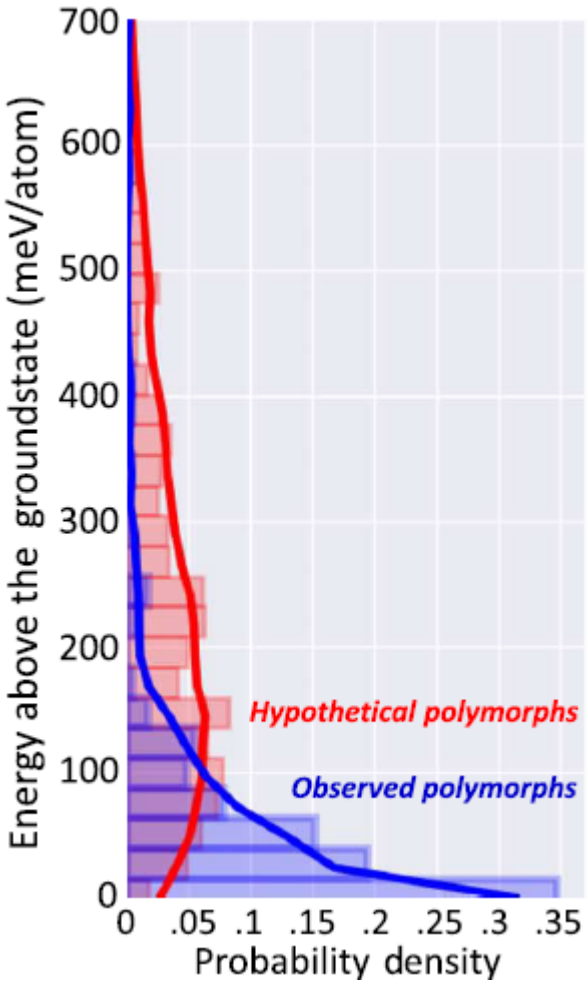
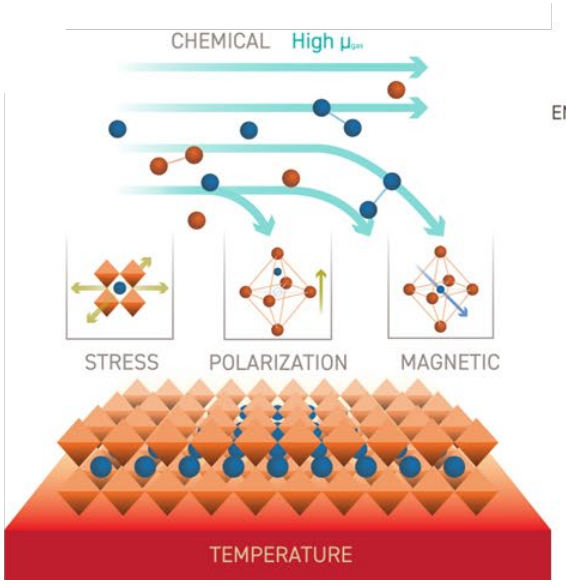
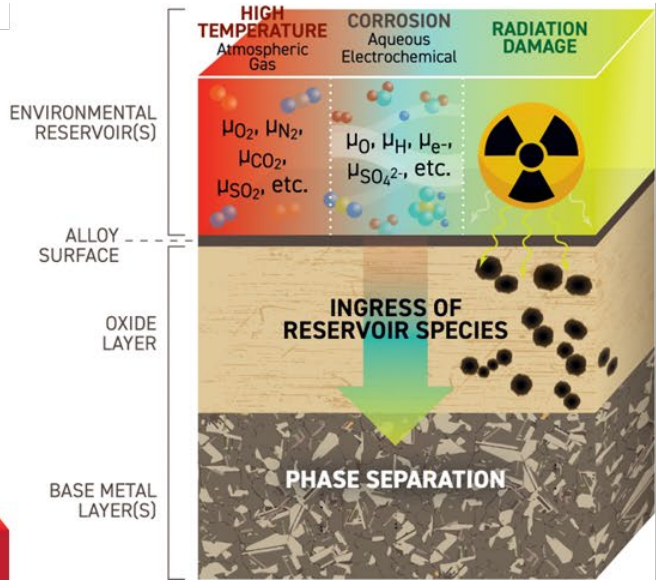
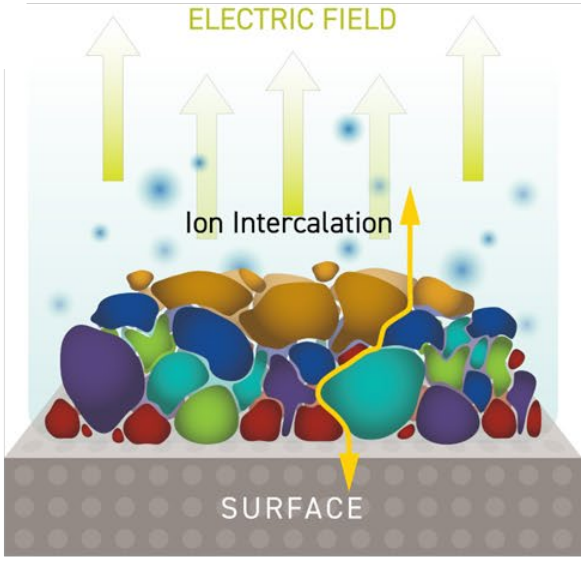


*W. Sun, *et al.*, *Science Advances* (2016)

*Metastability in **complex** modern materials*







Multiferroic materials

- Electric polarization
- Magnetic polarization
- Epitaxial strain
- Gas fugacity
- Film composition
- Temperature

High-entropy alloys

- 5+ components
- Phase separation
- Environment
  - High temperature
  - Corrosion (*p*H, *E*)
  - Radiation (α, β, γ)

Solid-Liquid Interface

- Aqueous stability
- Phase Heterogeneity
- Electrical Double Layer
  - Chemisorption
  - Physisorption
  - Water polarization
  - Electric field

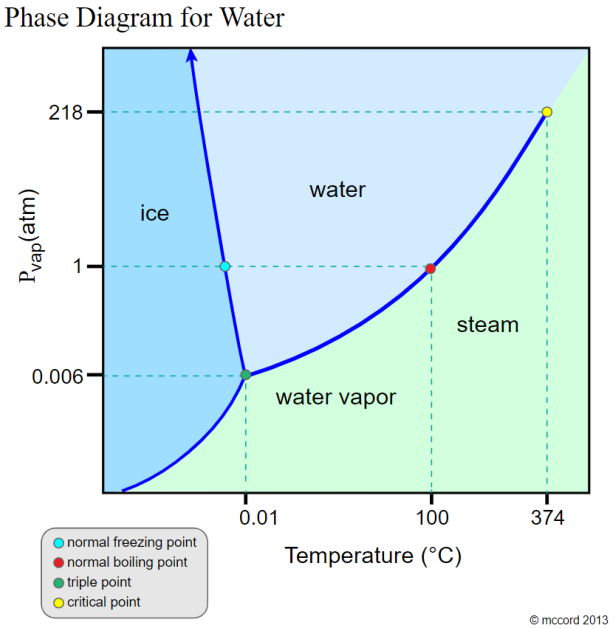
Evaluating stability is *confusing* with the bulk phase diagram …

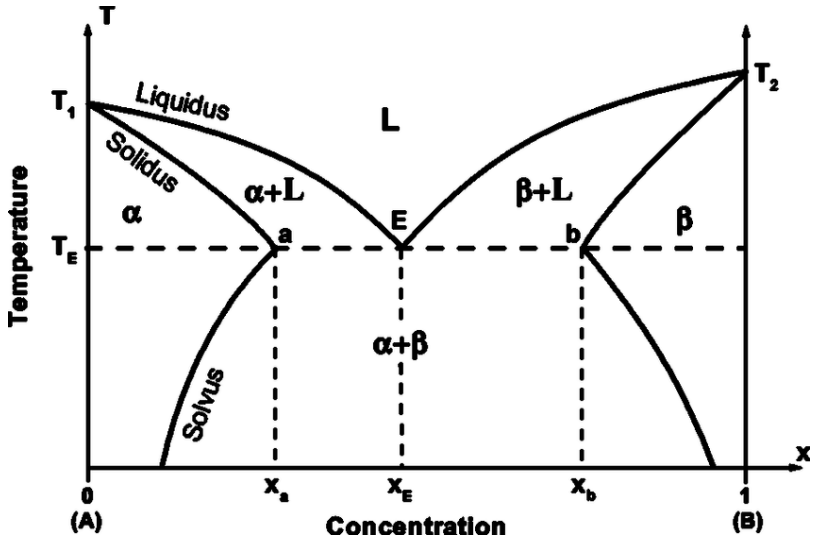
*Metastability in **complex** modern environments*

1. New axes with thermodynamic variables besides temperature, pressure and composition

$$dG = -SdT + VdP + \sum_i \mu_i dN_i$$

Classical Thermodynamics





*Metastability in **complex** modern environments*

1. New axes with thermodynamic variables besides temperature, pressure and composition

$$dG = -SdT + VdP + \sum_i \mu_i dN_i + \gamma dA + \phi dQ + \sigma_{ijkl} d\varepsilon_{ijkl} + \vec{\boldsymbol{E}} \cdot d\vec{\boldsymbol{P}} + \vec{\boldsymbol{B}} \cdot d\vec{\boldsymbol{M}} + \ldots$$

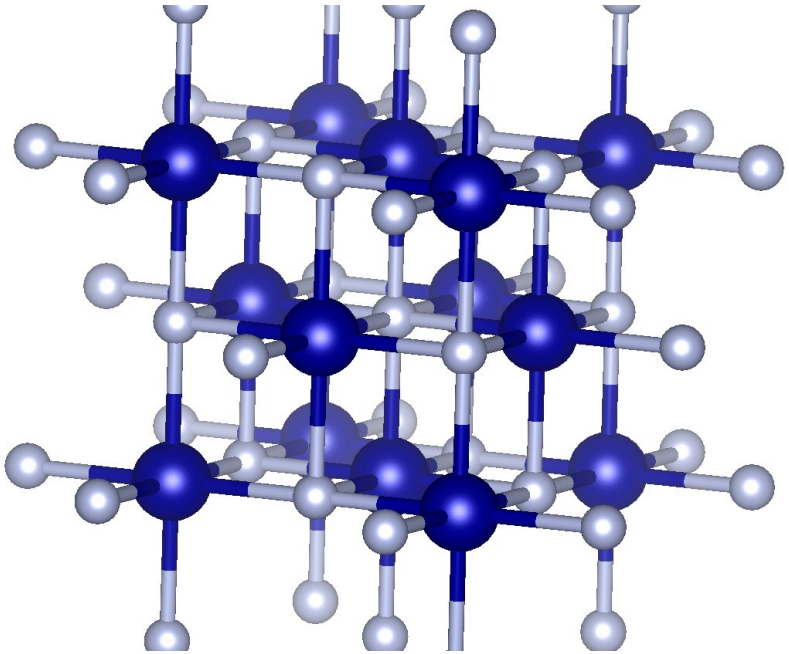
Classical Thermodynamics

Thermodynamic considerations in modern materials

Type of work	Intensive variable	Extensive variable	Differential work in dU
Mechanical			
Pressure-volume	$-P$	V	$-P\mathrm{d}V$
Elastic	f	L	$f\mathrm{d}L$
Gravitational	$\psi = gh$	$m = \sum M_i n_i$	$\psi \mathrm{d}m = \sum ghM_i \mathrm{d}n_i$
Surface	γ	A_s	$\gamma \mathrm{d}A_s$
Electromagnetic			
Charge transfer	ϕ_i	Q_i	$\phi_i \mathrm{d}Q_i$
Electric polarization	$\boldsymbol{E}$	$\boldsymbol{p}$	$\boldsymbol{E}\bullet\mathrm{d}\boldsymbol{p}$
Magnetic polarization	$\boldsymbol{B}$	$\boldsymbol{m}$	$\boldsymbol{B}\bullet\mathrm{d}\boldsymbol{m}$
Chemical			
Chemical: no reactions	μ_i	n_i (species)	$\mu_i \mathrm{d}n_i$
Chemical: reactions	μ_i	n_{ci} (components)	$\mu_i \mathrm{d}n_{ci}$

**Robert Alberty, "Use of Legendre Transforms in Chemical Thermodynamics", IUPAC Technical Report*

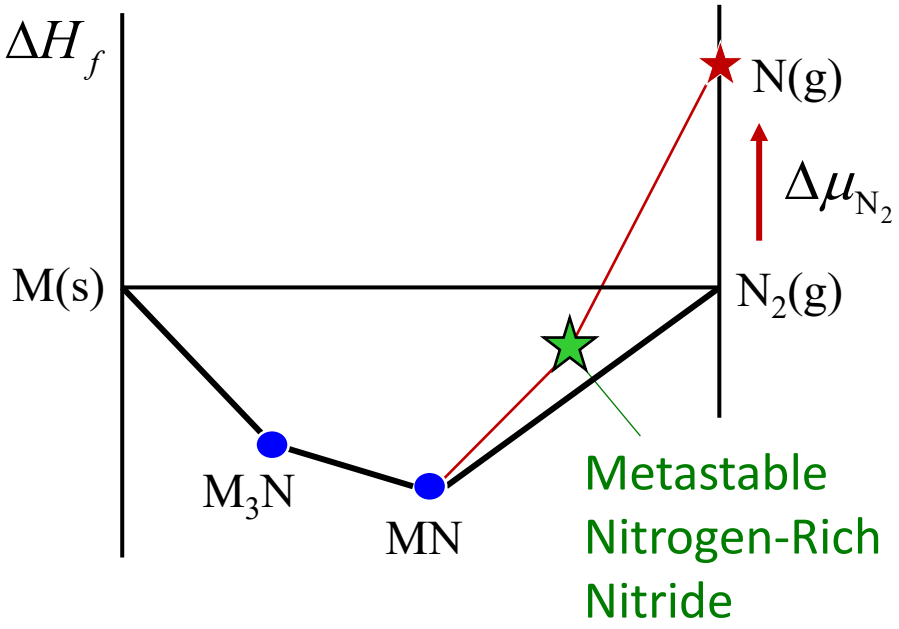
Thermodynamic routes to nitrogen-rich nitrides



TiN, CrN, MnN, MoN

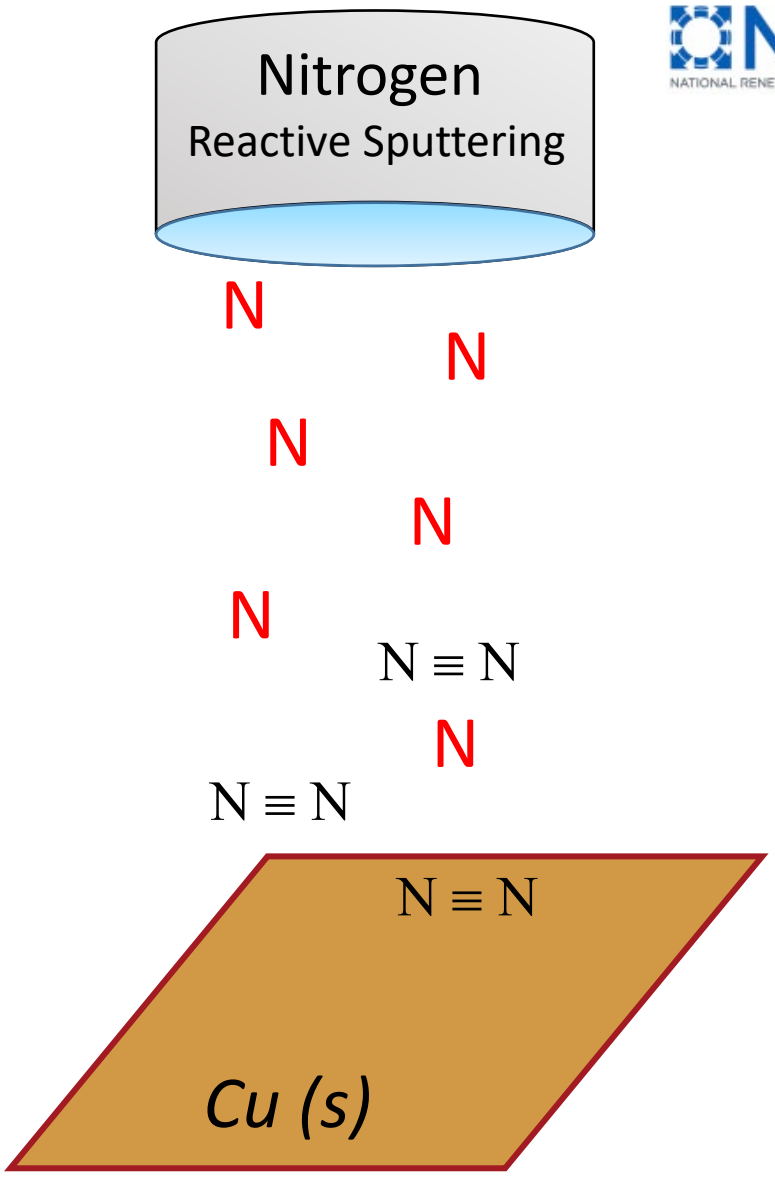
- Intermetallic electronic structure
- Not an ionic nitride (N^{3-}) ion
- ***Thermodynamics prefers sub-nitrides***

Control of $\Delta\mu_{N_2}$



W. Sun *et al.*, *Chem. Mater. (2017)*

Metastable, but experimentally accessible.



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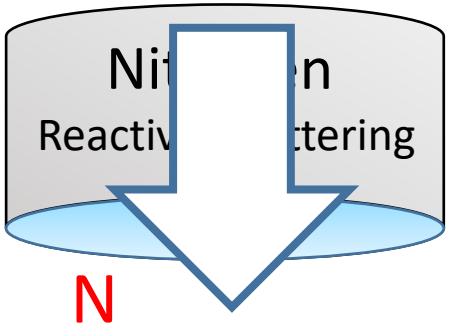
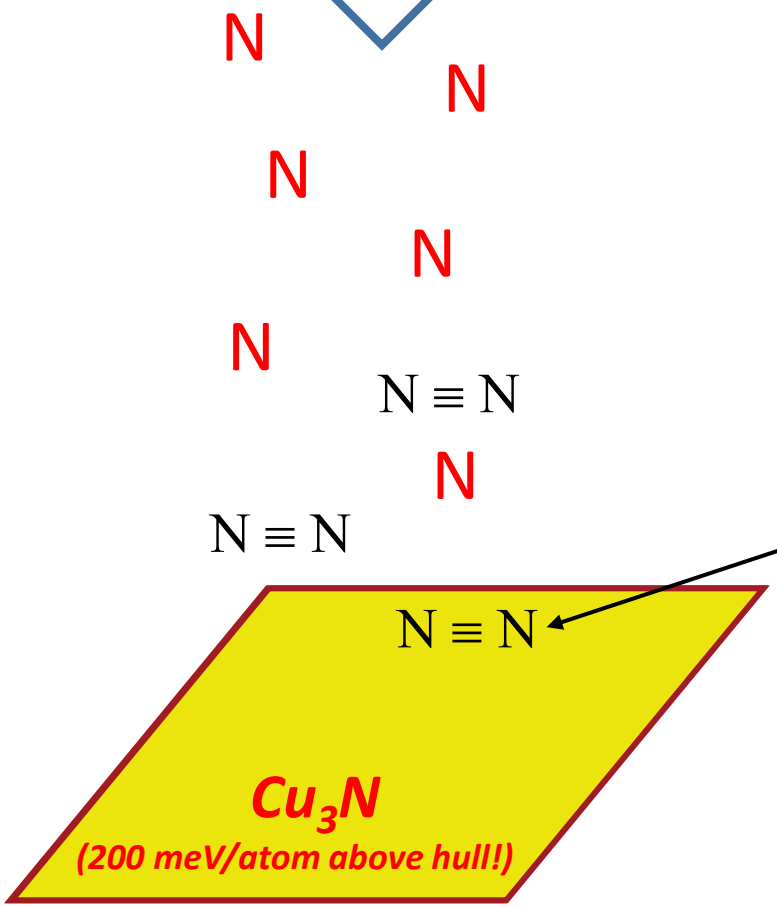
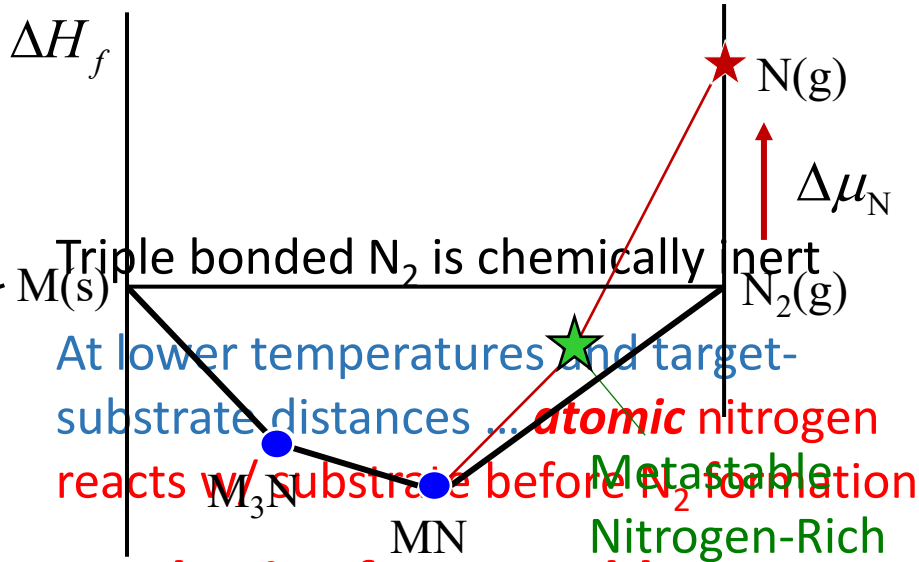


NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Plasma-cracked atomic nitrogen
can reach $\Delta\mu_N$ = +1 eV/N

C. Caskey et al, *Mater. Horiz. (2014)*



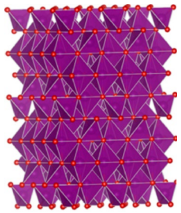


Synthesis of metastable Cu_3N

Metastable manganese oxides

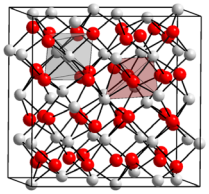
30+ Polymorphs over 5 Manganese oxidation states
(MnO, Mn_3O_4, Mn_2O_3, $MnOOH$, MnO_2, Mn_2O_7)

Supercapacitor



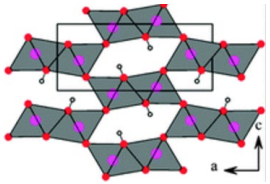
Mn_3O_4

Photocatalyst



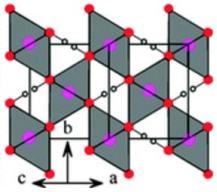
Mn_2O_3

Microbial Redox



α-MnOOH

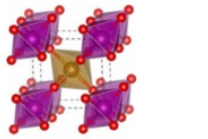
Heavy-Ion Soil Transport



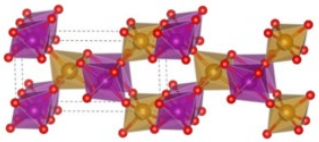
γ-MnOOH

MnO_2

Stable MnO_2 Polymorph



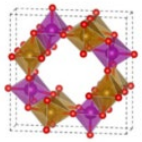
Pyrolusite (β) - $P4_2/mnm$



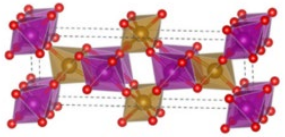
Ramsdellite (R) - Pnam

Alkaline Batteries

Molecular Sieves



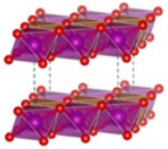
Hollandite (α) - I4/m



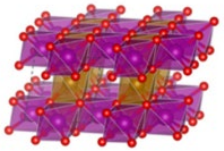
Intergrowth (γ) - C2/m

Alkaline Batteries

Heavy-ion soil transport



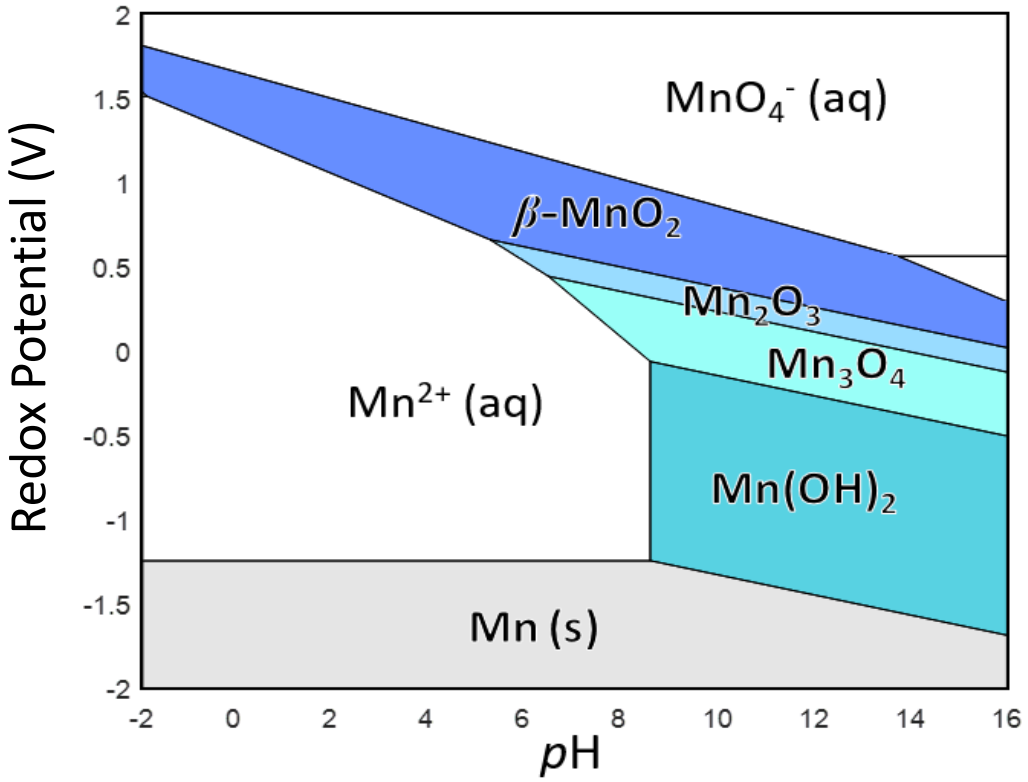
Layered (δ) - $R\bar{3}m$



Spinel (λ) - $Fd\bar{3}m$

Lithium-Ion Batteries

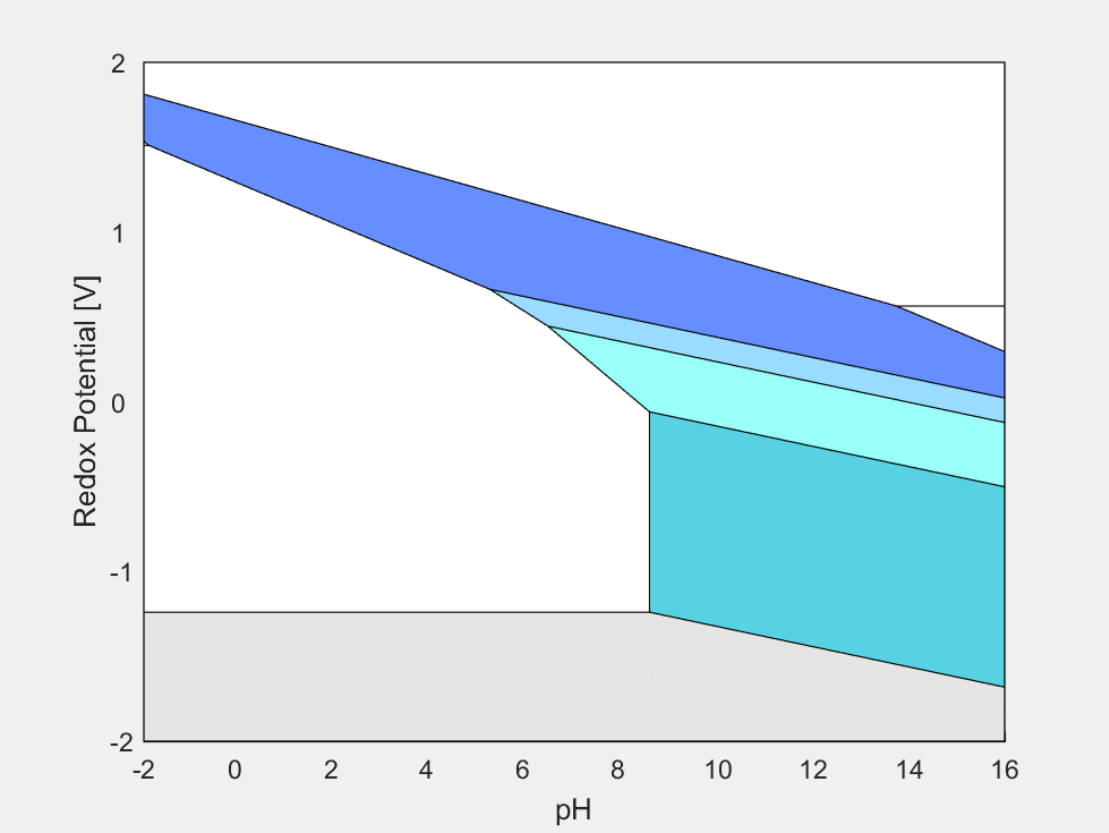
Metastable materials in aqueous synthesis



***Legendre Transformation* of *G*(T,P) to $\Psi(pH, E)$**

$$\overline{\Psi}(pH,E) = \frac{G_{Bulk} - N_O \mu_{H_2O}}{N_M} + \frac{2N_O - N_H}{N_M}[pH] - \frac{2N_O - N_H + Q}{N_M}[E]$$

Metastable materials in aqueous synthesis



***Legendre Transformation* of *G*(T,P) to $\Psi(pH, E)$**

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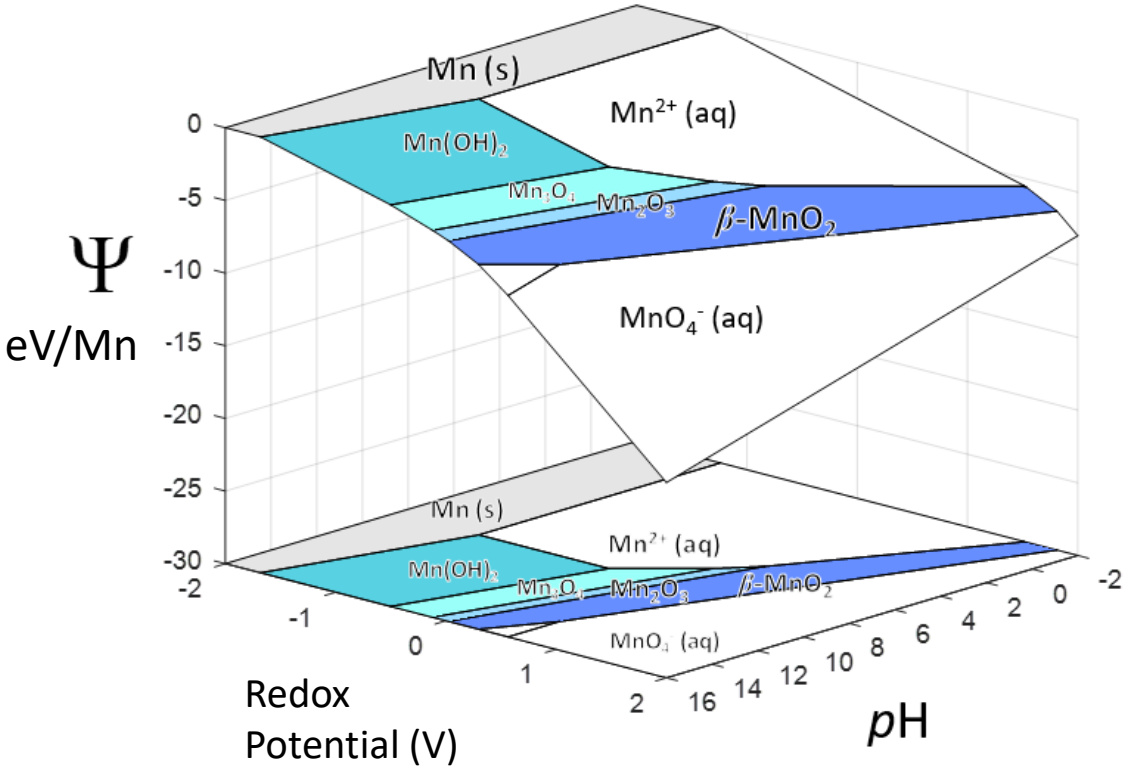
W. Sun et al., *Nature Communications (2019)*

Adding a free-energy axis to Pourbaix Diagrams

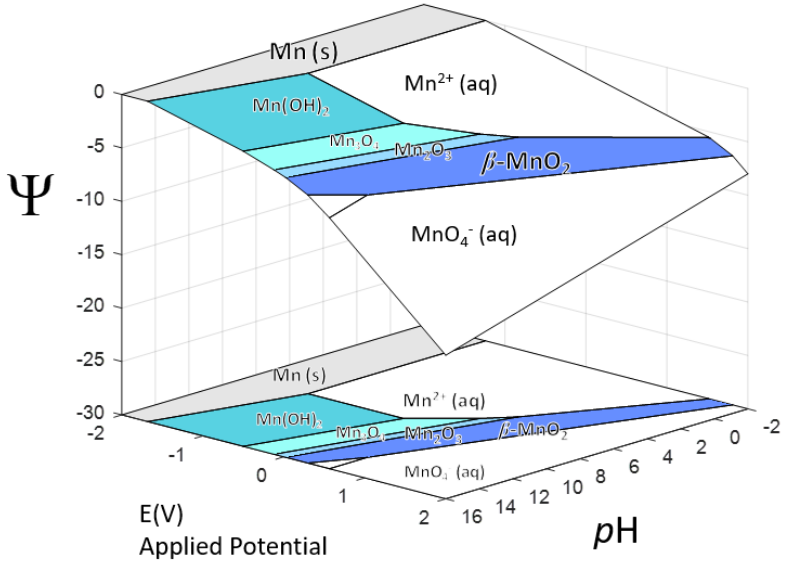


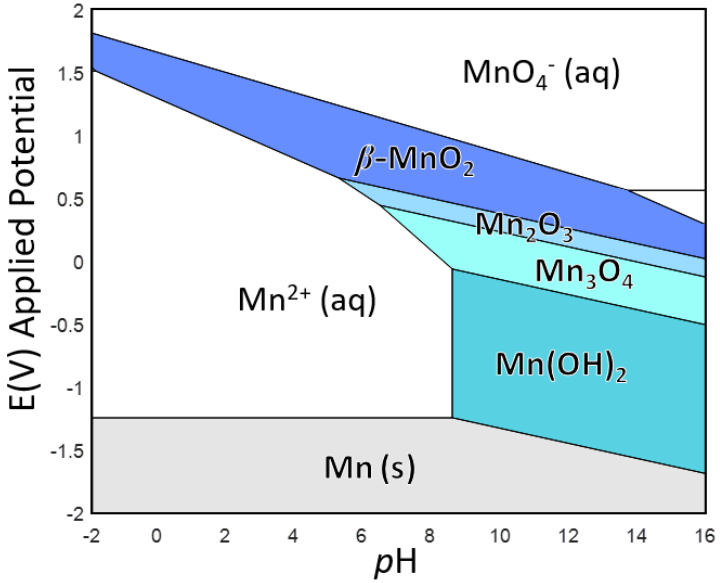
***Legendre Transformation* of *G*(T,P) to Ψ(*p*H, *E*)**

$$\overline{\Psi}(pH,E)=\frac{G_{Bulk}-N_O\mu_{H_2O}}{N_M}+\frac{2N_O-N_H}{N_M}[pH]-\frac{2N_O-N_H+Q}{N_M}[E]$$

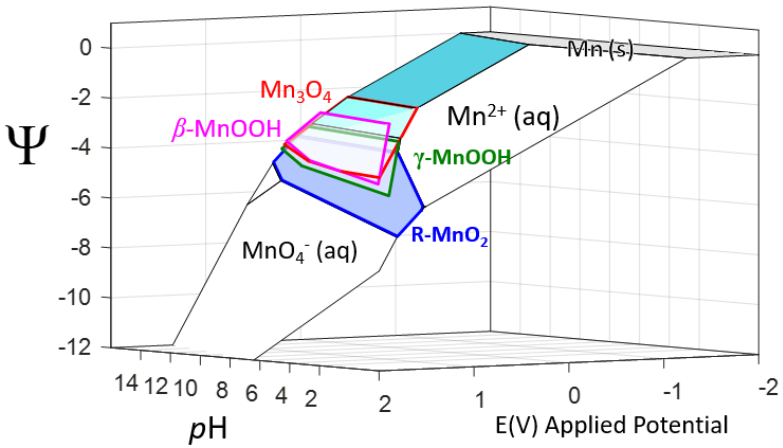
W. Sun et al., *Nature Communications (2019)*

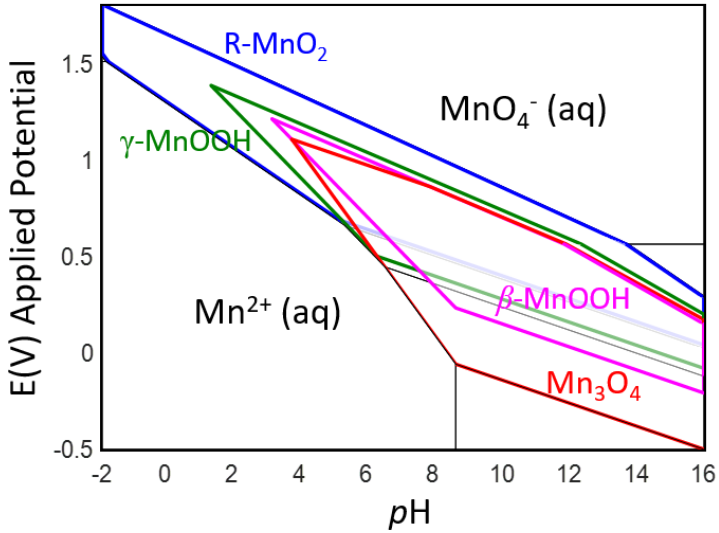
Pourbaix Diagram of ***Stable*** Phases



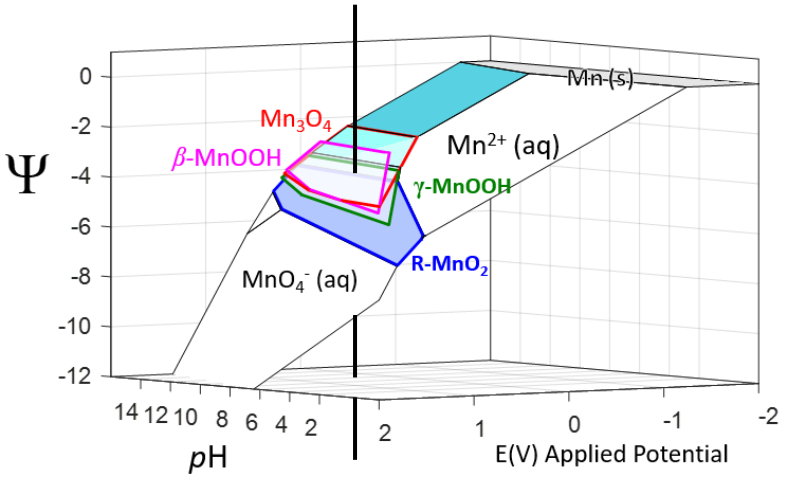


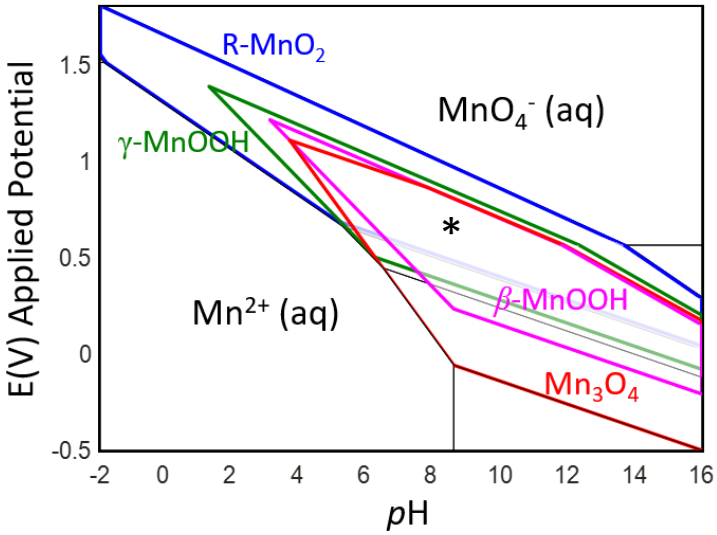
Pourbaix Diagram of ***Metastable*** Phases





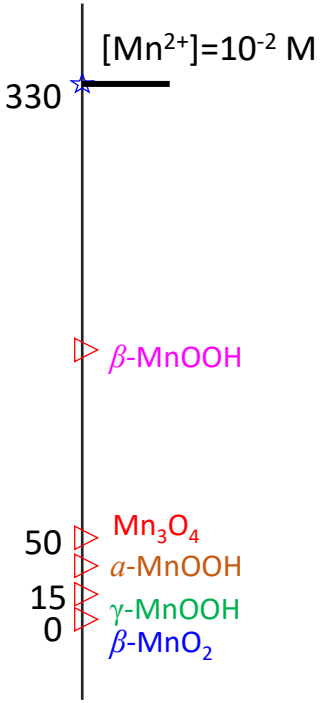
Directly compare free-energies between metastable phases





$\overline{\Psi}_{Bulk}$

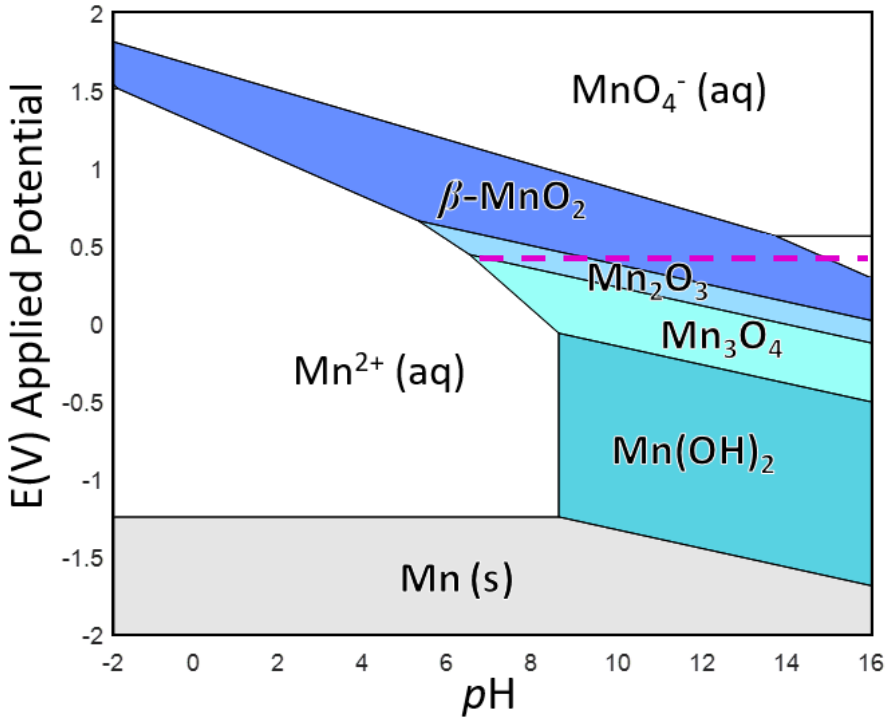
Pourbaix
Free Energy
[meV/Mn]



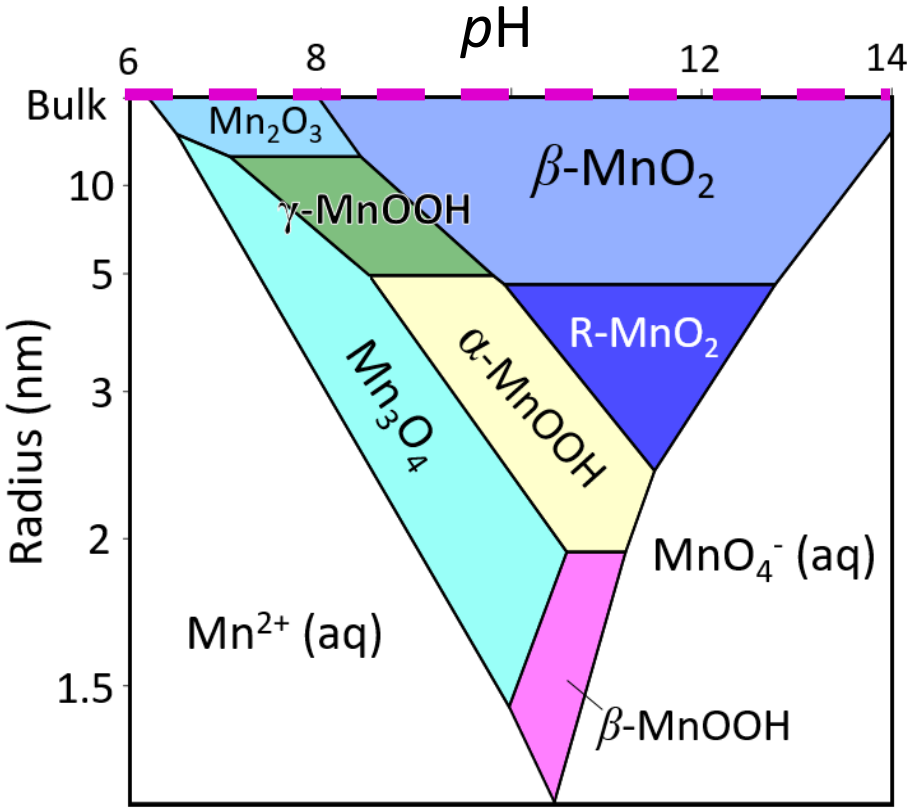
We can now extend our free-energy axis to include other thermodynamic terms

W. Sun et al., *Nat. Comms. (2018)*

Nanoscale Pourbaix Diagrams



Many metastable MnOxides are stabilized at small particle sizes



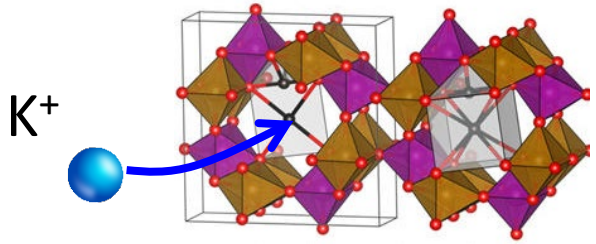
$$\overline{\Psi}(R) = \overline{\Psi}_{Bulk} + \gamma\left(\frac{A}{V}\right)\rho_{\mathrm{M}}$$

Projecting Pourbaix potential onto the ***p*H, Size** axes:

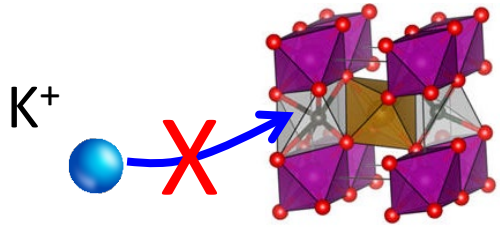
W. Sun et al., *Nature Communications (2019)*

Composition-dependent Pourbaix Diagrams

Cation intercalation can stabilize polymorphic frameworks at off-stoichiometric compositions



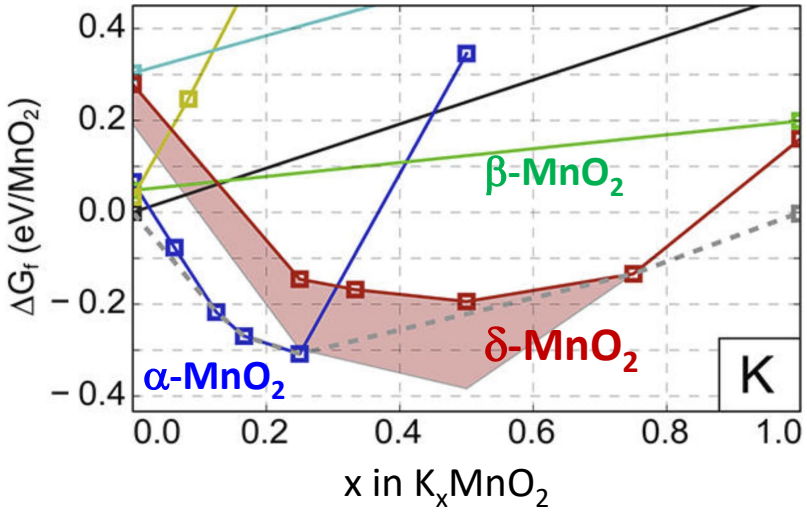
Hollandite (α) - **Metastable**

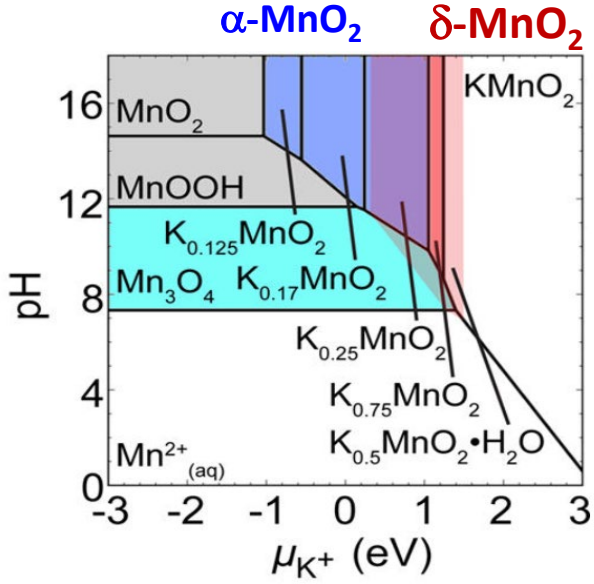


Pyrolusite (β) - **Stable**

$$\overline{\Psi}_{K_xMnO_2} = \overline{\Psi}_{MnO_2} - \mu_K N_K$$

Projecting Pourbaix potential onto the ***p*H, Size** axes:





D. Kitchaev, W. Sun *et al.*, *JACS (2017)*

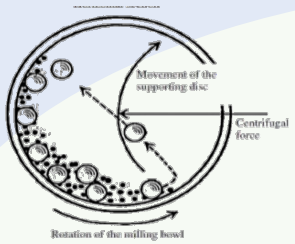
Different **synthesis methods** leverage different forms of thermodynamic work

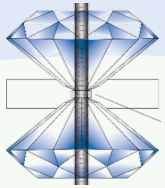
$$dG = -SdT + VdP + \sum_i \mu_i dN_i + \gamma dA + \phi dQ + \sigma_{ijkl} d\varepsilon_{ijkl} + \vec{E} \cdot d\vec{P} + \vec{B} \cdot d\vec{M} + \ldots$$

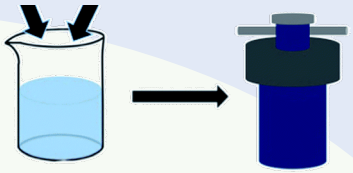
Pressure

*p*H, *E*

Shear







Epitaxial strain

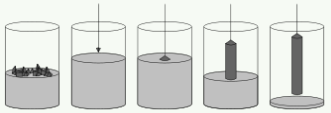
Diamond Anvil

Solvothermal

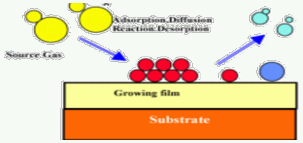
Solvent chemistry

Mechanochemistry

Target Phase



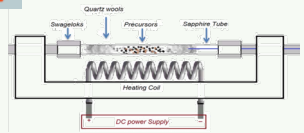
Liquidus surface



Flux Growth

Nucleation Surface Energy

Thin-film deposition



Temperature

Solid-State Synthesis

Plasma Fugacity

Precursor chemical potential

The geometry of high-dimensional phase diagrams

Construct → **I.** Generalized Gibbs Phase Rule
Interpret → **II.** The duality between open and closed chemical systems
Navigate → **III.** Engineering relative stability in 4 dimensions

$$dG = -SdT + VdP + \sum_i \mu_i dN_i \quad + \gamma dA + \phi dQ + \sigma_{ijkl} d\varepsilon_{ijkl} + \vec{E} \cdot d\vec{P} + \vec{B} \cdot d\vec{M} + \ldots$$

Classical Thermodynamics

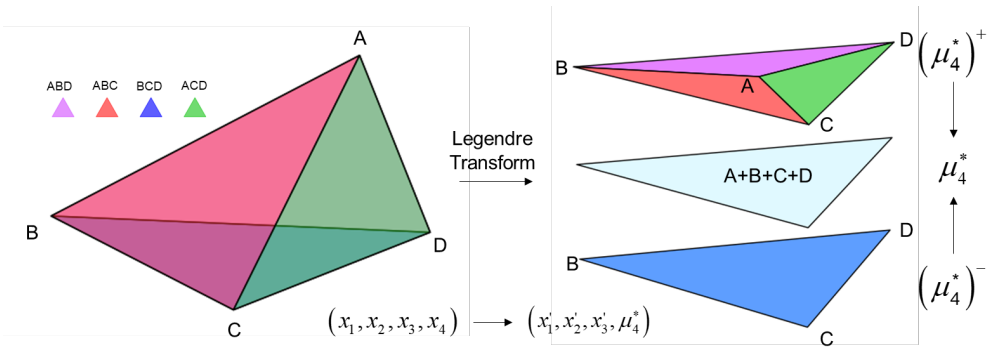
Thermodynamic considerations in modern materials

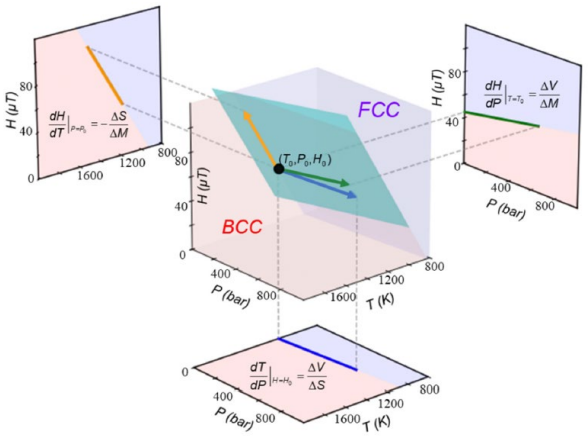
Phase diagrams with any axes, in any dimension

Combinatorial Geometry of Phase Coexistence

Legendre transformations

High-dimensional Phase Boundaries





AI-Guided Discovery of Metastable Materials

NATIONAL ACADEMIES Sciences Engineering Medicine

The Overprediction Problem

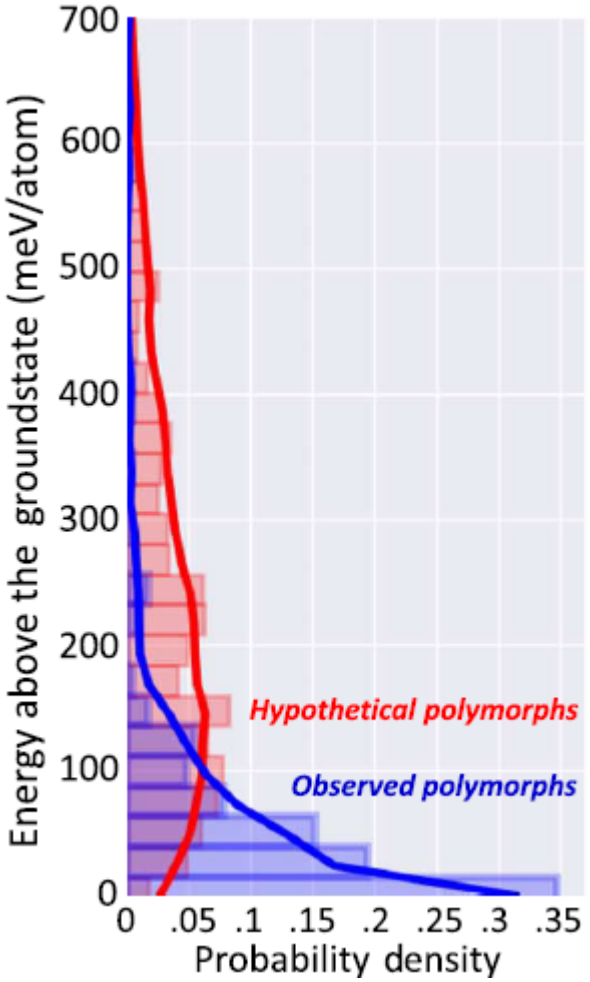
1) Which metastable materials can form?

Remnant Metastability

2) Which metastable materials *will* form, under my conditions of synthesis?

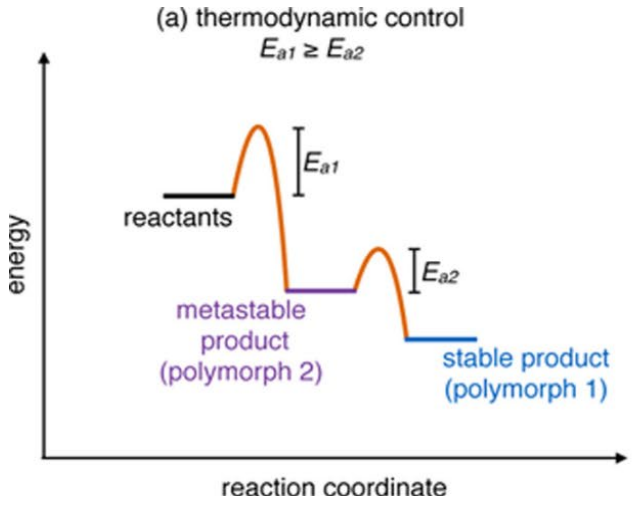
High-dimensional phase diagrams

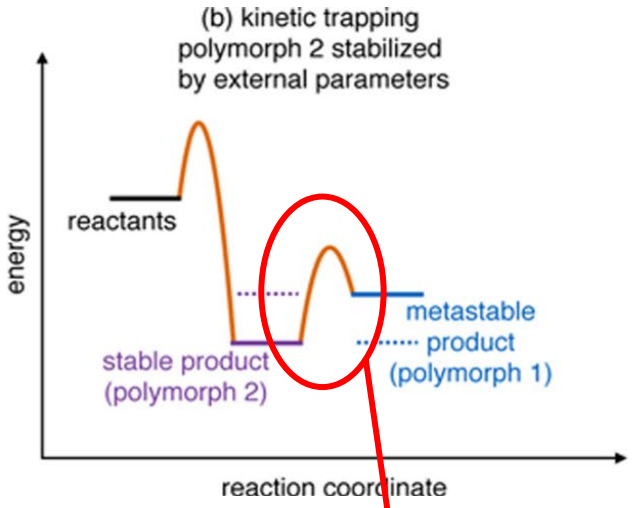
3) How can I keep (or get rid of) metastable materials that have formed?

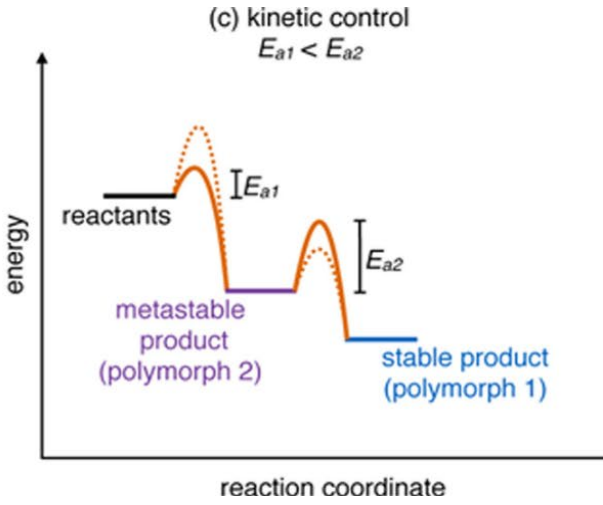


*W. Sun, *et al.*, *Science Advances* (2016)

Persistence of a metastable phase







Martinolich, Neilson *Chemistry of Materials* (2017)

Jamie Neilson
Colorado State Uni.

Cannot put **"reaction coordinate"** into AI

What **mechanism** is the kinetic barrier? (Rate limiting step?)

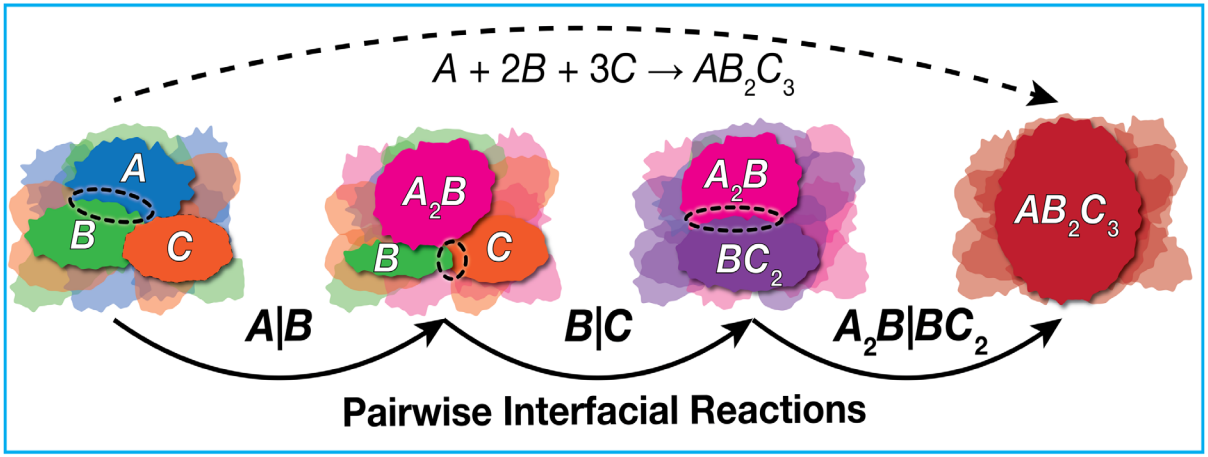
Nucleation?
Diffusion? Growth?

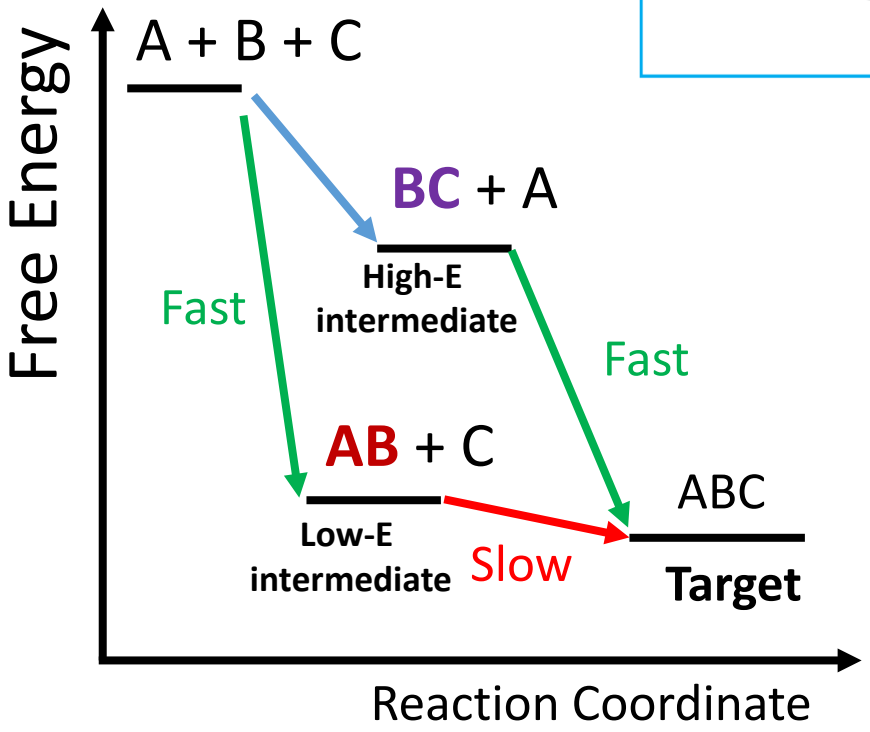
Diffusion-limited	Nucleation-limited	Growth-limited
Solid-State Synthesis	*Solution-Synthesis*	*Defect-Mediated*

Diffusion-limited | Nucleation-limited | Growth-limited

Solid-State Synthesis | *Solution-Synthesis* | *Defect-Mediated*

Reactions between 3+ precursors occur **only 2 at a time**



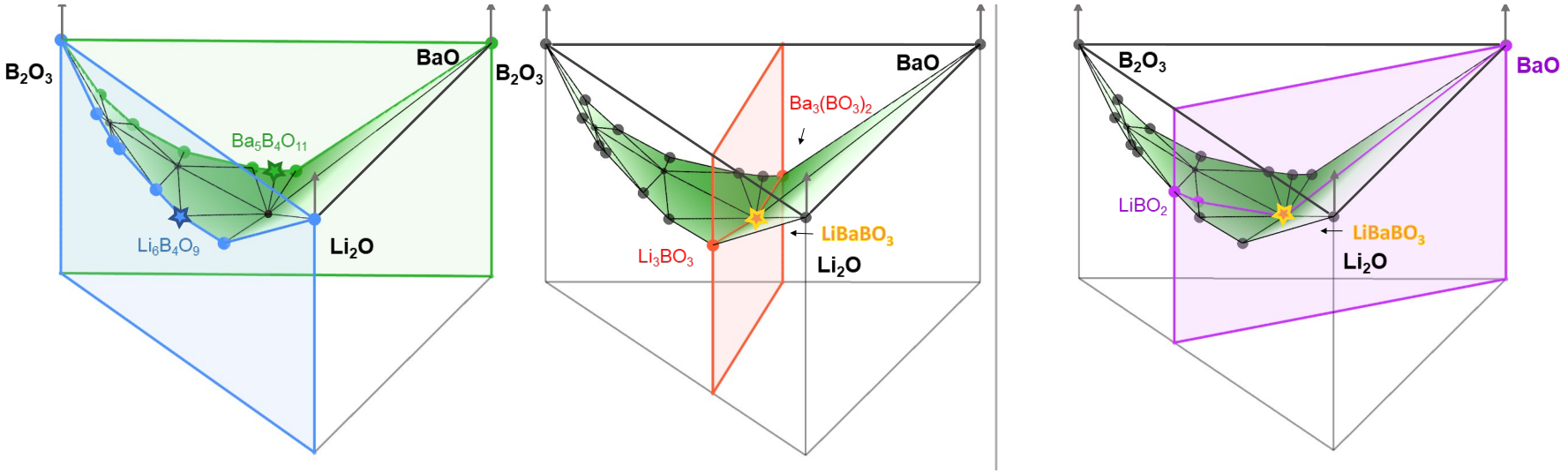


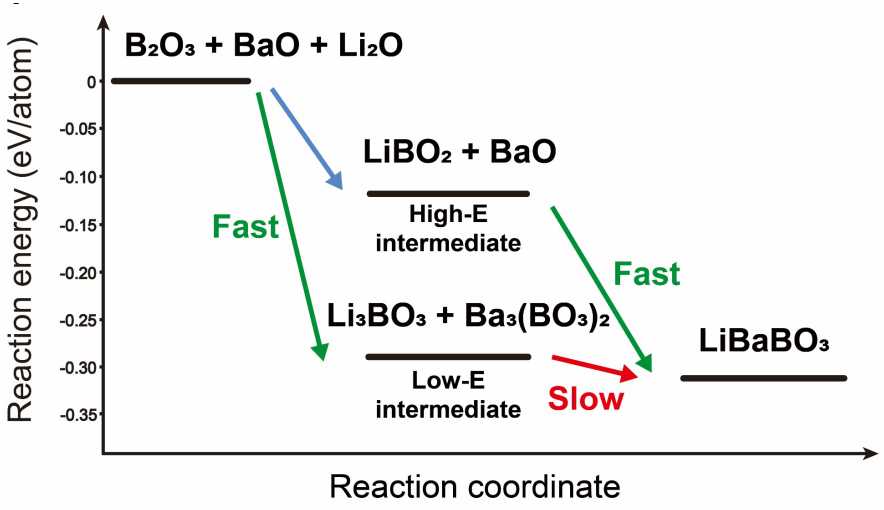
If A+B → AB consumes most of the driving force, the final step becomes slow

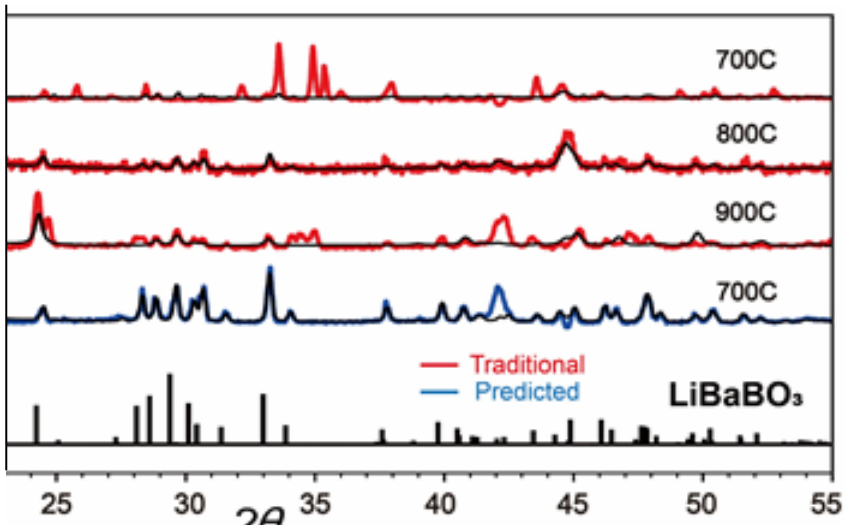
If you synthesize BC first, you can save the reaction energy for the last step!

Diffusion-limited | Nucleation-limited | Growth-limited

Solid-State Synthesis | *Solution-Synthesis* | *Defect-Mediated*







J. Chen, S. Cross, E. Wang, W. Sun *et al.*, Nature Synthesis (2024)

Diffusion-limited | Nucleation-limited | Growth-limited

Solid-State Synthesis | *Solution-Synthesis* | *Defect-Mediated*

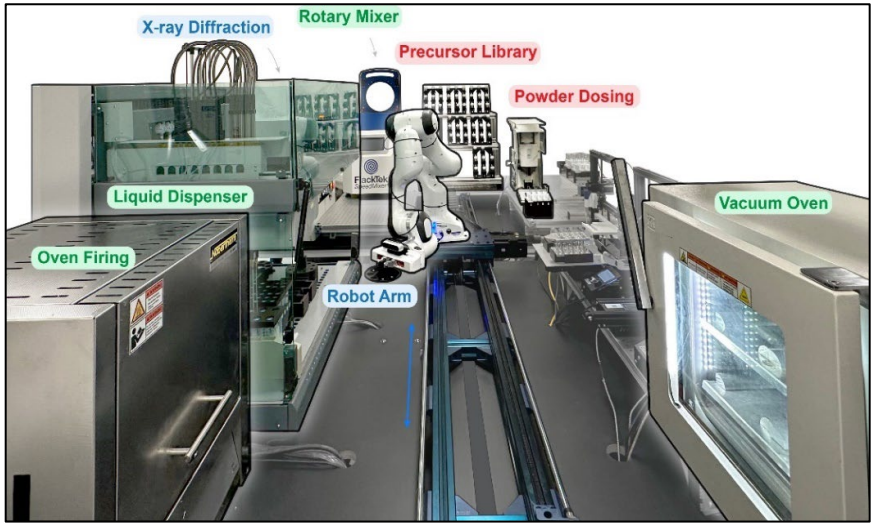
nature synthesis

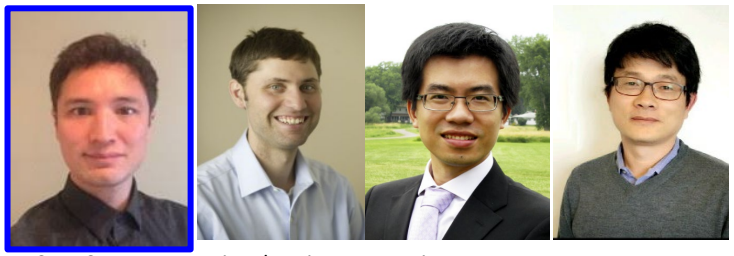
astralQ

Article | Open access | Published: 09 April 2024

Navigating phase diagram complexity to guide robotic inorganic materials synthesis

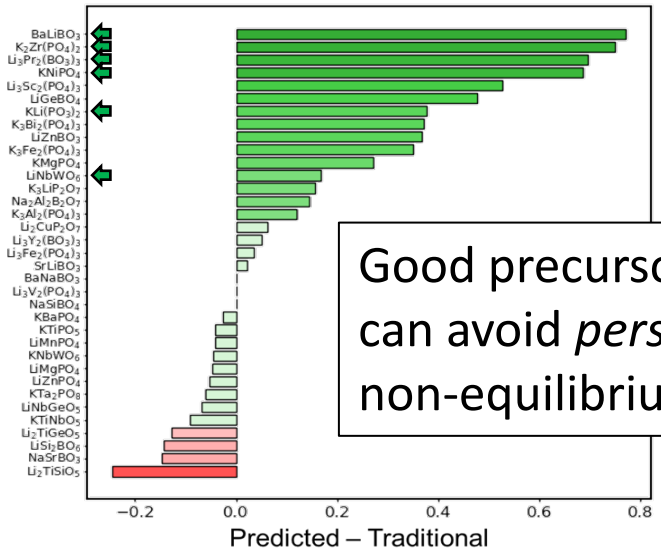
Jiadong Chen, Samuel R. Cross, Lincoln J. Miara, Jeong-Ju Cho, Yan Wang & Wenhao Sun





Sam Cross | Lincoln Miara | Eric Wang | J.J. Cho

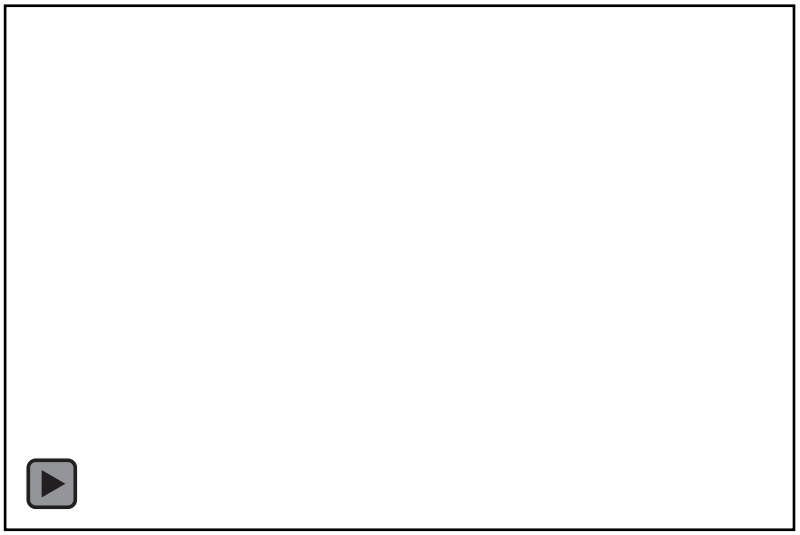
Target	Traditional Precursors	Predicted Precursors
$BaLiBO_3$	Li_2CO_3, B_2O_3, BaO	BaO, $LiBO_2$
$K_2Zr(PO_4)_2$	K_2CO_3, $NH_4H_2PO_4$, ZrO_2	KPO_3, ZrO_2
$Li_3Pr_2(BO_3)_3$	Li_2CO_3, B_2O_3, Pr_6O_{11}	$LiBO_2$, Pr_6O_{11}
$KNiPO_4$	K_2CO_3, $NH_4H_2PO_4$, NiO	KPO_3, NiO
$Li_3Sc_2(PO_4)_3$	Sc_2O_3, Li_2CO_3, $NH_4H_2PO_4$	Sc_2O_3, $LiPO_3$
$LiGeBO_4$	Li_2CO_3, B_2O_3, GeO_2	$LiBO_2$, GeO_2
$KLi(PO_3)_2$	Li_2CO_3, K_2CO_3, $NH_4H_2PO_4$	$LiPO_3$, KPO_3
$LiNbWO_6$	Li_2CO_3, Nb_2O_5, WO_3	$LiNbO_3$, WO_3
$LiZnBO_3$	Li_2CO_3, ZnO, B_2O_3	$LiBO_2$, ZnO
$K_3Fe_2(PO_4)_3$	K_2CO_3, $NH_4H_2PO_4$, Fe_2O_3	KPO_3, Fe_2O_3
$KMgPO_4$	K_2CO_3, $NH_4H_2PO_4$, MgO	MgO, KPO_3



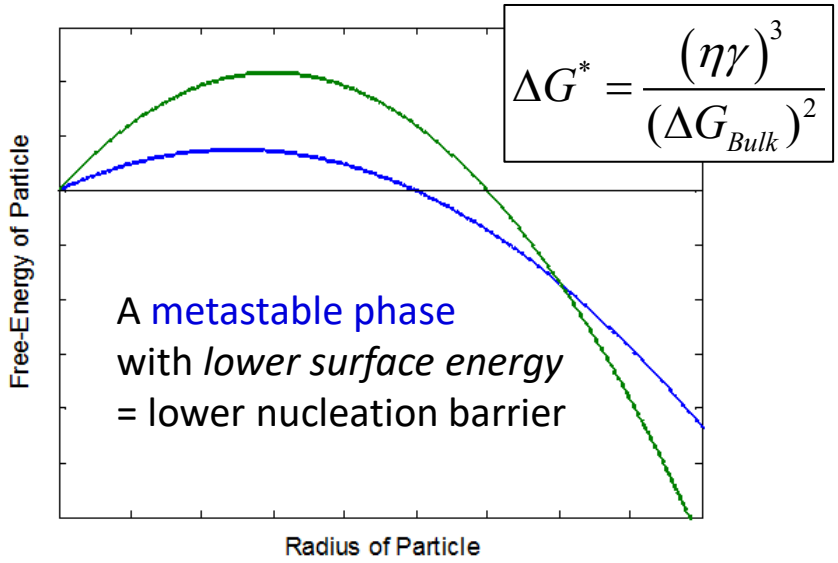
Good precursor selection can avoid *persistent* non-equilibrium phases

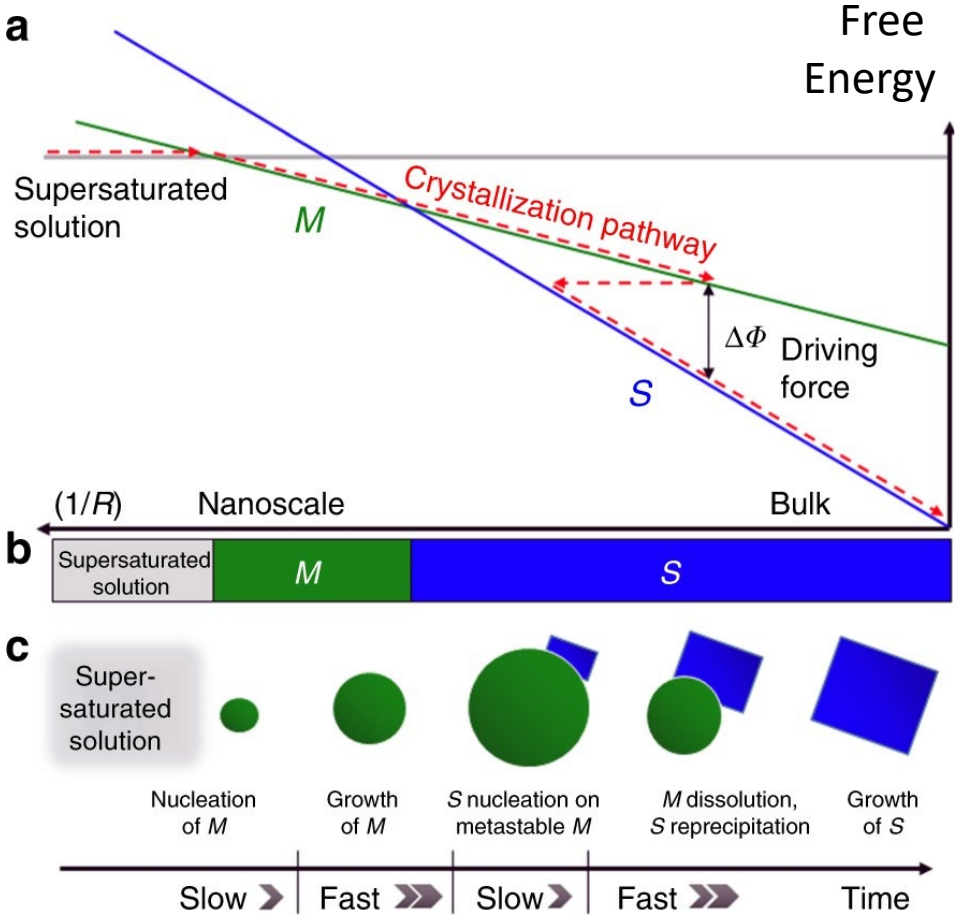
Diffusion-limited | **Nucleation-limited** | Growth-limited

Solid-State Synthesis | ***Solution-Synthesis*** | *Defect-Mediated*



MH Nielson, J. Deyoreo, *Science* (2014)





B.R. Chen*, W. Sun*, *et al, Nat. Comms (2018)*

Diffusion-limited | **Nucleation-limited** | Growth-limited

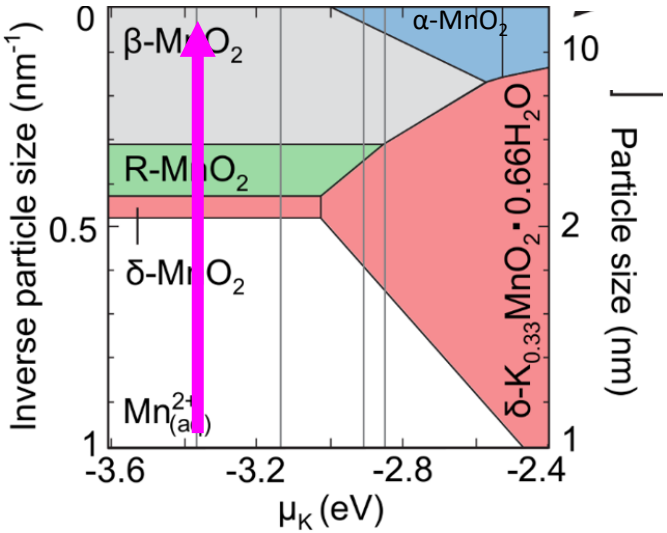
Solid-State Synthesis | ***Solution-Synthesis*** | *Defect-Mediated*

Theory

β

R(γ')

δ



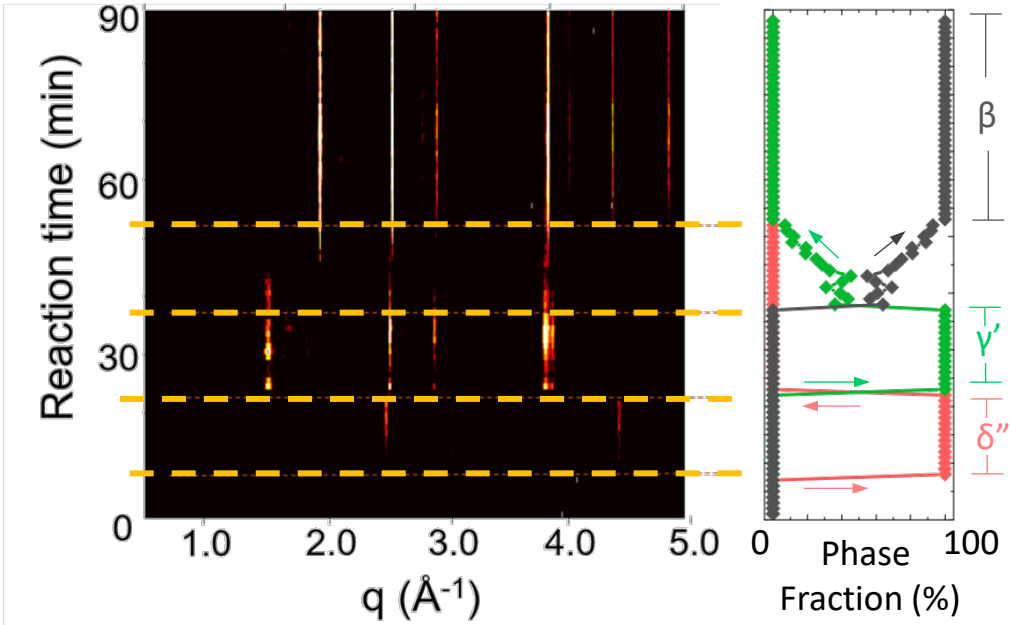
Bor-Rong Chen Mike Toney Laura Schelhas

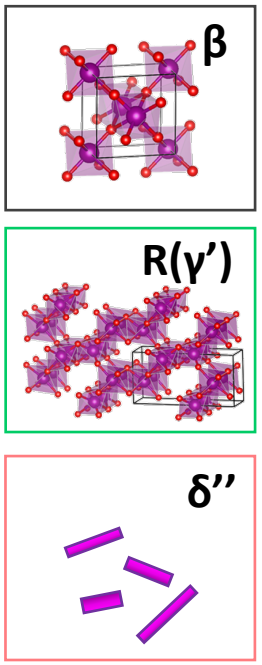
Observation

β

γ'

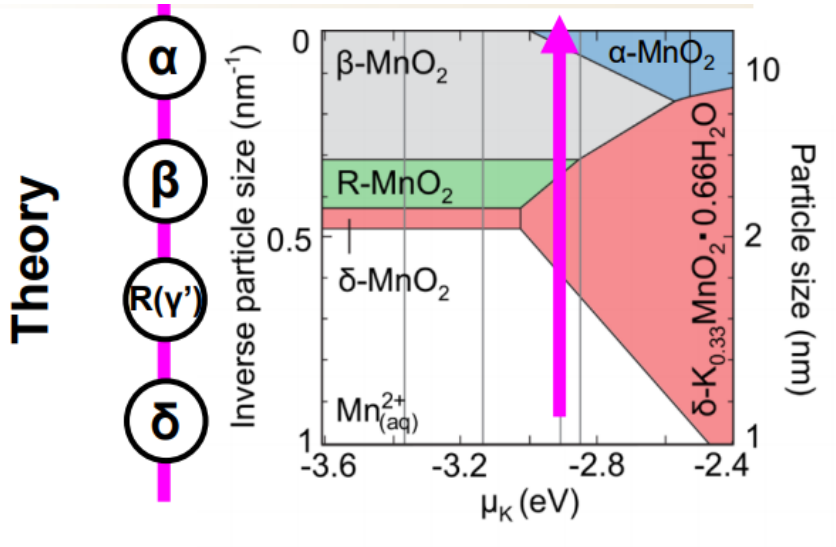
δ''

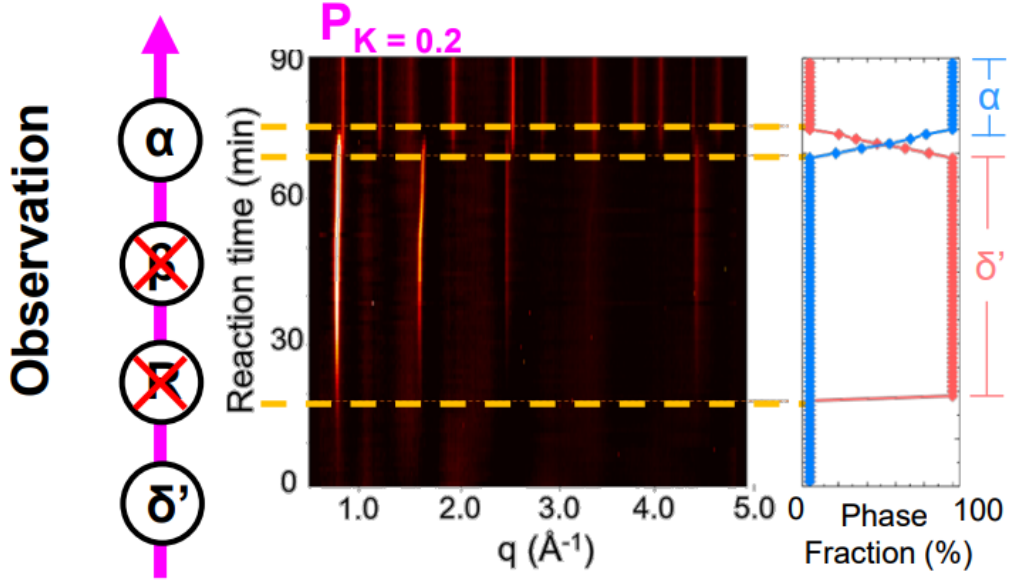




Diffusion-limited | **Nucleation-limited** | Growth-limited

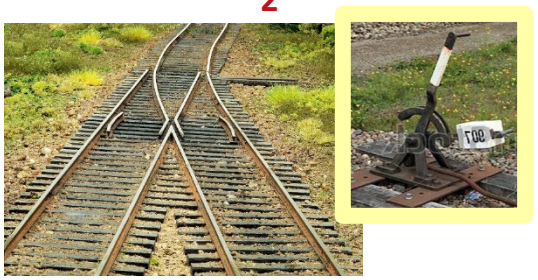
Solid-State Synthesis | ***Solution-Synthesis*** | *Defect-Mediated*





High [K⁺] regime has different crystallization pathway

δ-MnO_2



[K⁺]

R-MnO_2 **α-MnO_2**

β-MnO_2

We capture ***which*** metastable MnO_2 phases appear, and their **order**

B.R. Chen*, W. Sun*, *et al, Nat. Comms (2018)*

Diffusion-limited | Nucleation-limited | **Growth-limited**

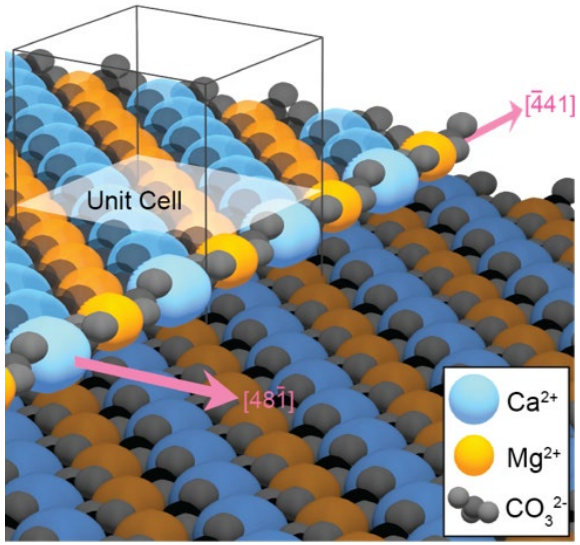
Solid-State Synthesis | *Solution-Synthesis* | ***Defect-Mediated***

Dolomite $CaMg(CO_3)_2$ comprises mountain ranges in nature, *but cannot readily grow in the laboratory*.

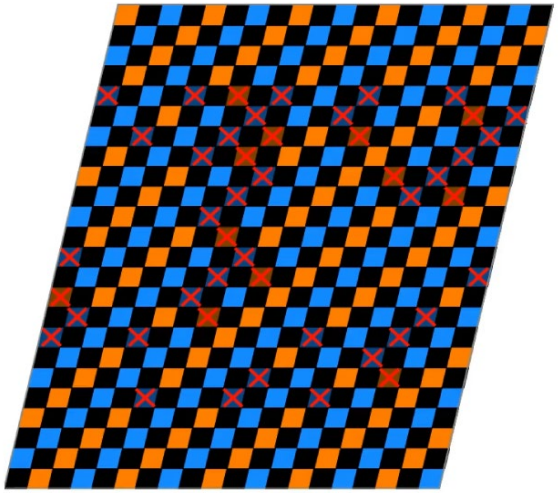
Ca/Mg disordering blocks dolomite growth

Needs dissolution to activate its growth

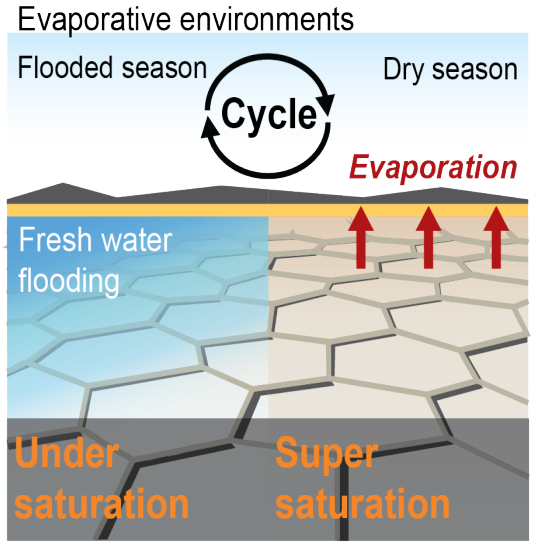
Washes away growth-limiting defects



J. Kim, *et al.* W. Sun*, *Science* (2023)



X indicates wrong cation on site



Diffusion-limited	Nucleation-limited	Growth-limited
Solid-State Synthesis	*Solution-Synthesis*	*Defect-Mediated*

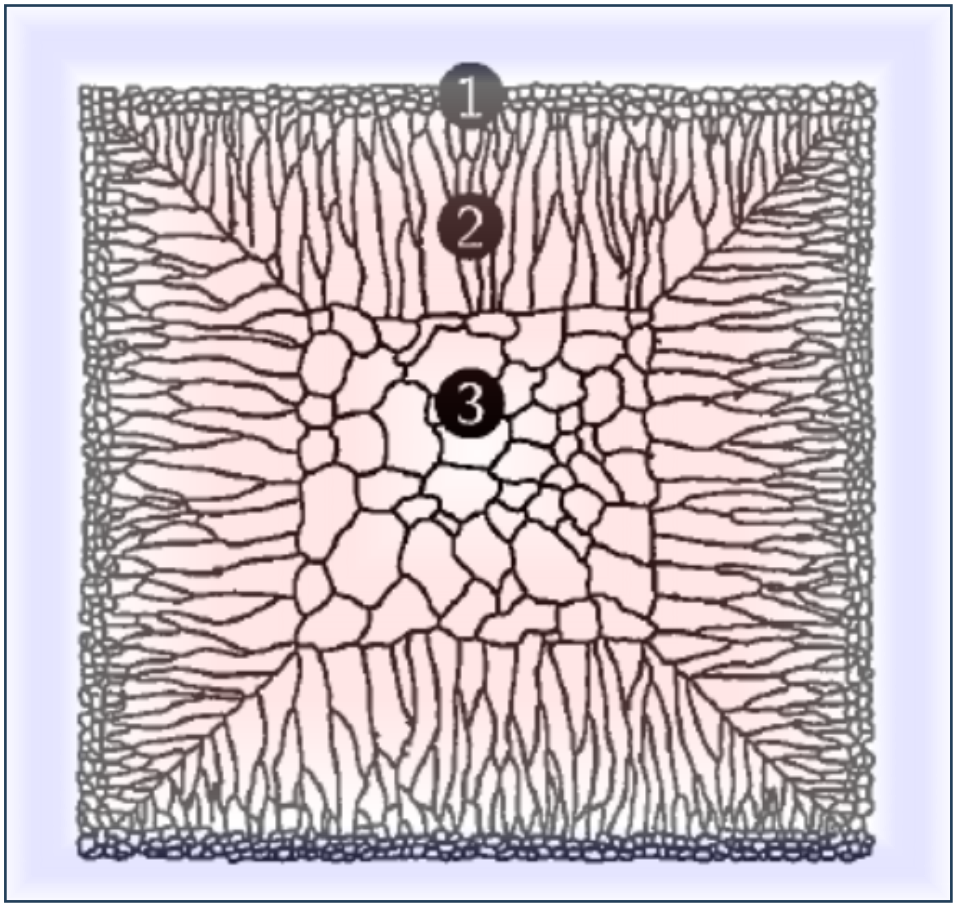
Rate-limiting kinetics change with length-scales

1) **Big Thermal Gradient**
   Fast nucleation, Slow Growth

3) **Thermal diffusion-limited**
   Slow nucleation, fast growth

*Kinetics in **lab-scale** may be **different** than in the **manufacturing** scale*

Solidification Microstructure



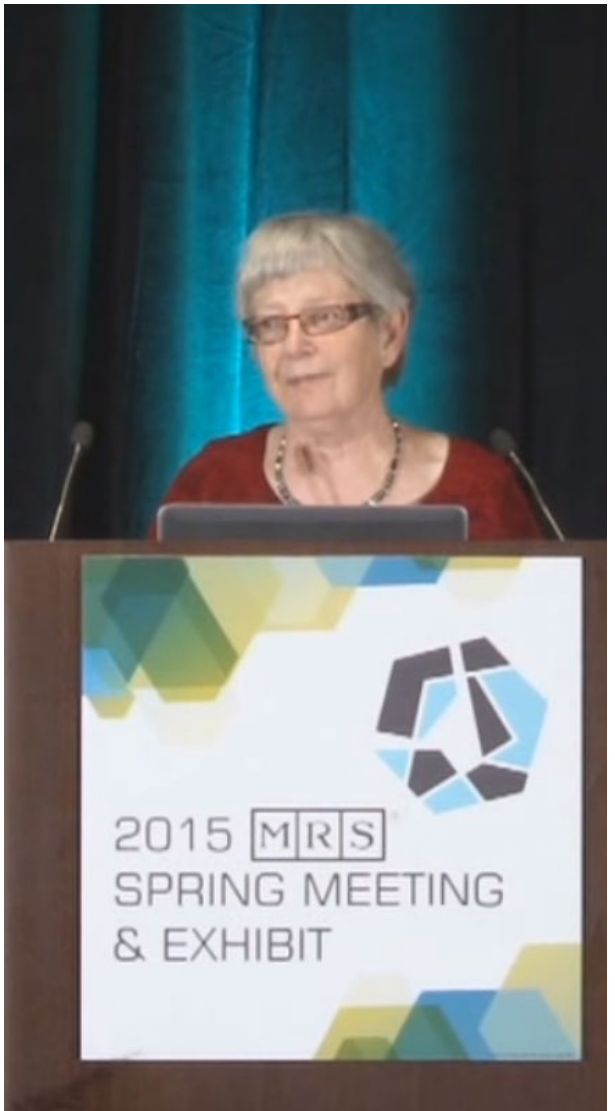
Are metastable polymorphs *kinetic* byproducts?

“Many of the things we have ascribed to kinetics are in fact thermodynamically driven.

“When you don’t understand something in archaeology, you say something has ‘ceremonial purposes’

When you don't understand something in chemistry and materials science, you say it is 'kinetically controlled’.”

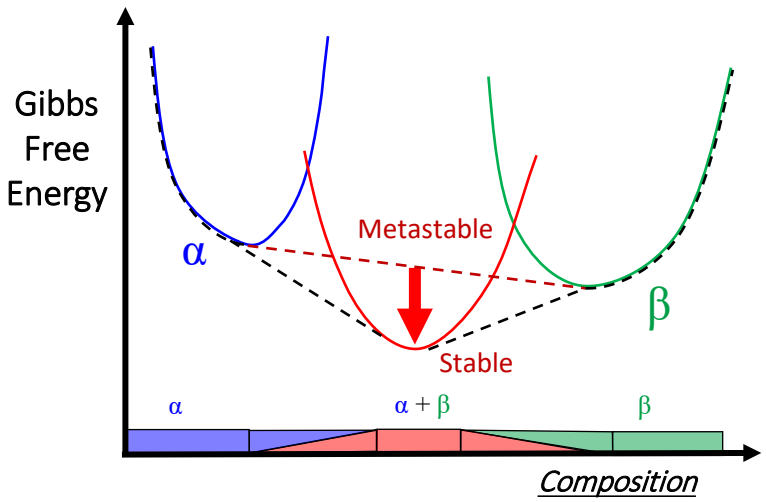
- Alexandra Navrotsky
MRS 2015 Symposium X

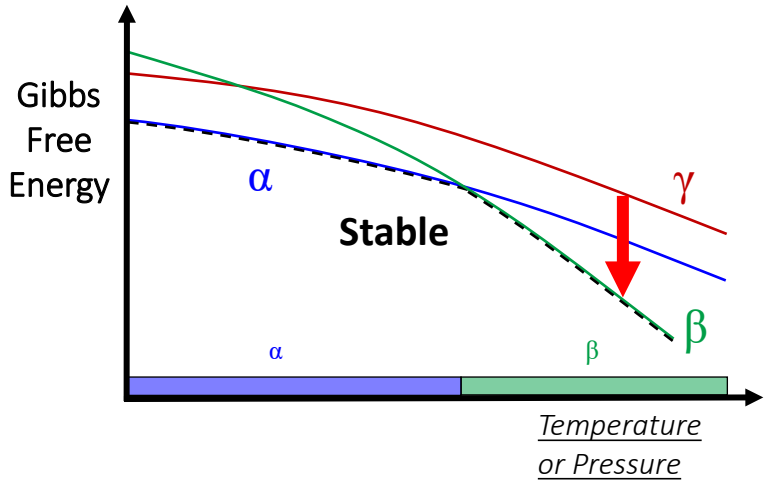


The interplay between Thermodynamics and Kinetics

Metastable Precursor → Equilibrium Target

Thermodynamic Driving Force





Diffusion (Fick's Law)

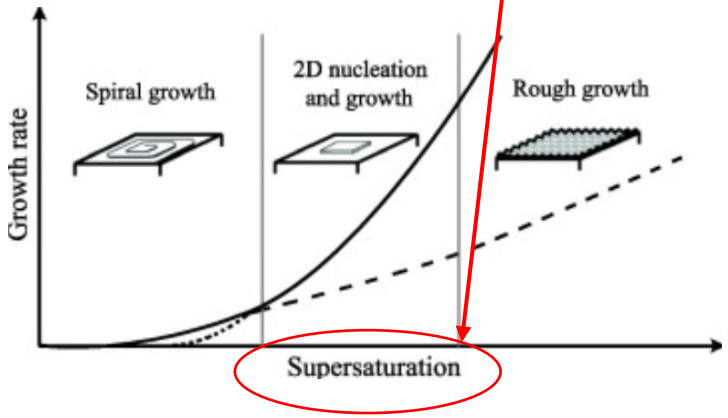
$$J = \frac{Dc_i}{RT}\frac{\partial \mu_i}{\partial x}$$

Nucleation Barrier

$$\Delta G_c \propto \frac{\gamma^3}{(\Delta G_{bulk})^2}$$

Thermodynamic Driving Force!

Crystal Growth



AI-Guided Discovery of Metastable Materials

NATIONAL ACADEMIES Sciences Engineering Medicine

The Overprediction Problem

1) Which metastable materials can form?

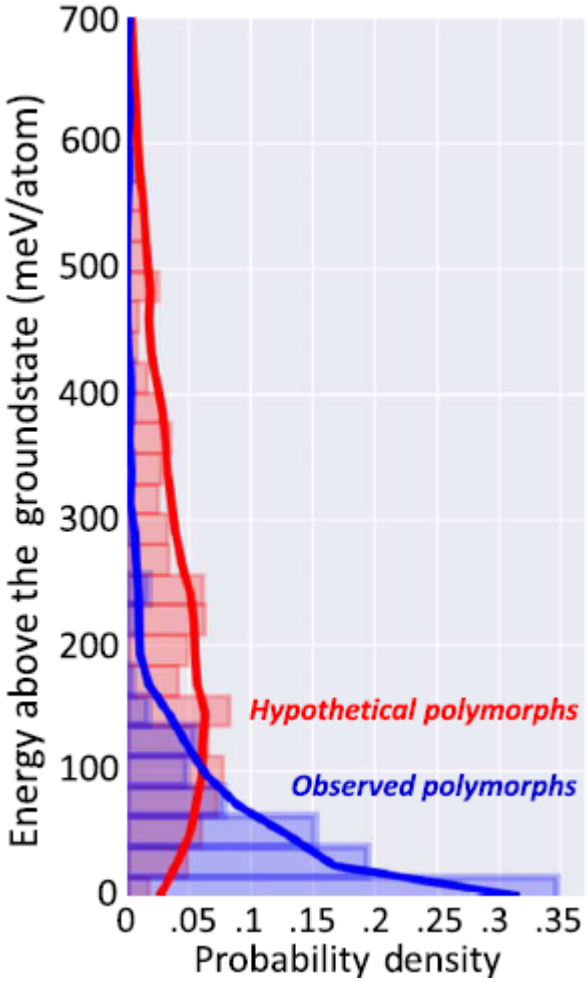
Remnant Metastability

2) Which metastable materials *will* form, under my conditions of synthesis?

High-dimensional phase diagrams

3) How can I keep (or get rid of) metastable materials that have formed?

Navigating kinetic rate limiting steps



*W. Sun, *et al.*, *Science Advances* (2016)

AI-Guided Discovery of Metastable Materials

NATIONAL ACADEMIES Sciences Engineering Medicine

The thermodynamic scale of inorganic crystalline metastability
W. Sun, K.A. Persson, G. Ceder, et al., Science Advances (2016)

The geometry of high-dimensional phase diagrams
J. Chen, M. Powell Palm, Wenhao Sun., *Arxiv* (2024)

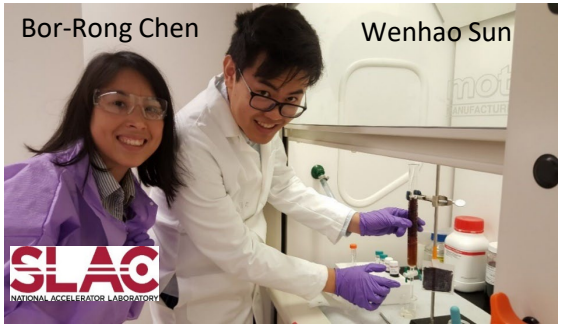
Understanding Crystallization Pathways leading to manganese oxide polymorph formation
B.R. Chen, W. Sun, *et al.*, *Nature Communications* (2018)

Navigating phase diagram complexity to design more efficient solid-state syntheses
Jiadong Chen, Sam Cross, Lincoln Miara, Wenhao Sun *et al.*, *Nature Synthesis* (2024)

Dissolution enables dolomite crystal growth near ambient conditions
J. Kim, Wenhao Sun, *et al.*, *Science* (2023)

CNGMD Incorporating Metastability


Gerbrand Ceder




Jiadong Chen


Joonsoo Kim


Sam Cross

EARLY CAREER AWARD

AI-Guided Discovery of Metastable Materials

NATIONAL ACADEMIES Sciences Engineering Medicine

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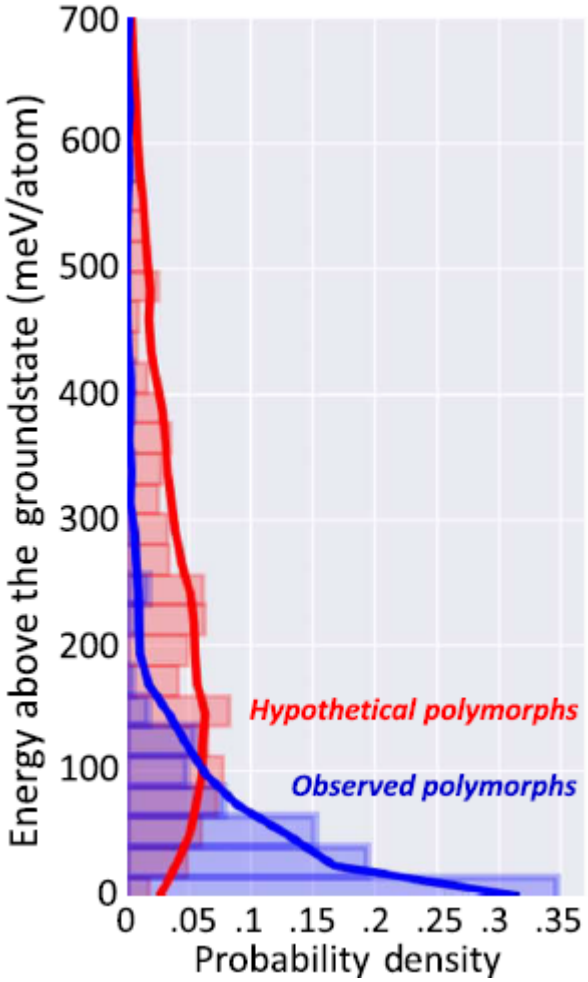
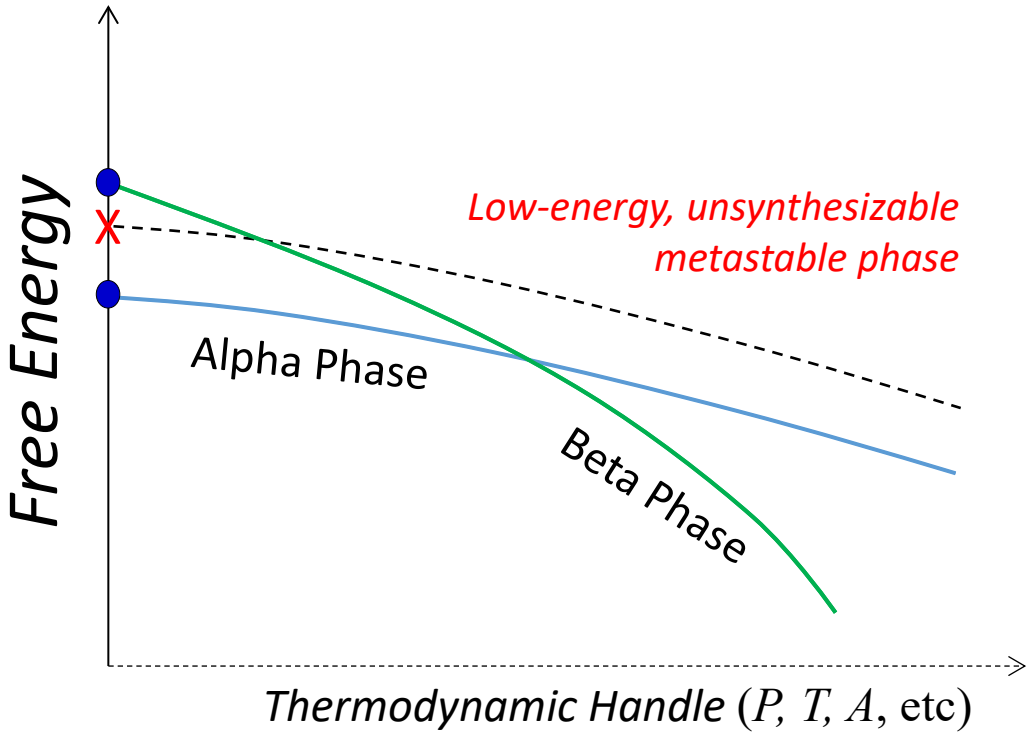


*W. Sun, *et al.*, *Science Advances* (2016)

"Remnant" Metastability Hypothesis

Observed metastable phases are generally remnants of thermodynamic conditions where they were once the lowest free-energy phase.



Extensive Advantage

- A **high-entropy** metastable phase should be synthesized at **high Temps**
- A **low-volume** metastable phase should be synthesized at **high Pressure**
- A **nitrogen-rich** metastable phase should be synthesized at **high μ_N**
- A **polar p**olymorph should be synthesized under applied ***E*-fields**

W. Sun, *Science Advances*, 2016