Forum on the Future of Synthesis
MRS Fall 2024

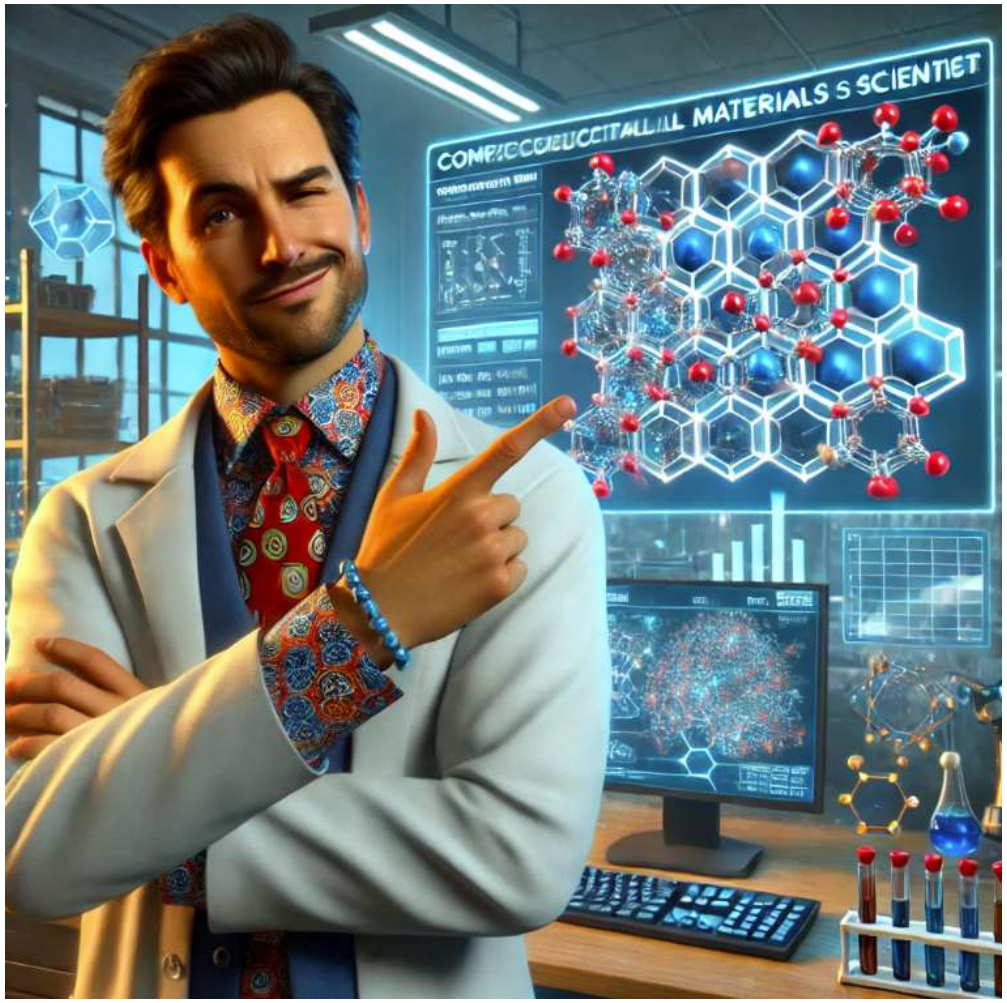
Evaluating the ***synthesis*** and ***synthesizability*** of computationally-predicted materials

(… a bold perspective of the Future of Synthesis)

Wenhao Sun
Dow Early Career Professor
Materials Science and Engineering
University of Michigan

Show of hands!

- How many of you are primarily experimentalists?
- How many of you are primarily computationalists?
- Have done a ‘closed-loop MGI’ computational/experimental collaboration?
- **Were given, or gave, a predicted material that *could not be synthesized*?**
- How many of you tried for >6 months? >1 Year? >2 years?



Give me a picture of a smug computational materials scientist who is making theoretical predictions of new materials that probably can't be made but they are very confident in their predictions

Well, it's on the convex hull,
so it should be synthesizable.

Well it's metastable, but only above the hull by 10 meV/atom, so you can make it *if you're clever enough*.

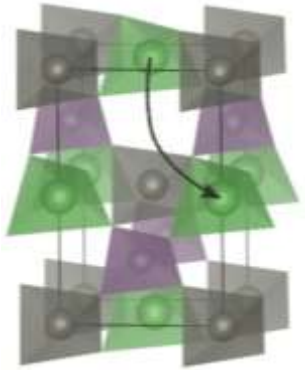
Well AXZ exists, so AYZ should be easy to make, since Y is similar to X.

Well, my AI synthesis predictor has a good RMSE/F1 score, and it says this material is 82% likely to be synthesizable

Predicted next-gen battery materials still awaiting experimental realization

JCESR | JOINT CENTER FOR ENERGY STORAGE RESEARCH

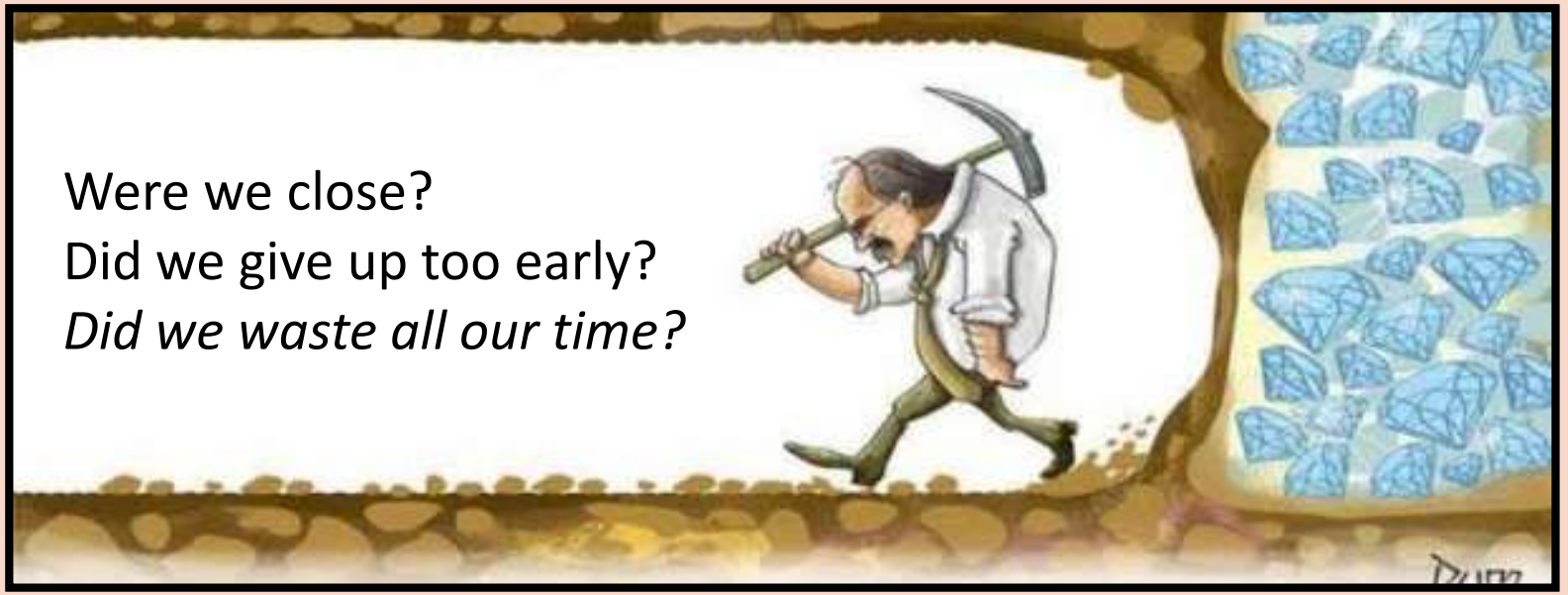
$Li_2Zn_{0.5}PS_4$ $Na_3Mo_2(PO_4)_3F_3$ $MgMo_2(PO_4)_3O$ $MgV_{1.25}Ti_{0.75}O_4$



W. Richards, *EES* (2016)

+ Fastest Li-Ion Conductor
+ 10 meV/atom above hull

- Cannot synthesize at high enough Li/Zn ratios
- Phase impurities



Linda Nazar
U. Waterloo

Ken Poeppelmeier
Northwestern U.

Jordi Cabana
U Illinois Chicago

These would be game-changing materials

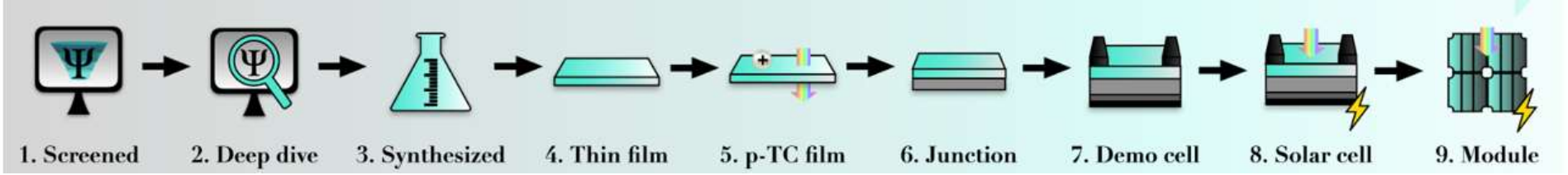
Expert solid-state chemists devote years to attempt their synthesis…

PRX Energy

PERSPECTIVE | OPEN ACCESS

From Design to Device: Challenges and Opportunities in Computational Discovery of *p*-Type Transparent Conductors

Rachel Woods-Robinson [1,2,3,*], Monica Morales-Masis [4], Geoffroy Hautier [5], and Andrea Crovetto [6]



	Material	P-type TC "design-to-device" progress	Bottleneck
Computational predictions	(a) $ZnZrN_2$		Synthesizability challenges
	(b) ZrSO		Thin film challenges
	(c) $Cs_4Cd_2SbCl_{12}$		DFT errors
	(d) BP		Poor crystal quality
	(e) CaCuP		Spurious absorption
	(f) Ta_2SnO_6		Dopability challenges
	(g) $CrMn_2O_4$		Doping reduces transparency
	(h) TaIrGe		Insufficient research attention
	(i) Ba_2BiTaO_6		Dopability challenges

What does "synthesizable" *mean*?

- Is it even **possible** to make this material?
- What experimental **method** would be best to synthesize it? (Solid-State, Hydrothermal, Flux?)
- Within my method, what **recipe** should I use? (Precursors, Temp., Time*, etc…*)
- Can I make my material in the desired ***form***? (Powder, Thin-film, Bulk Single Crystal)
- Can I synthesize it with high ***quality*****?** (No killer defects)
- Can I synthesize it ***reliably*** *and* ***reproducibly***?
- Can I synthesize it ***efficiently***? (Time, Electricity, $$ Cost, Labor)
- Can I synthesize it ***at scale*** for manufacturing?

- Is my material operationally stable?

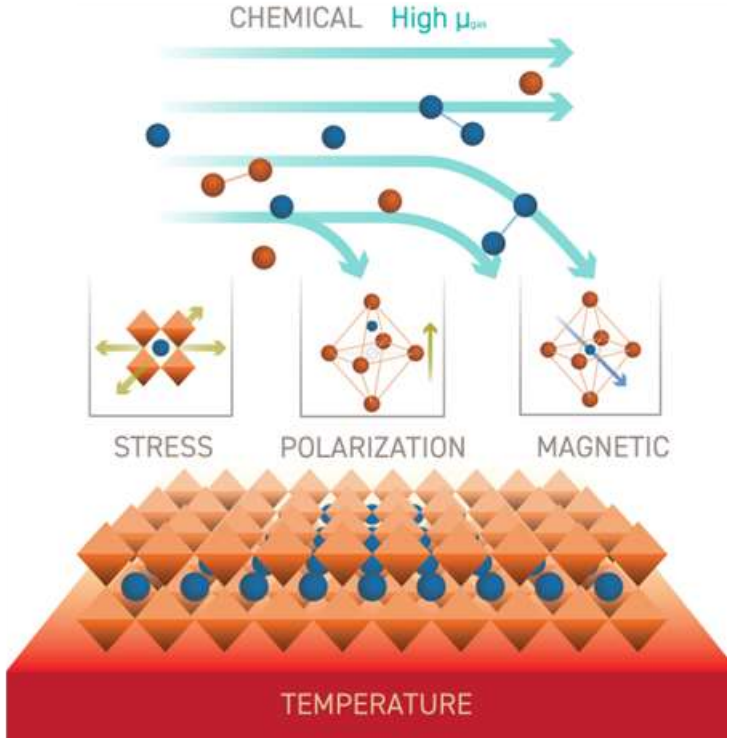
→Can I **avoid the synthesis** of undesired phases during operation?

Interfacial phases
Corrosion byproducts
Decomposition products

Predicting Synthesis and Synthesizability

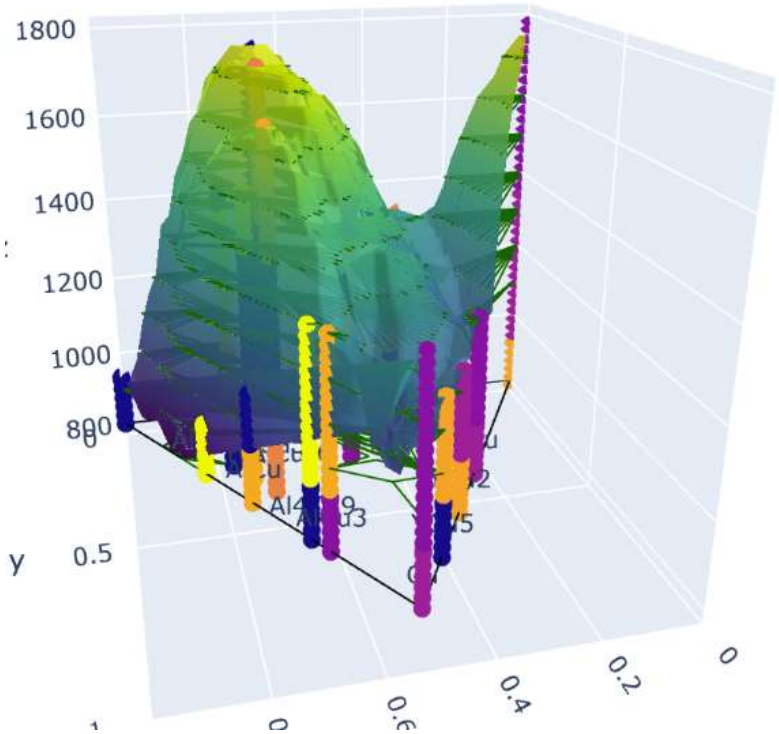
Thermodynamics

Epitaxial Thin Film



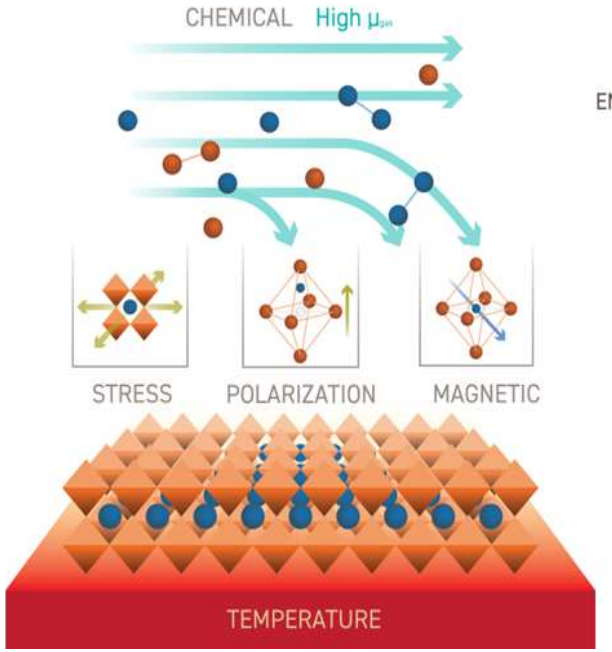
Kinetics

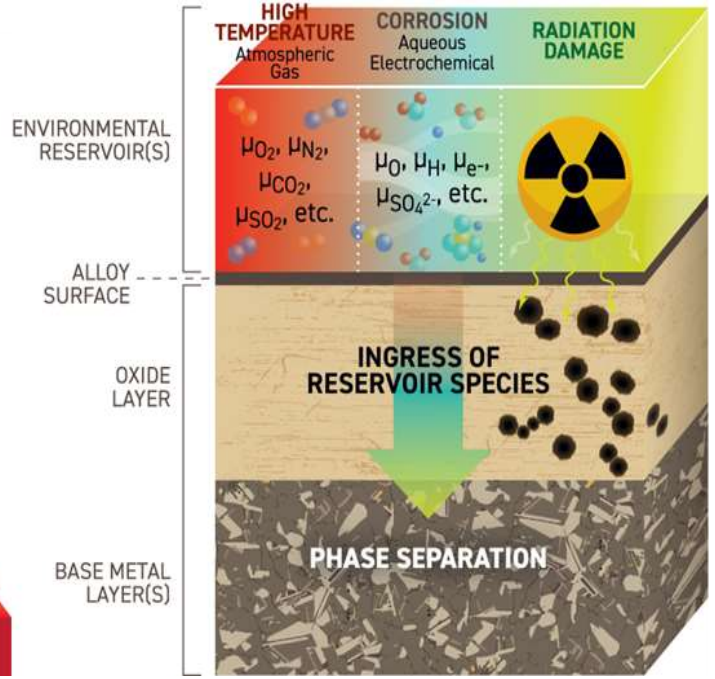
Bulk Crystal Growth

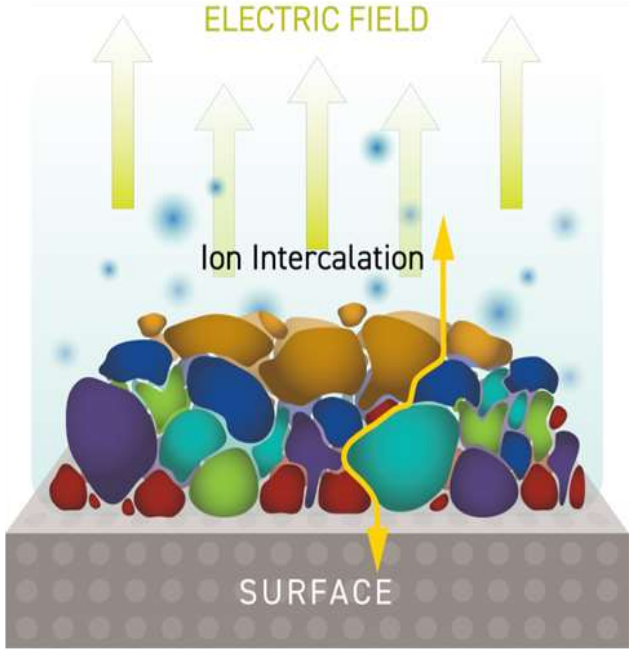


ML/AI Robotics

Modern materials are becoming very complicated ….







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)

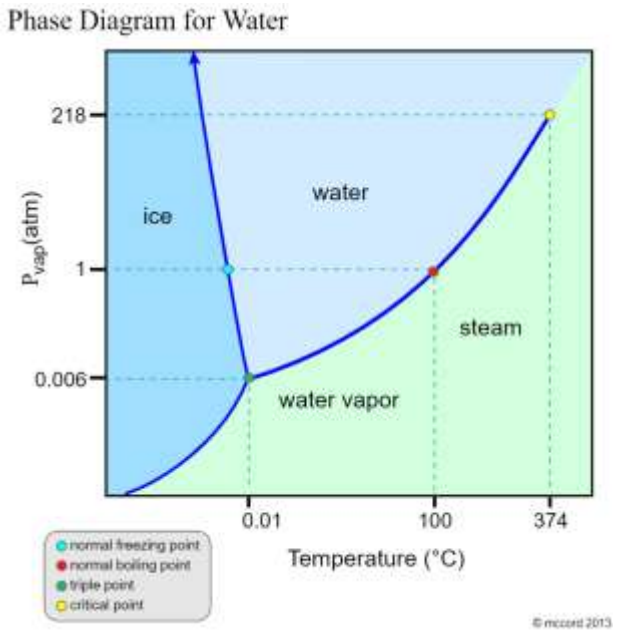
Solid-Liquid Interface

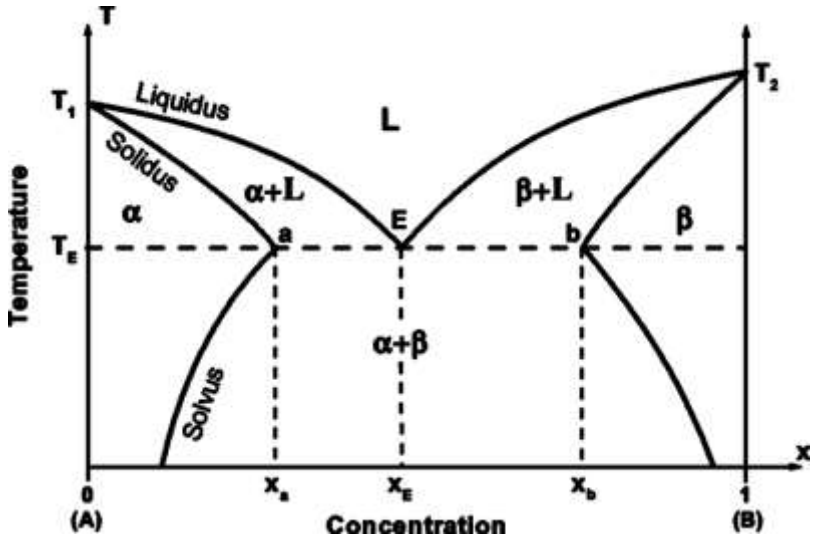
- Aqueous stability
- Phase Heterogeneity
- Electrical Double Layer
  - Chemisorption
  - Physisorption
  - Water polarization
  - Electric field

Phase diagrams are out of date!

Classical thermodynamics only has axes of temperature, pressure and composition

$$dG = \underbrace{-SdT + VdP + \sum_i \mu_i dN_i}_{\text{Classical Thermodynamics}}$$





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

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*

Phase diagrams are out of date!

Classical thermodynamics only has axes of temperature, pressure and composition

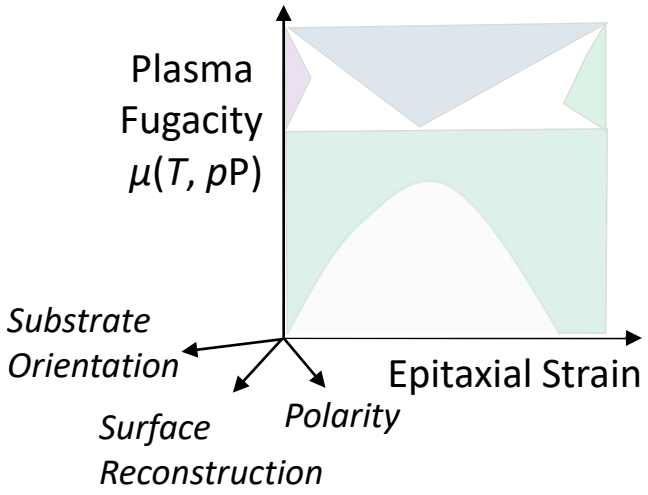
$$dG = -SdT + VdP + \sum_i \mu_i dN_i + \gamma dA + \phi dQ + \sigma_{ijkl} d\varepsilon_{ijkl} + \vec{E} \cdot d\vec{P} + \vec{B} \cdot d\vec{M} + \ldots$$

Classical Thermodynamics

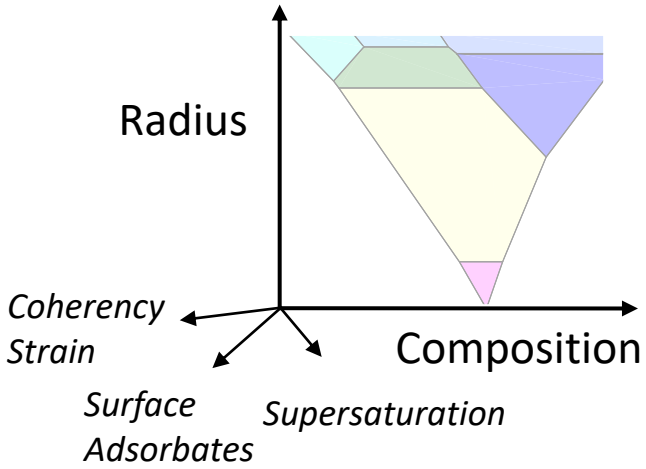
Thermodynamic considerations in modern materials

2) May become intrinsically high-dimensional

Vapor Deposition (MBE, MOCVD, *etc*)



Nanoparticle Stability



The geometry of high-dimensional phase diagrams

Construct →
Interpret →
Navigate →

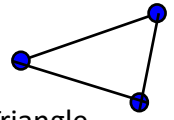
I. Generalized Gibbs Phase Rule
II. Duality between open and closed chemical systems
III. Engineering Relative Stability in 4 Dimensions

Dr. Jiadong Chen

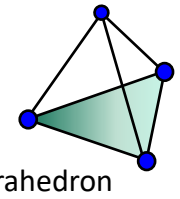
Phase Coexistence Regions in *U*(*S*,*X*) are *N-dimensional triangles* (Simplices)

0 dimension

1 dimension



2 dimensions

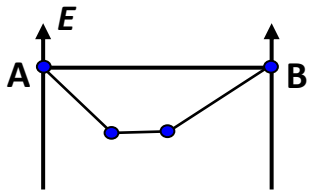


3 dimensions

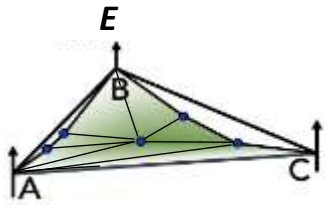
'5-cell'

4 dimensions

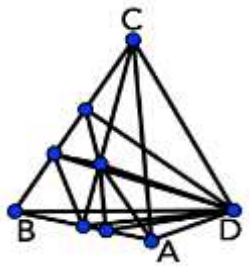
Thermodynamic Convex Hulls



1 variable



2 variables

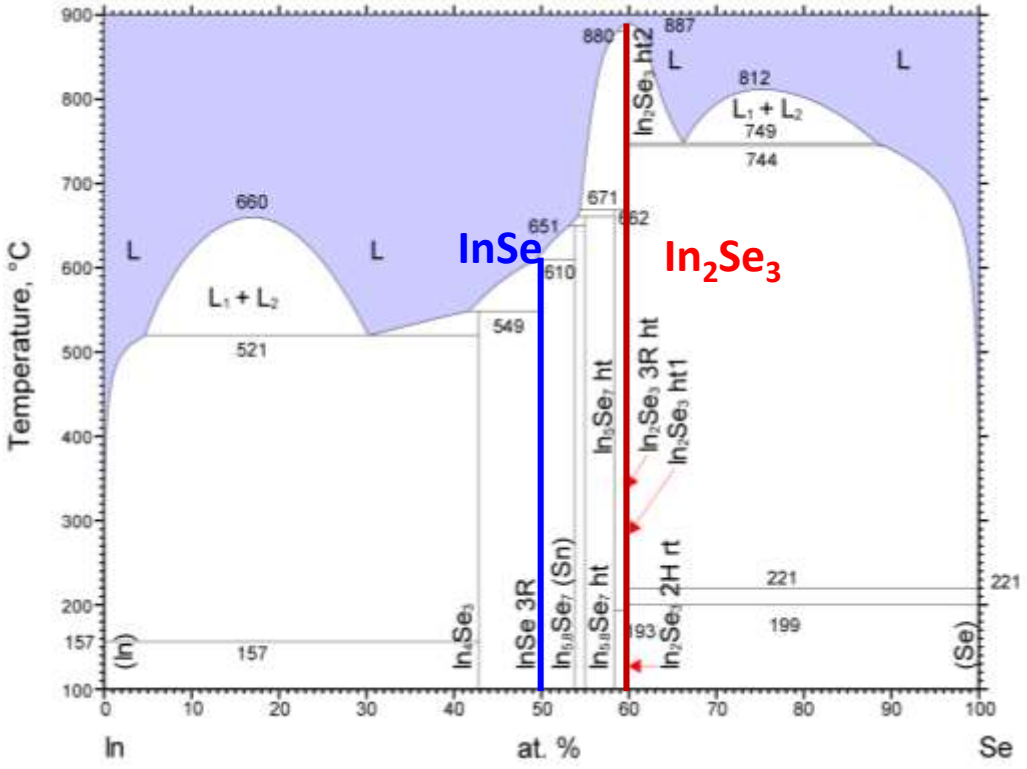


3 variables

Lack of Formalism

≥4 variables

In thin-film growth, the Temperature-Composition diagram is useless



To make thin films, you control
gas chemical potential, not composition!

MBE: Chamber pressure, Knudsen cell aperture, Plasma (RF/DC), Gas flow rate

MOCVD: Molecular precursor, gas ratios, flow rates

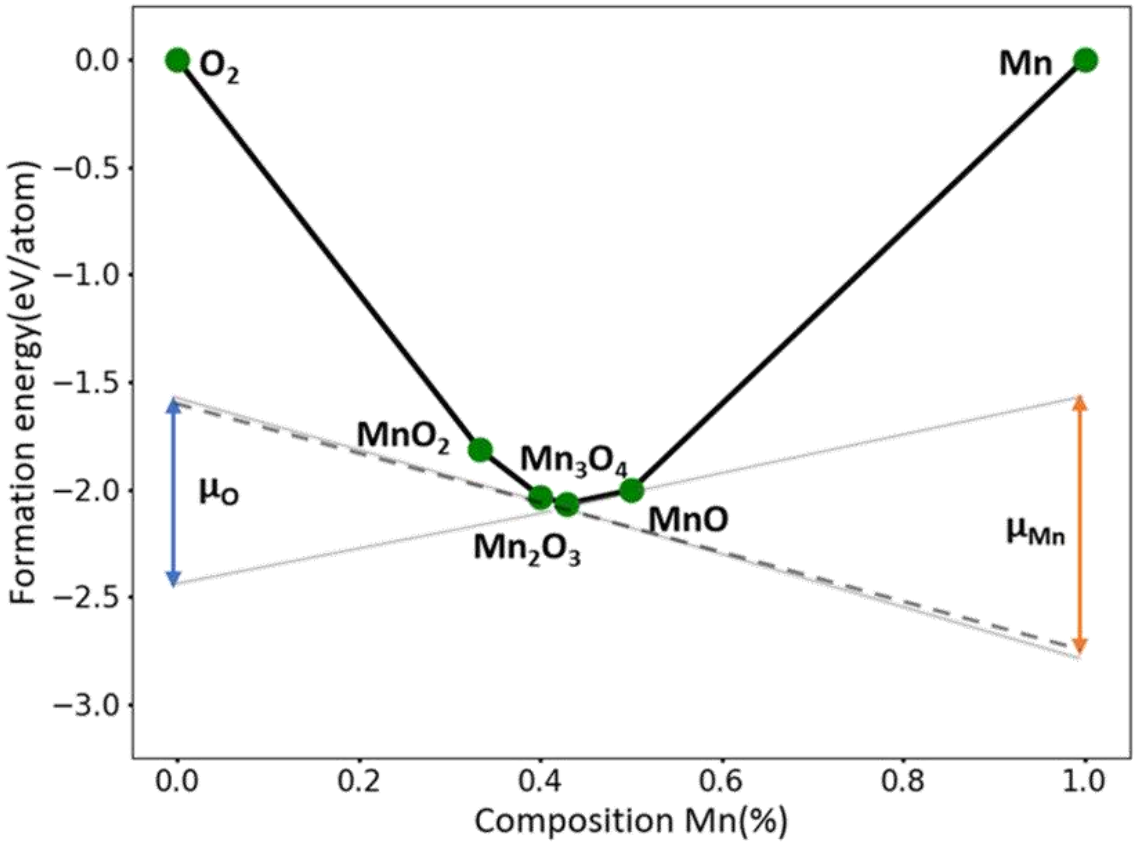
PLD: Laser energy, Fluence, Target-Substrate Distance

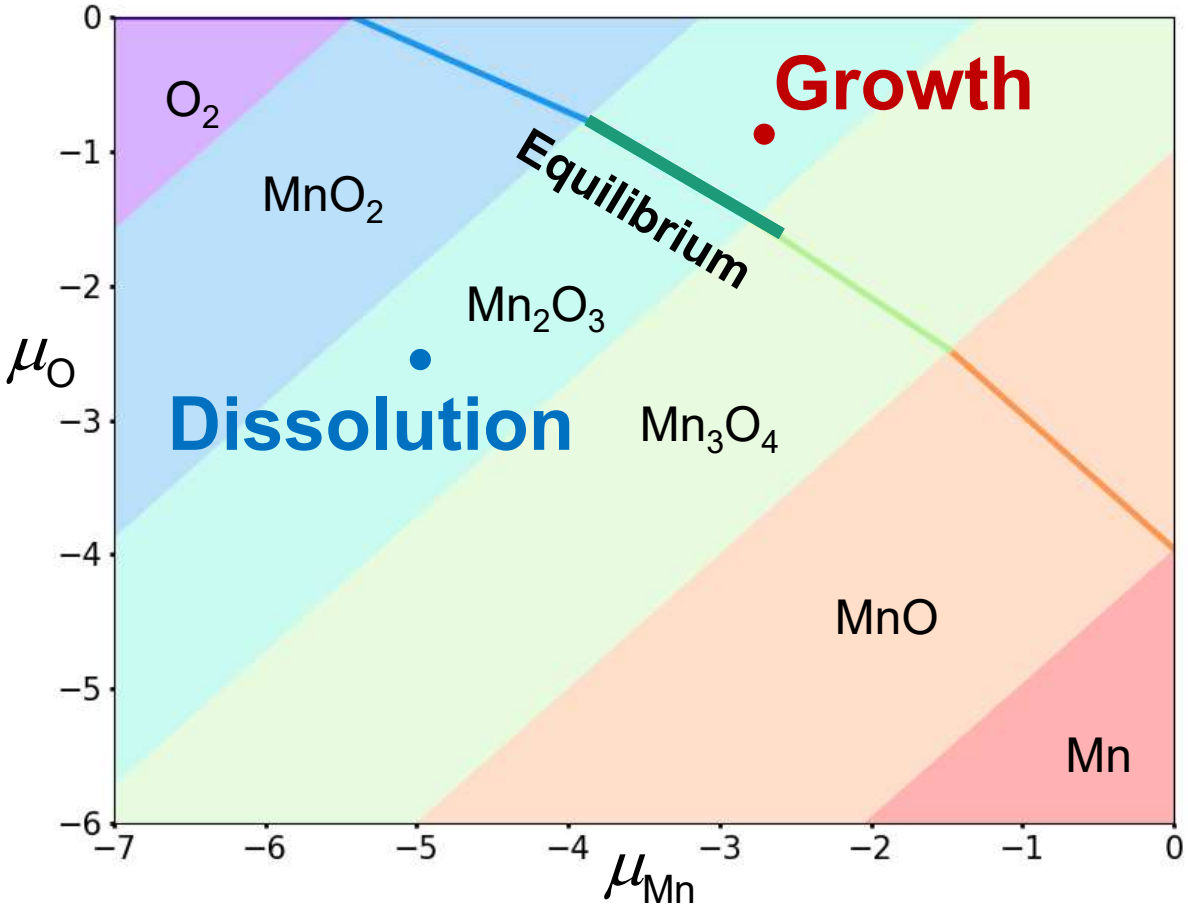
"I want InSe, but keep depositing In_2Se_3"

Andy Mannix
Stanford University

The Geometry of High Dimensional Phase Diagrams II:

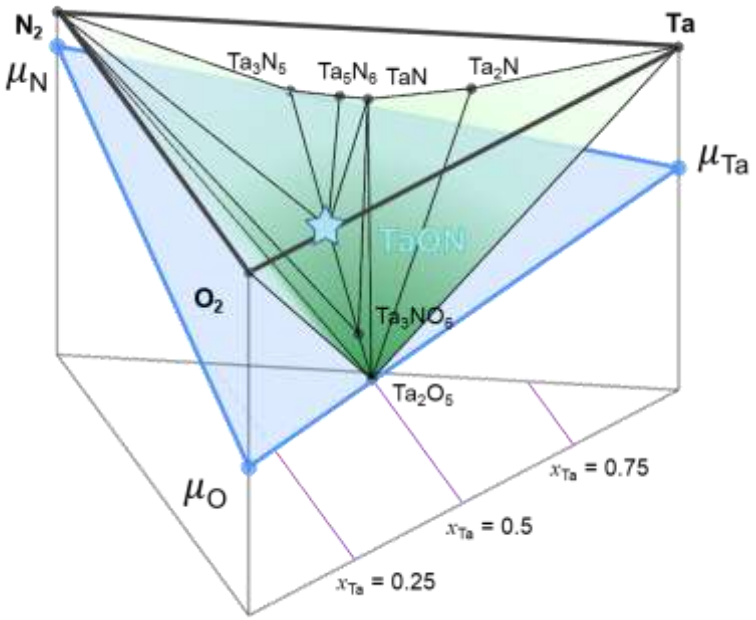
The **duality** between convex hulls and chemical potential diagrams

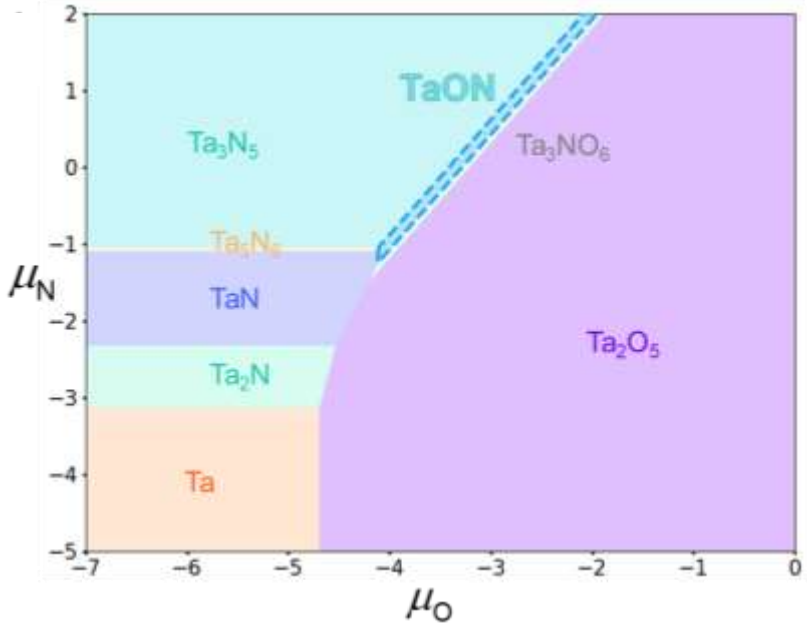




Jiadong Chen, M. Powell-Palm, Wenhao Sun, *Arxiv* 2404.05197 (2024)

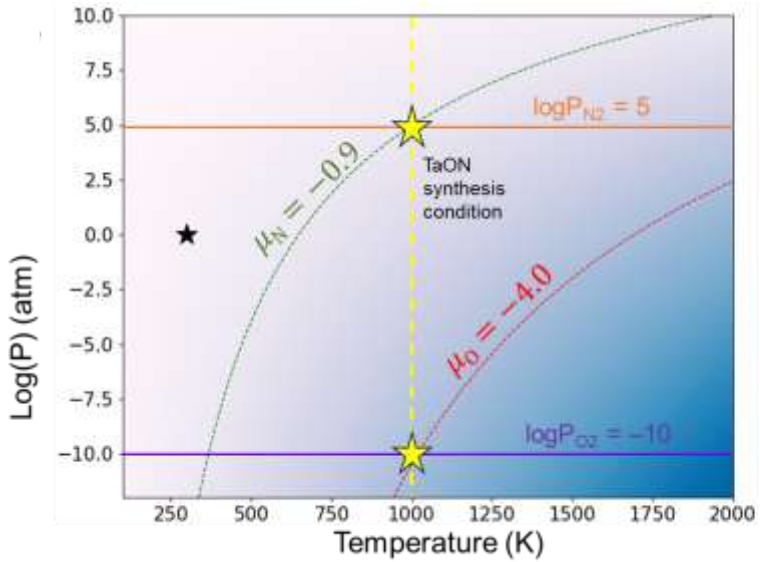
TaON is stable on convex hull

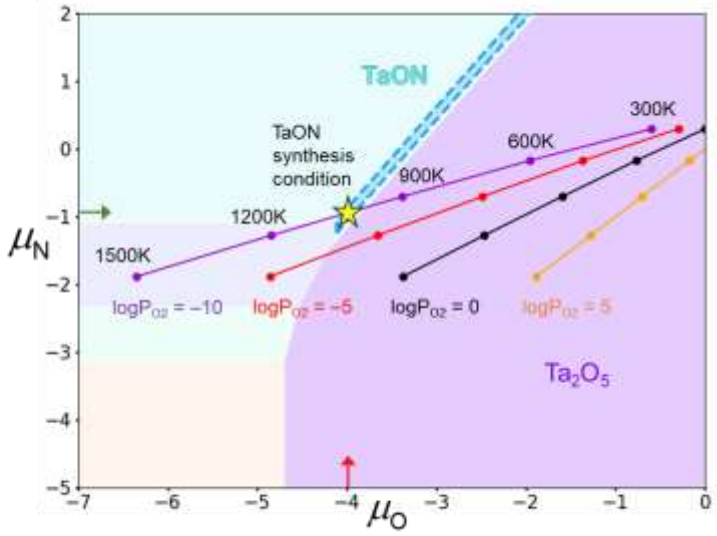




But has very narrow chemical potential window

Need **precise** temperature, **very low** oxygen pressure, **very high** nitrogen fugacity





Jiadong Chen, M. Powell-Palm, Wenhao Sun, *Arxiv* 2404.05197 (2024)

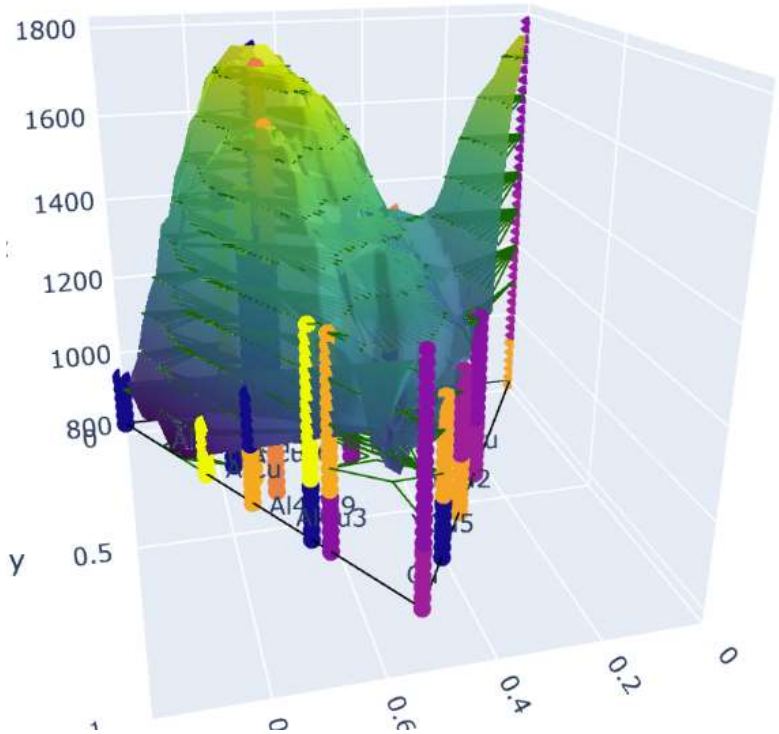
Predicting Synthesis and Synthesizability

Thermodynamics

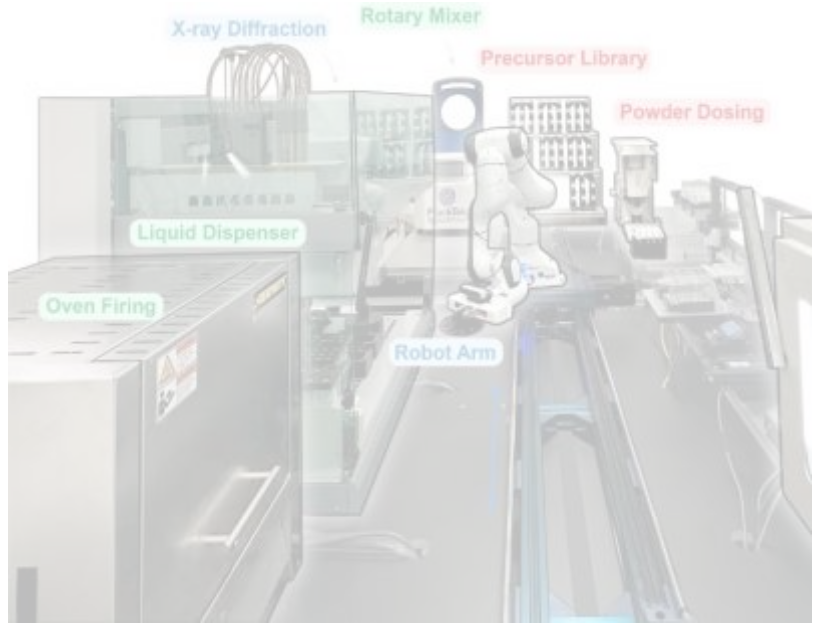
Epitaxial Thin Film

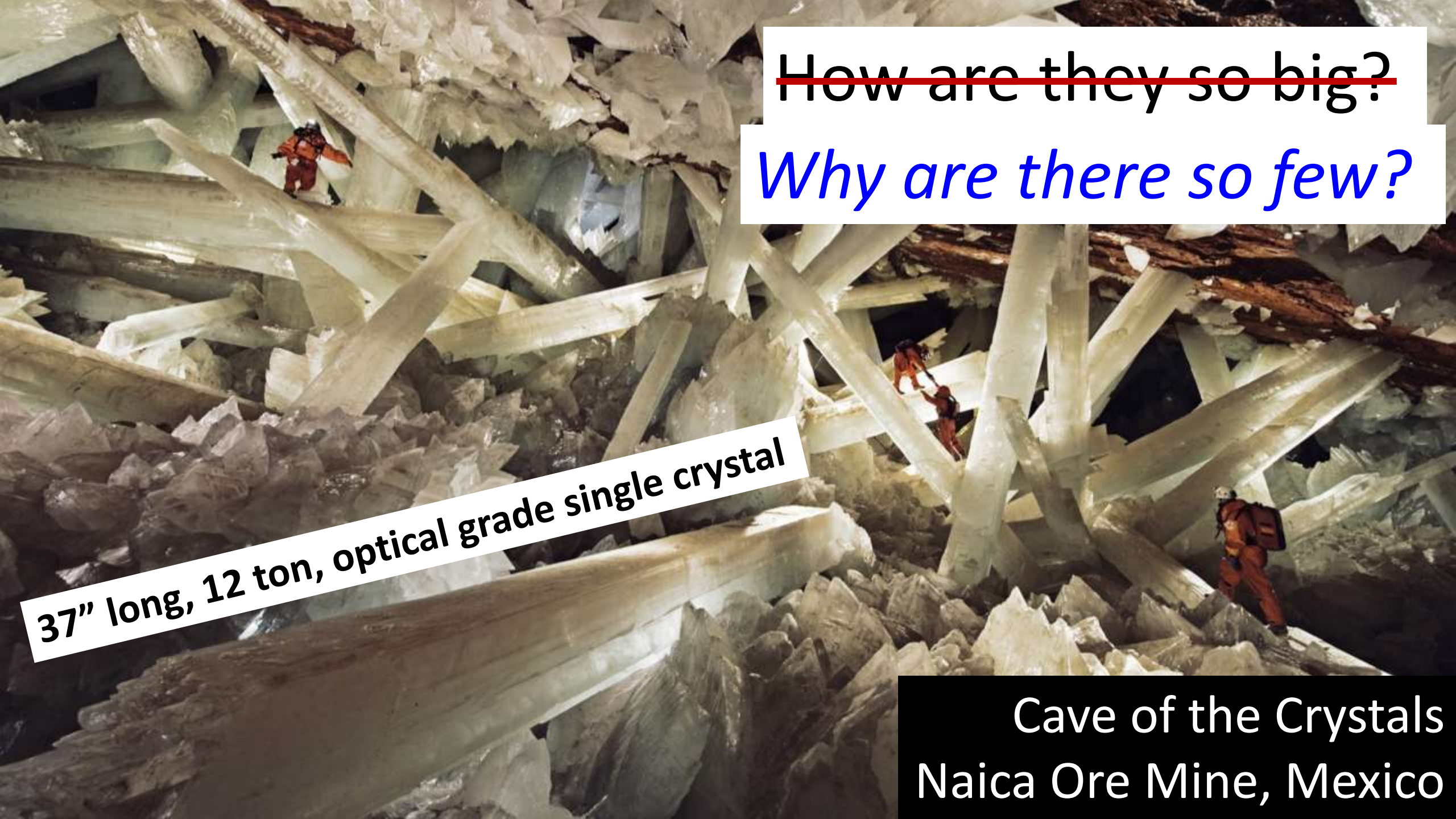
Kinetics

Bulk Crystal Growth

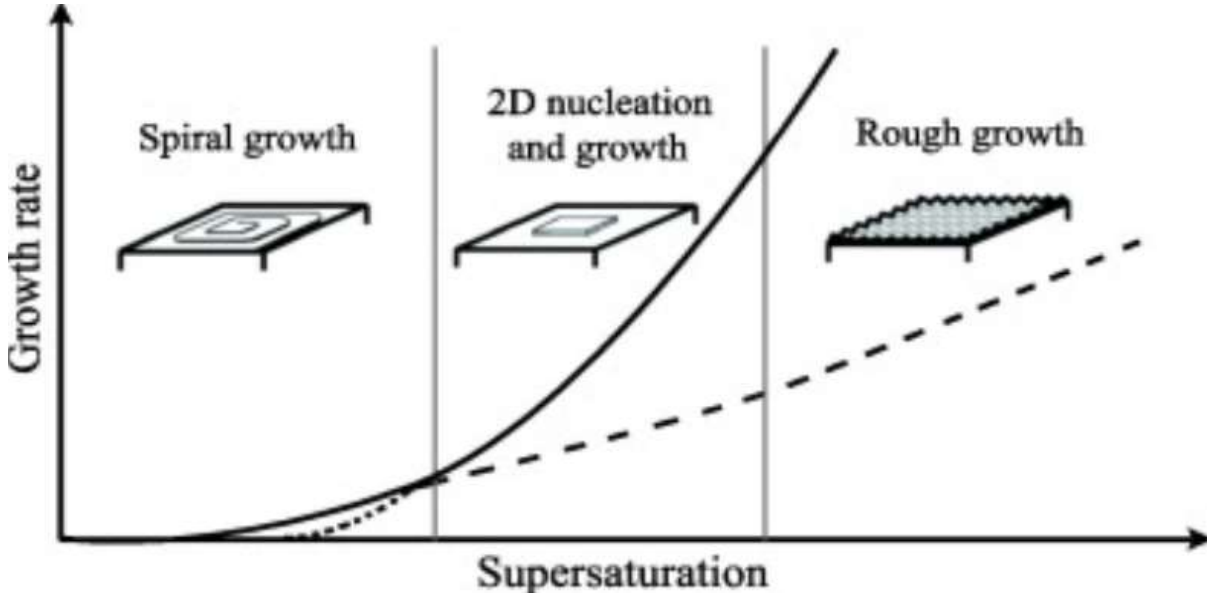


ML/AI
Robotics

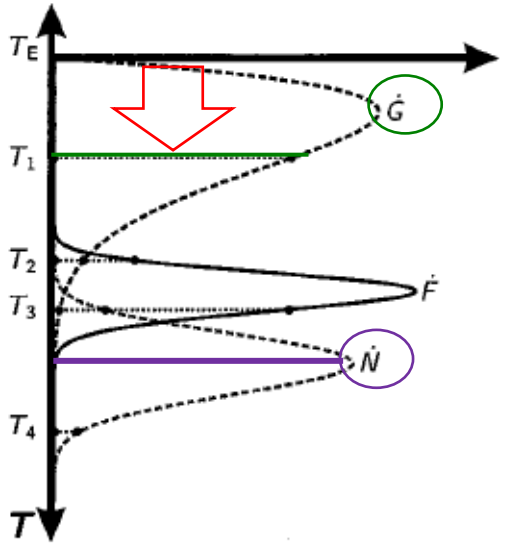


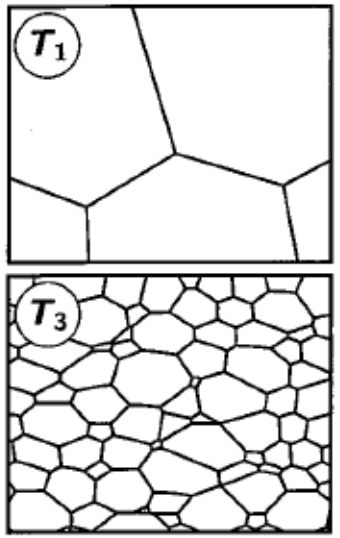

~~How are they so big?~~
Why are there so few?
37” long, 12 ton, optical grade single crystal
Cave of the Crystals
Naica Ore Mine, Mexico

Supersaturation from solution



Solidification by Cooling from Melt





Low undercooling

High undercooling

Thermodynamic driving force

(supersaturation, undercooling) needs to be:

1) **Big enough** to promote crystal growth

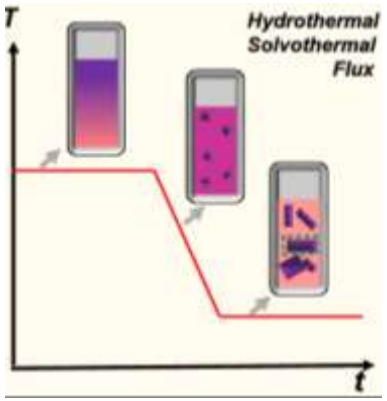
2) **Not so big** that it triggers secondary nucleation

REVIEW | May 16, 2024

Tools and Tricks for Single Crystal Growth

Tanya Berry*, Nicholas Ng*, and Tyrel M. McQueen*

Chemistry of Materials > Vol 36/Issue 10



Need the Liquidus!

- The system you want isn't in Thermocalc/Factsage

- DFT is only for solids, not liquids

Bulk crystal growth

Design of Fluxes for Growth of 'Buried Intermetallics'

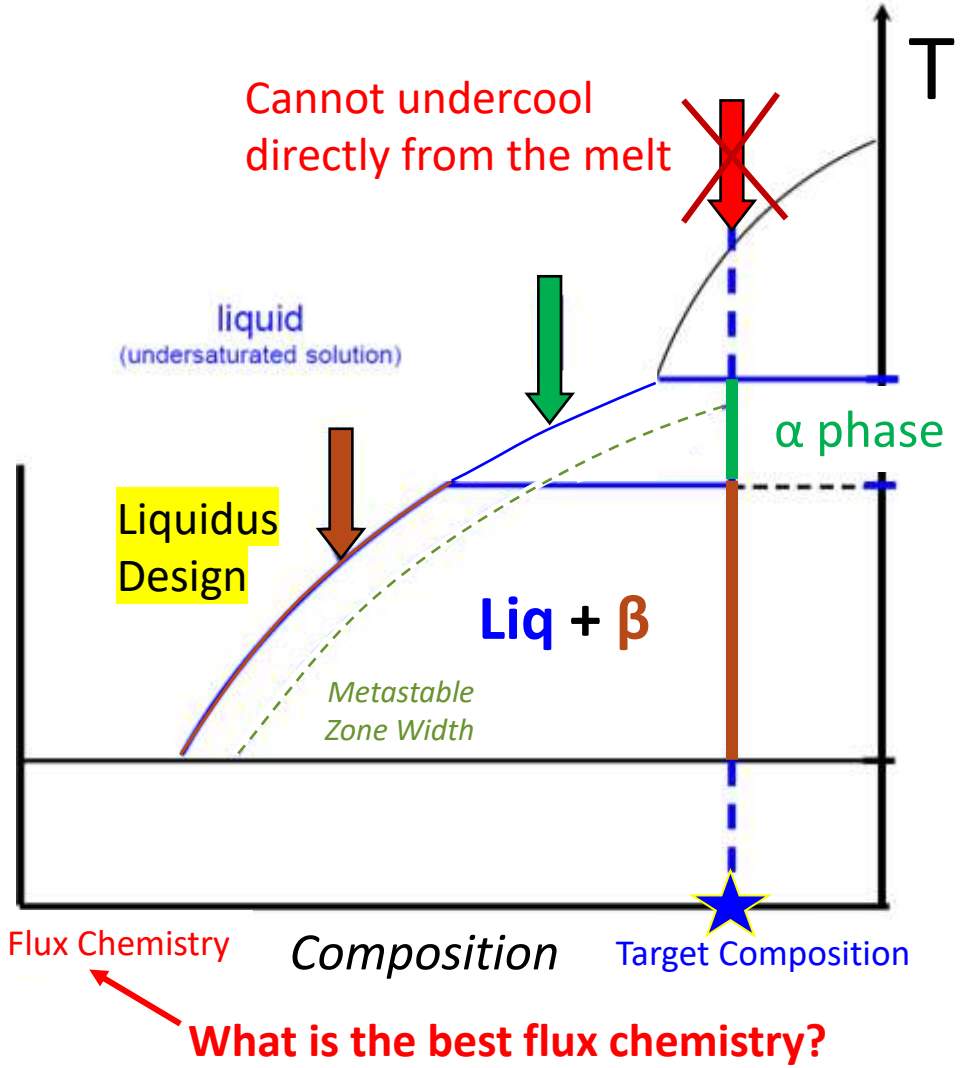
* Crystals which do not melt congruently :
  chemical or peritectic decomposition

* Crystal structure transition (polymorphism)
  strain and fractures

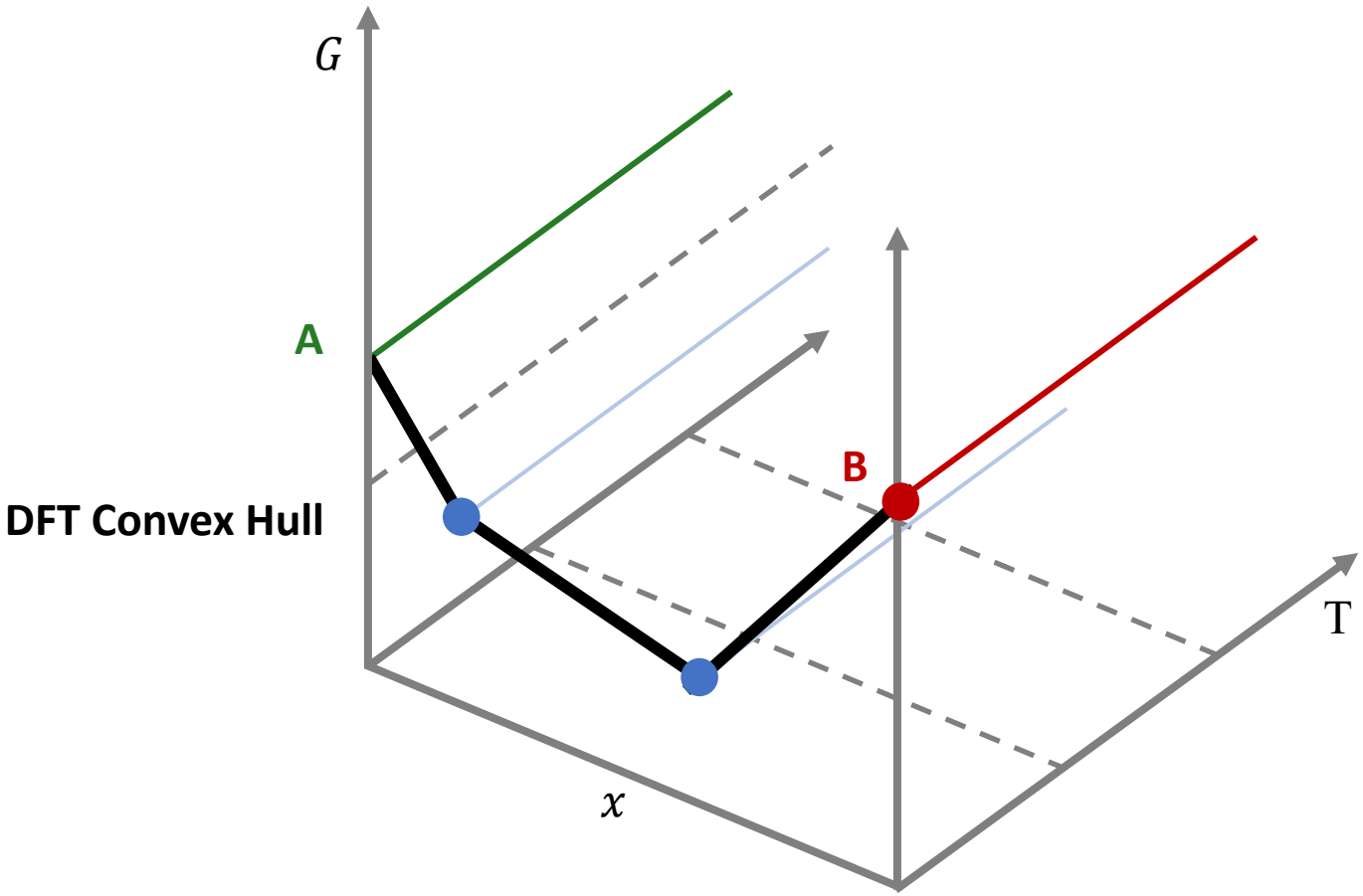
* Highly refractory materials
  delicate and expensive growth from the melt

* High vapor pressure above Tm

* Volatile constituent in the melt



If you have a DFT convex hull, **there exists** some G_{liquid} that reproduces the liquidus curve



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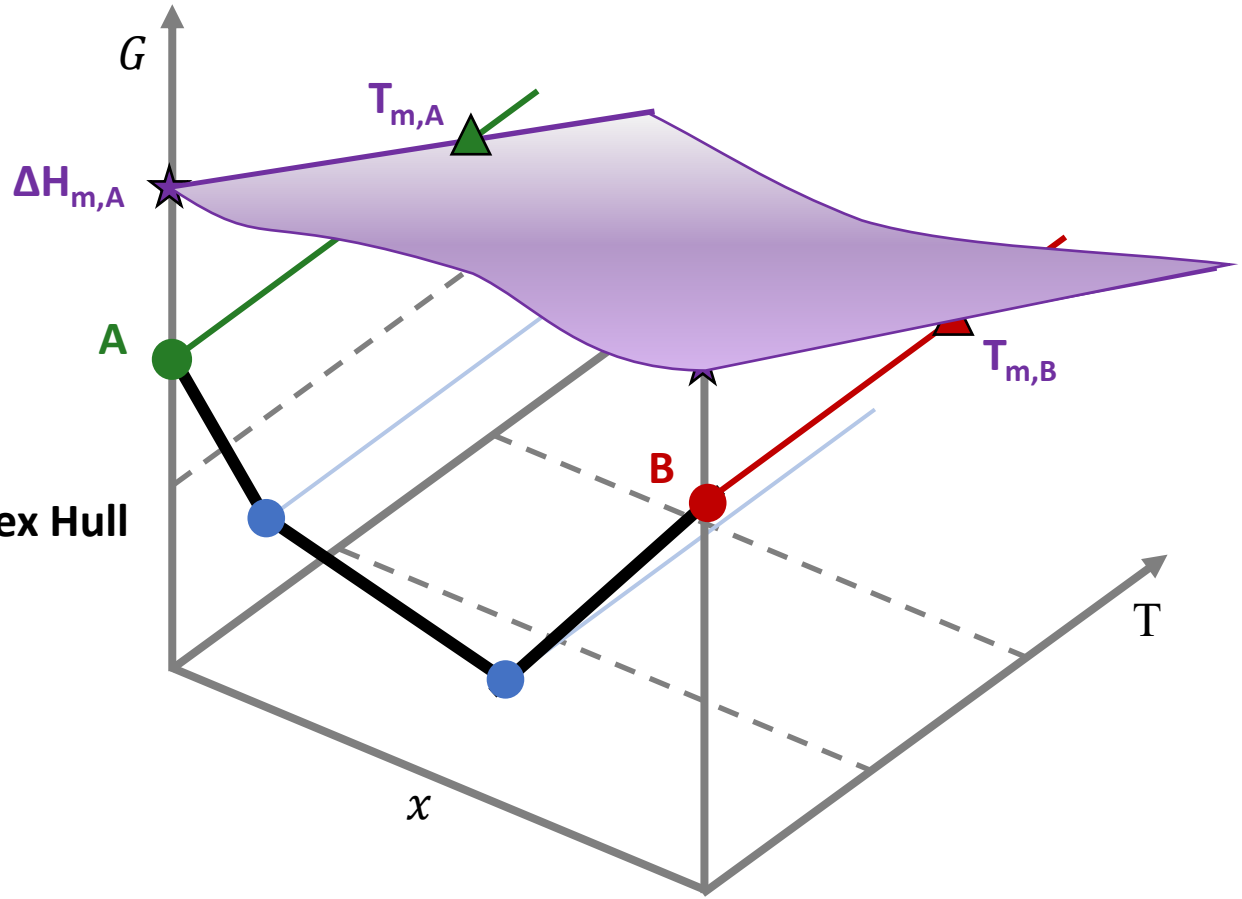
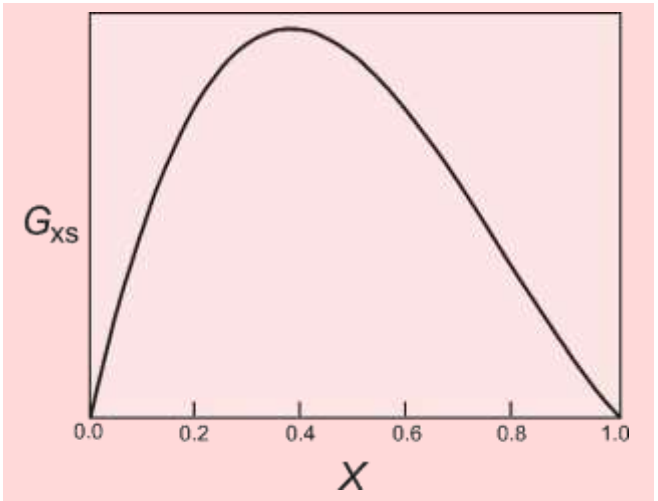


DFT Convex Hull

$$G_{Liq} = x_A \, {}^{\circ}G_A + x_B \, {}^{\circ}G_B + RT(x_A \ln x_A + xB \ln x_B) + \Delta G_m^{xs} \; (Nonideal)$$



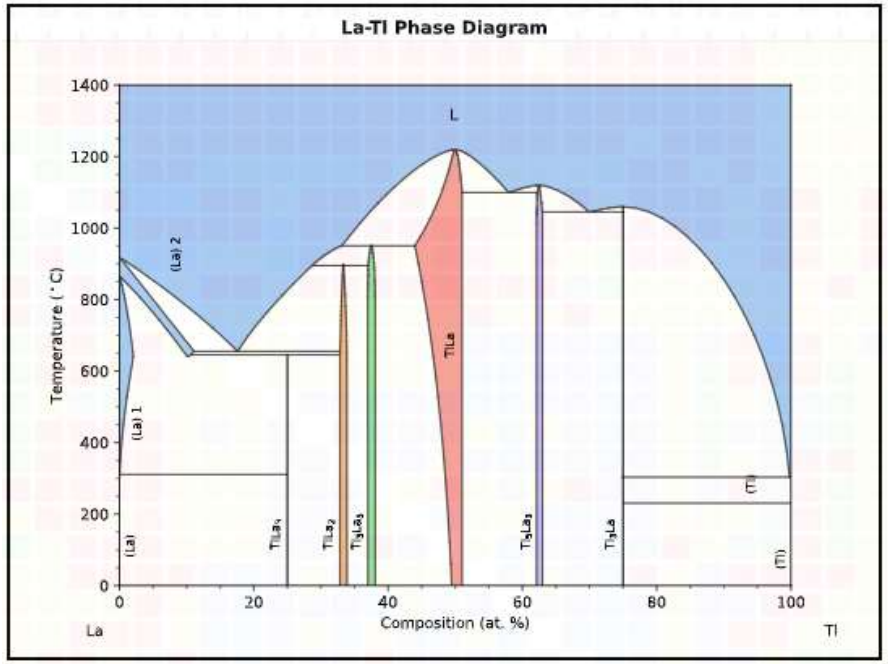
$$L_0 = a + bT$$
$$L_1 = m + nT$$

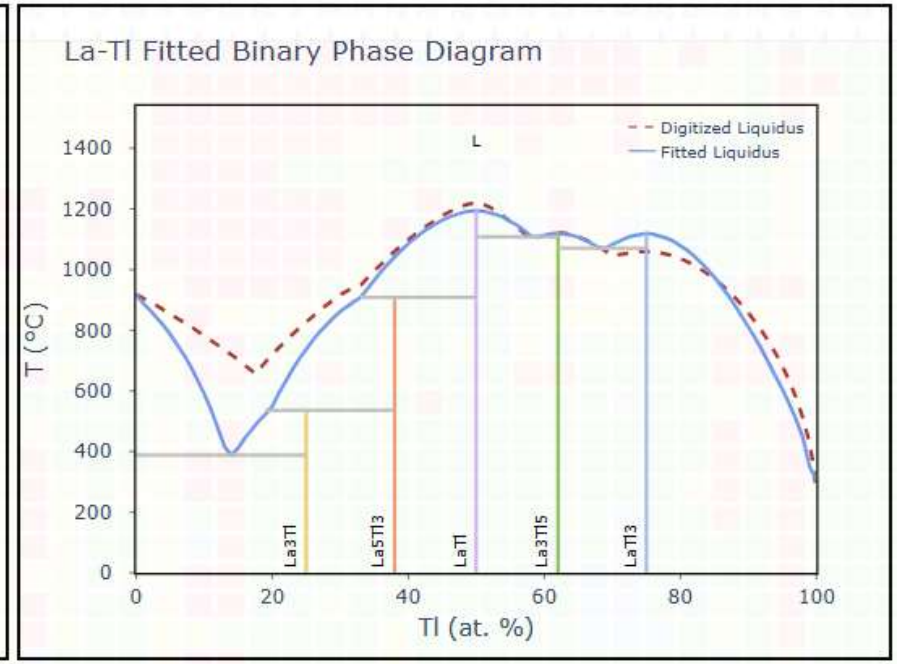
Only 4 terms!

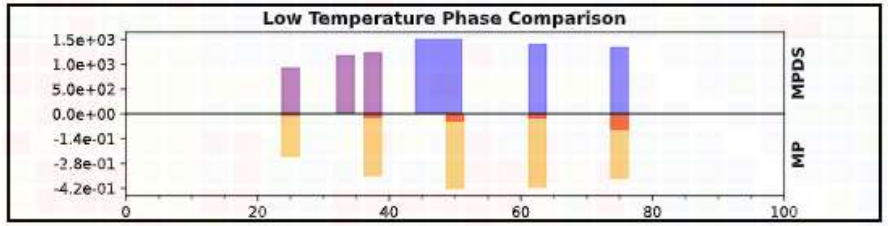
$$\Delta G_m^{xs} = x_A x_B \boldsymbol{L_0} + x_A x_B (x_A - x_B) \boldsymbol{L_1}$$

Regular Solution Mixing Energy (Parabola)

Skews Parabola Left or Right







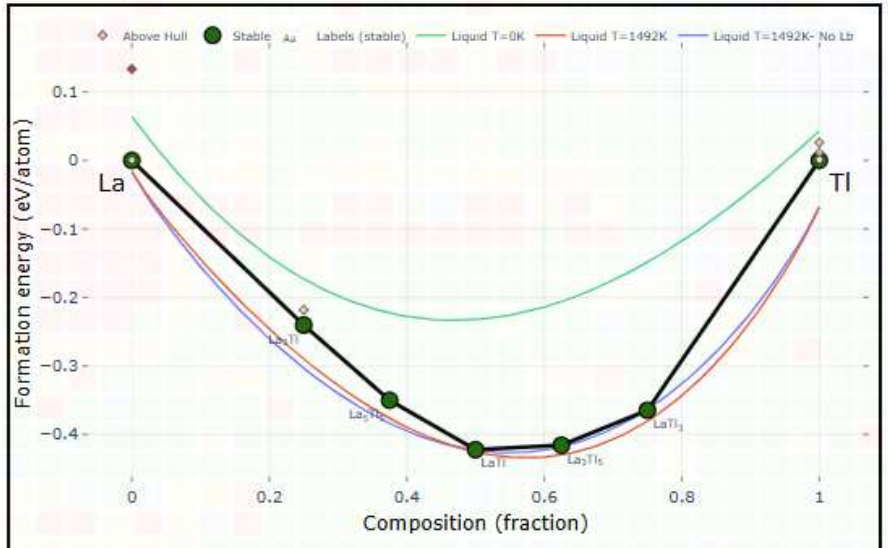
Fitted Parameters - Liquidus MAE: 63.2 K, RMSE: 96.6 K

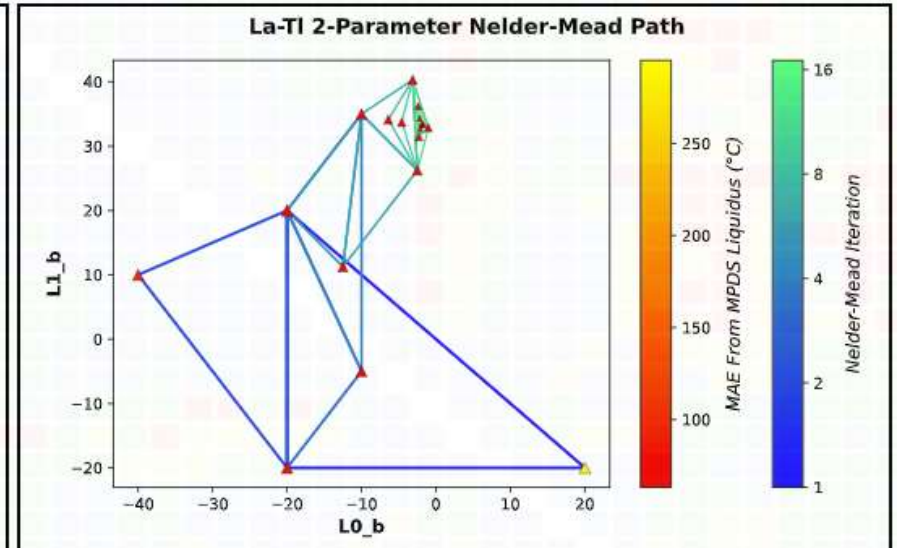
L0_a	L0_b	L1_a	L1_b
-110,300	-2.184	-17,970	34.3

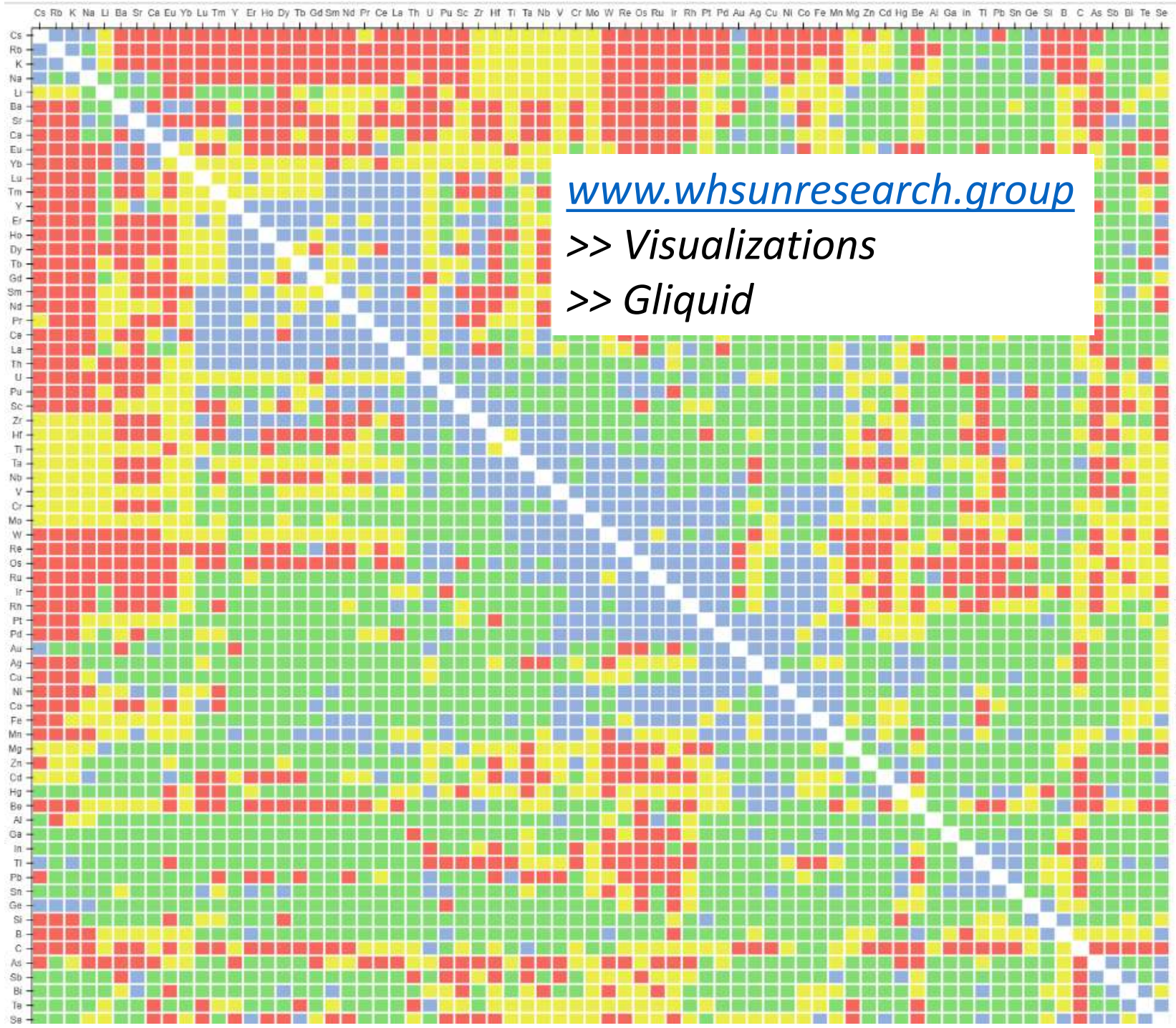
Phase Diagram Source: Delfino et al. (1990)
DFT Energies: Materials Project GGA

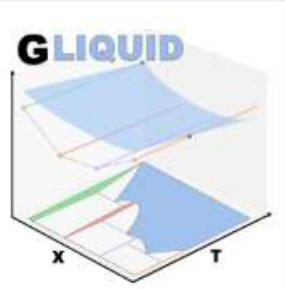
Invariant Point Counts

PD Source	Eutectics	Congruent Melting	Peritectics	Liquid Misc Gaps
MPDS	4	3	2	0
Fitted	3	3	2	0









Liquid Mixing Parameters Fitted
Complete Liquidus Data Available
Phase Diagram Data Available
No Phase Diagram Data Availble

Show Predicted Phase Diagrams

Coloring Scheme

Fitting Data Availability

Axis Ordering

Pettifor Chemical Similarity

DFT-Referenced Binary Phase Diagram Map
by Joshua Willwerth (willwerj@umich.edu)

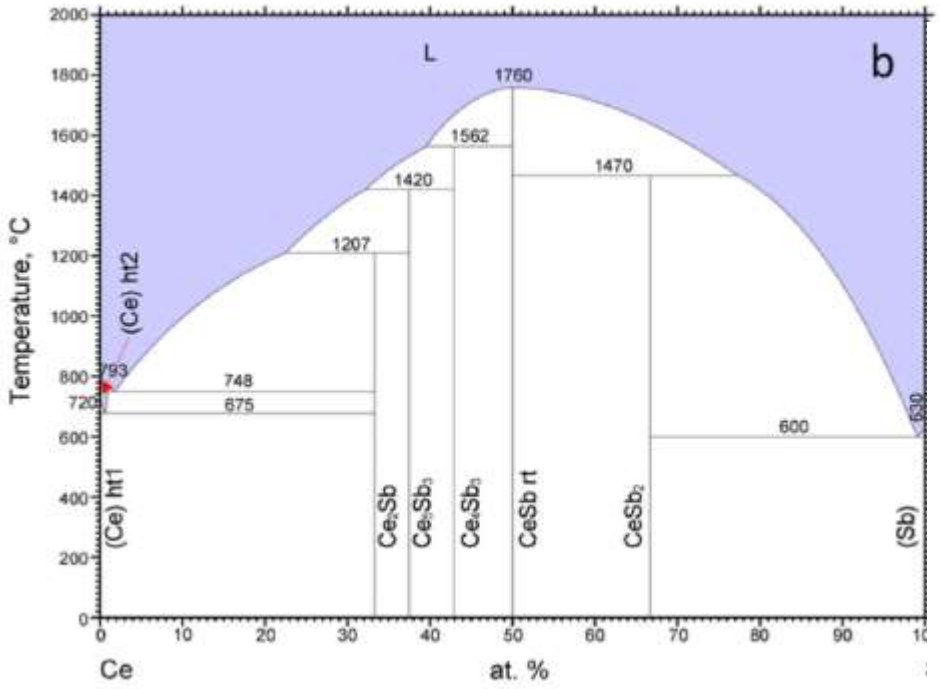
This app can be used to explore the results of the G-Liquid project by Joshua Willwerth, Shibo Tan, Abar Rauf & Wenhao Sun (Sun Research Group, University of Michigan)

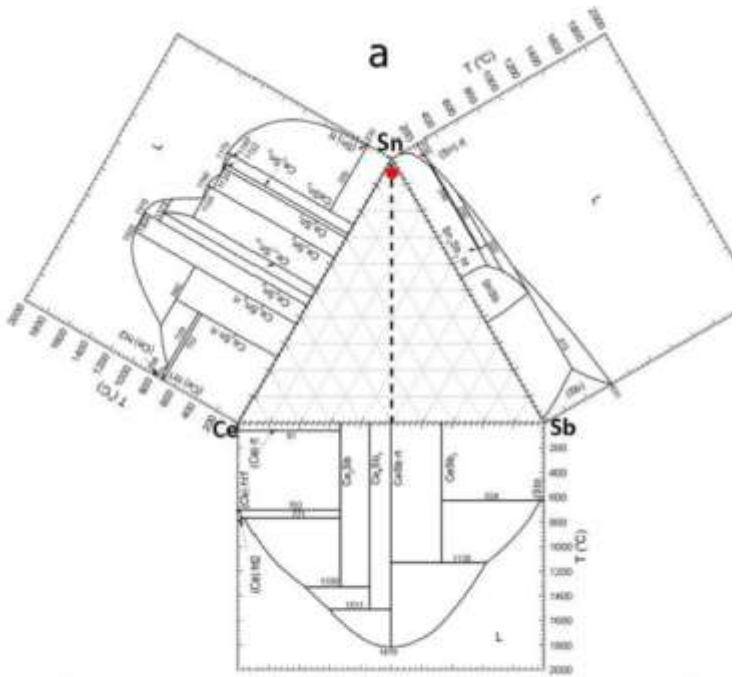
This project is made possible by funding from the U.S. Department of Energy (DOE) Office of Science, Basic Energy Sciences Award No. DE-SC0021130

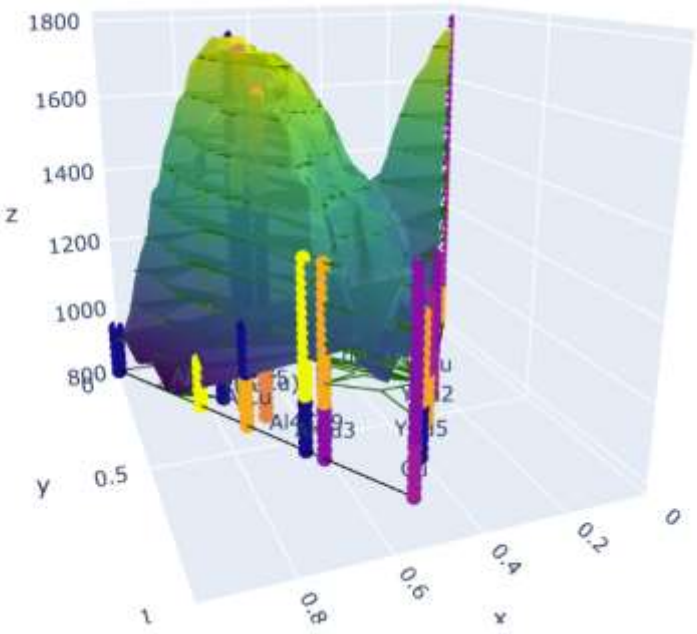
Ternary Interpolation App

Predictions and prediction confidence are a work in progress and will be updated in a future version of this map

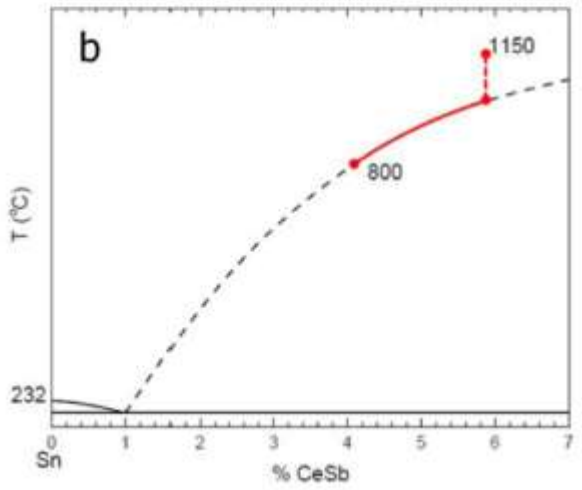
Can interpolate from 3 binaries to a ternary







Paul Canfield used a Ce-Sb-Sn ternary to grow CeSb at lower temperatures



Can now predict and search for these 3rd flux elements

Paul Canfield, *New Materials Physics*
Rep. Prog. Phys. 83 016501

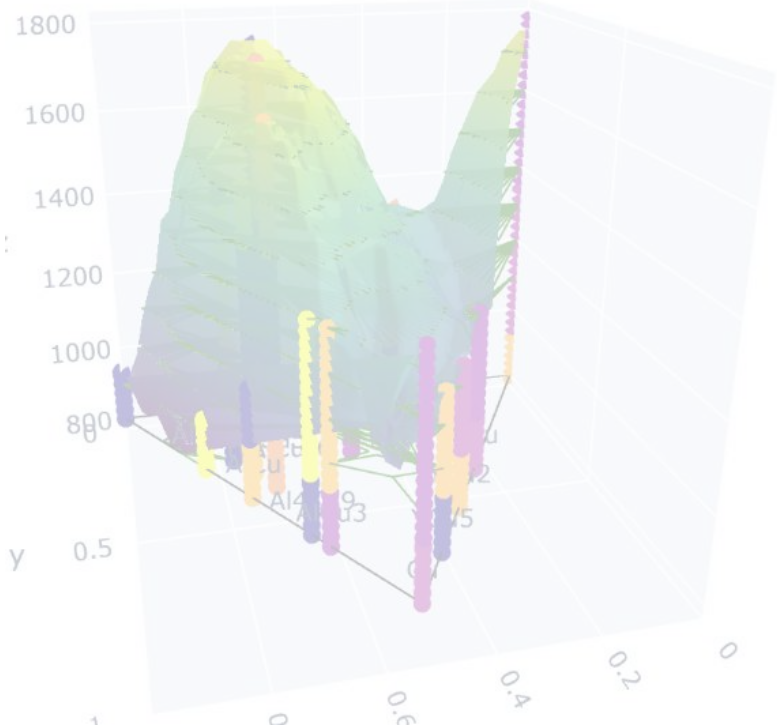
Predicting Synthesis and Synthesizability

Thermodynamics

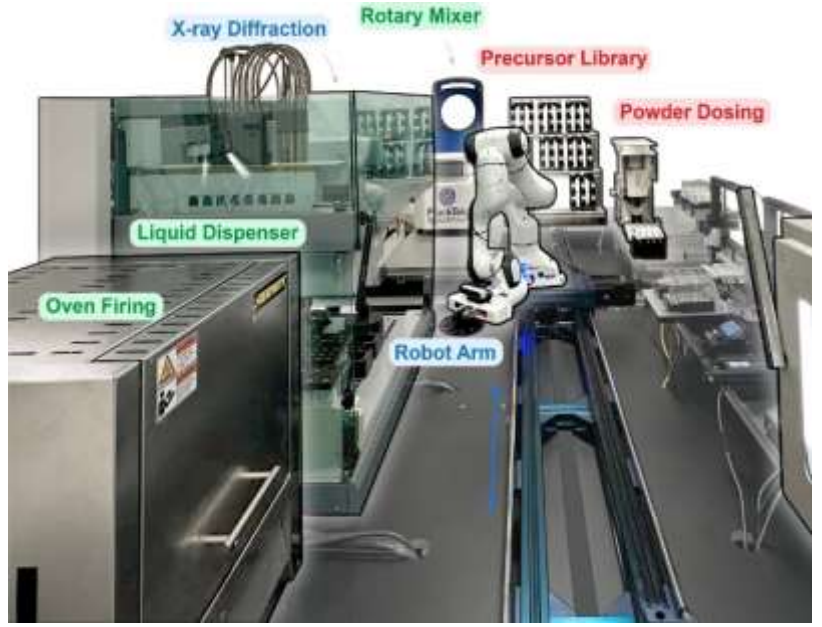
Epitaxial Thin Film

Kinetics

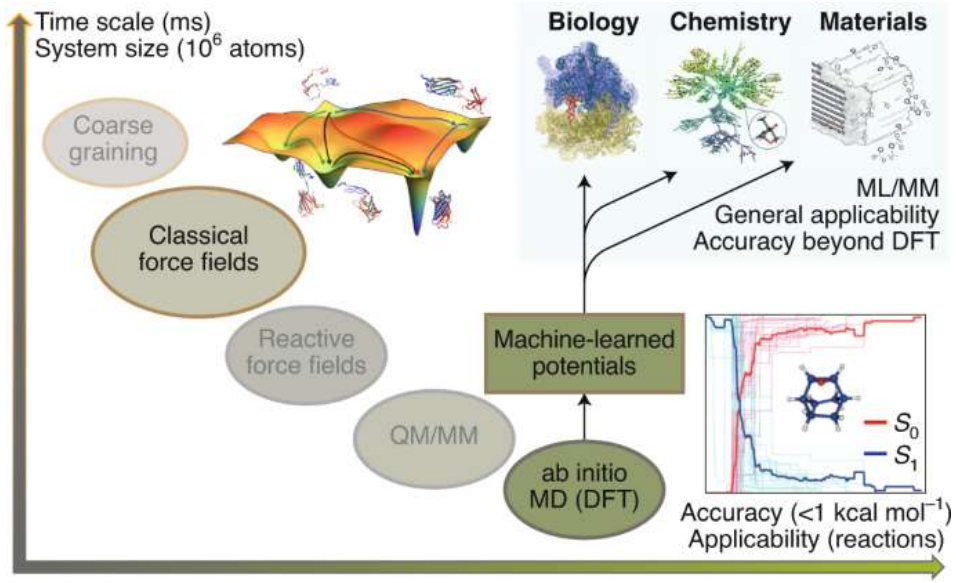
Bulk Crystal Growth



ML/AI Robotics



My opinion: Probably can't simulate your way to predictive synthesis even with machine-learned potentials



Friedrich, Aspuru-Guzik *et al.*, *Nature Materials* (2021)

Even with >10^{12} atoms + millisecond timescales:

- Cannot simulate over every synthesis condition.
- Cannot explore which synthesis method to use
- ML-potentials are expensive to train, don't have (good) chemical transferability.
- Hard to assess competitive phase formation

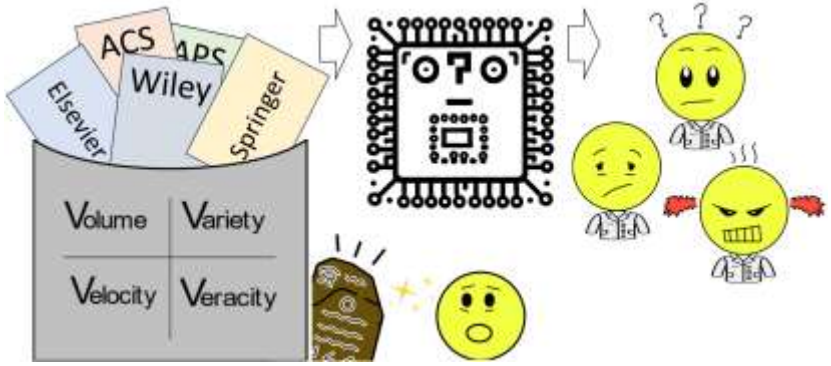
+ Understand dynamics, mechanisms, rate-limiting steps
+ Interrogate synthesis *science*, learn generalizable principles

My opinion: Text-Mining + ChatGPT can't directly predict synthesis

Faraday Discussions
Cite this: DOI: 10.1039/d4fd00112e
ROYAL SOCIETY OF CHEMISTRY
PAPER
View Article Online
View Journal

A critical reflection on attempts to machine-learn materials synthesis insights from text-mined literature recipes

Wenhao Sun †* and Nicholas David †



In the Ceder Group, I helped build text-mined recipes for 30,000+ solid-state syntheses and 50,000+ solution-based syntheses

- ML models capture how chemists *think* about synthesis, rather than something fundamental.

- ML predictions are not much different than what chemists would try anyway.

+ We can test new synthesis hypotheses against large historical datasets

+ Unusual/Anomalous recipes can be very insightful

nature synthesis

Article | Open access | Published: 30 January 2024

Optimal thermodynamic conditions to minimize kinetic by-products in aqueous materials synthesis

Zheren Wang, Yingzhi Sun, Kevin Cruse, Yan Zeng, Yuxing Fei, Zexuan Liu, Junyi Shangguan, Young-Woon Byeon, KyuJung Jun, Tanjin He, Wenhao Sun ✉ & Gerbrand Ceder ✉

Nature Synthesis **3**, 527–536 (2024) | Cite this article

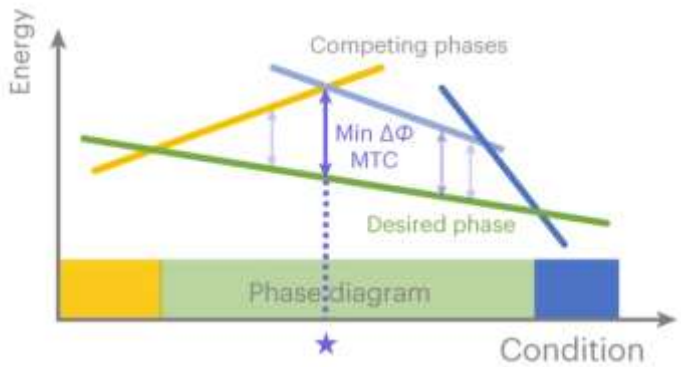
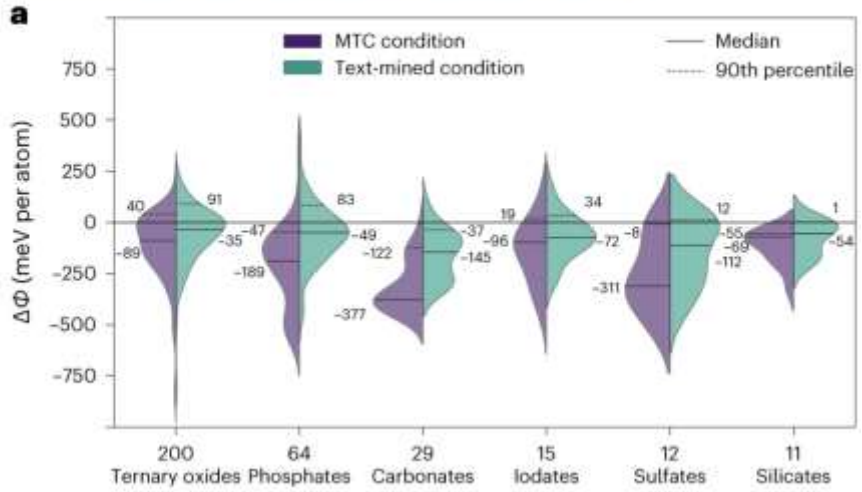


Fig. 2: Thermodynamic competition analysis on text-mined dataset.

From: Optimal thermodynamic conditions to minimize kinetic by-products in aqueous materials synthesis



nature synthesis

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 ✉

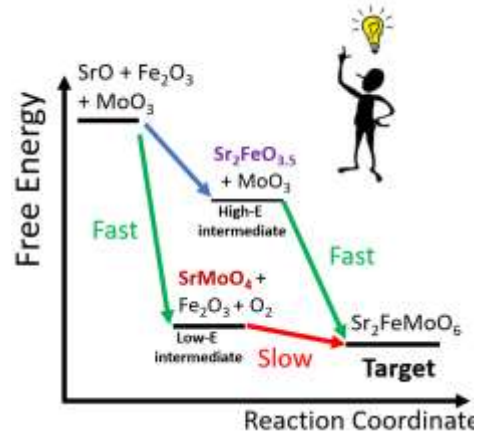
Nature Synthesis **3**, 606–614 (2024) | Cite this article

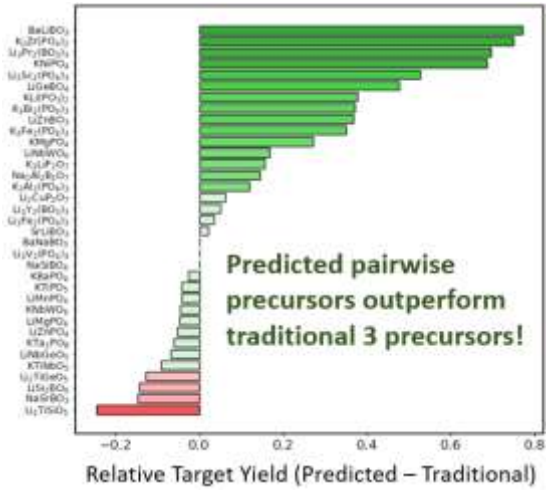
Sr_2FeMoO_6 samples were prepared by solid-state reaction. Two elaboration processes have been used in order to improve the purity of the samples. For the first one, which is close to the protocol used by most of groups, stoichiometric amounts of $SrCO_3$, Fe_2O_3 and MoO_3 were mixed, **ground and calcined at 900°C for 2h** in an Ar atmosphere. The calcined mixtures were **reground**, pressed and reduced for 1h under current flow of 5% H2/95% Ar at 700°C. Afterwards the mixtures were **sintered at 1200°C** under argon flow during **10h**.

Unfortunately, the last protocol does not allow one to obtain a pure Sr_2FeMoO_6 compound. Instead, **$SrMoO_4$ is thermodynamically favored**. Therefore, a segregation occurs which makes it impossible to obtain a pure phase.

To get rid of this difficulty, we have developed a sintering process in which only one reaction is performed at each step in order to avoid the formation of $SrMoO_4$. Therefore, in the first step, stoichiometric amounts of $SrCO_3$, Fe_2O_3 were mixed, ground and calcined at 1000°C during 5h under an Ar flow giving rise to $Sr_2FeO_{3.5}$ compound. Then stoichiometric amounts of $Sr_2FeO_{3.5}$, MoO_3 and MoO_3 were mixed, ground, pressed and sintered at **1200°C during 2h** under N_2/H_2 flow.

doi.org/10.1016/j.cattod.2005.12.019

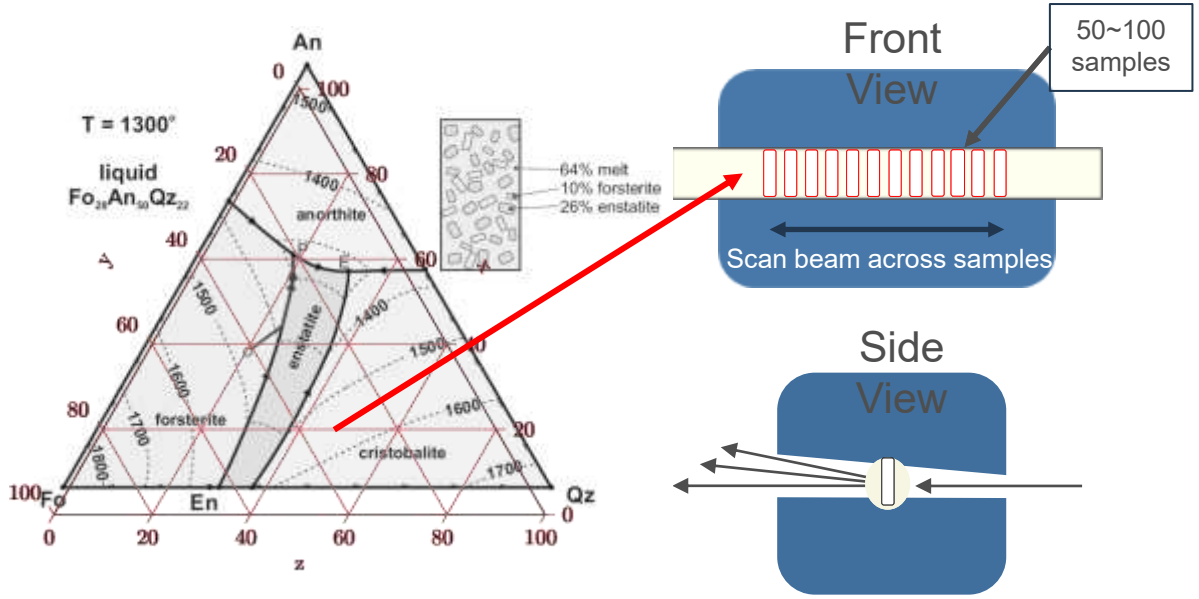


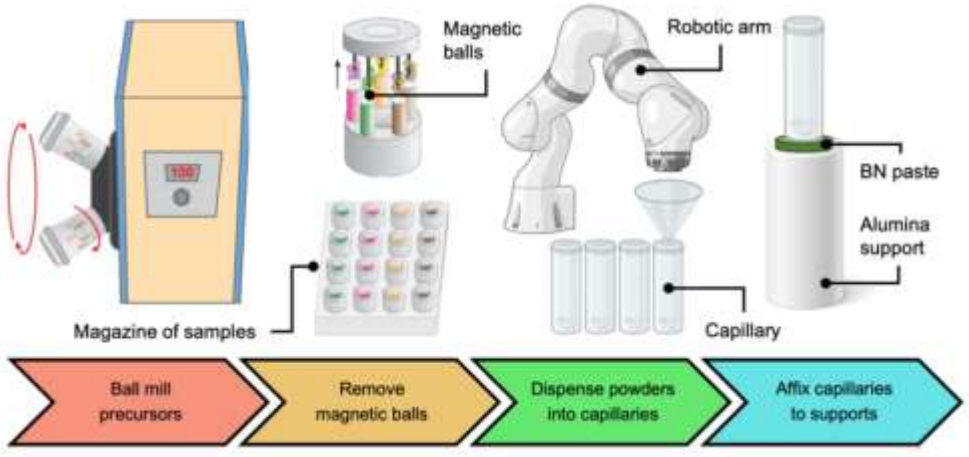


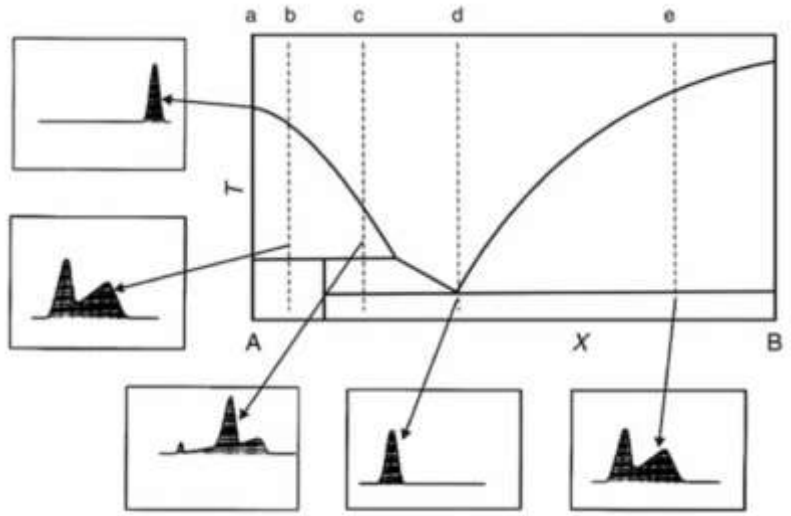
My opinion: There is more to robotic labs than ‘self-driving’

Many materials properties are easier to measure than to calculate

- Melting Temperature
- Solubility in aqueous/organic solvents
- Critical Vapor Pressure





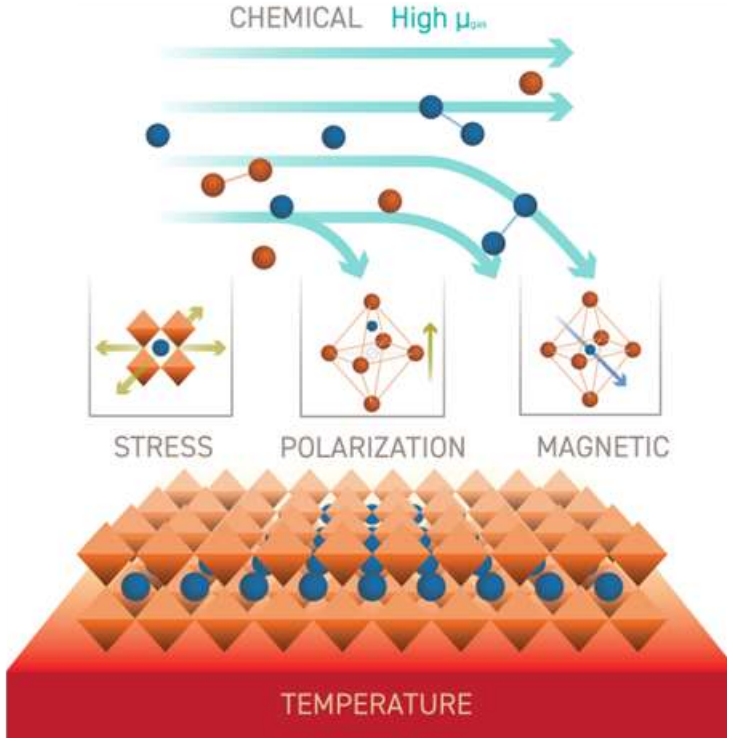


What about autonomous robotic phase diagram assessment?

Predicting Synthesis and Synthesizability

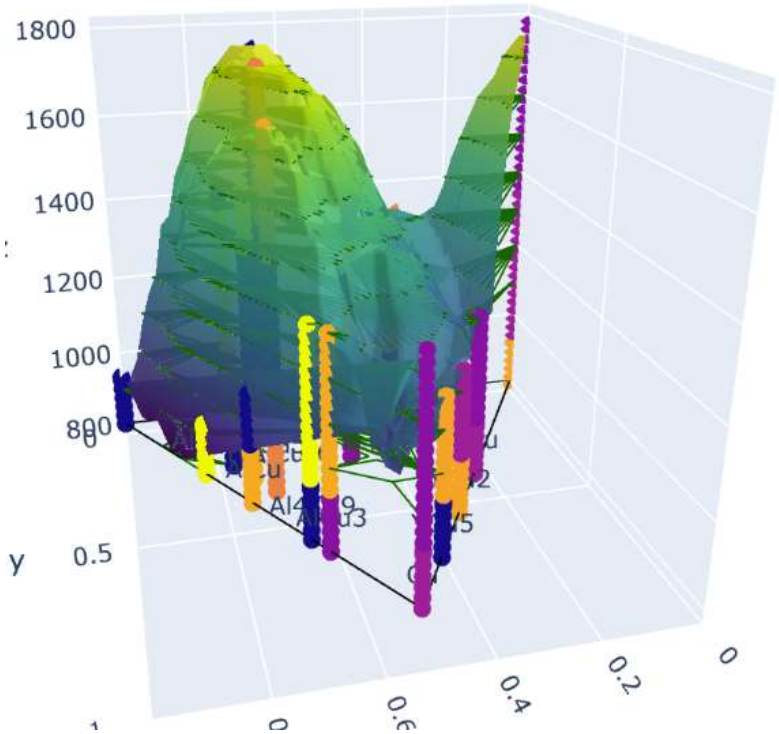
Thermodynamics

Epitaxial Thin Film



Kinetics

Bulk Crystal Growth



ML/AI Robotics

Predicting Synthesis and Synthesizability

Group Website: www.whsunresearch.group

The geometry of high-dimensional phase diagrams (arXiv)

Construct → **I.** Generalized Gibbs Phase Rule

Interpret → **II.** Duality between open and closed chemical systems

Navigate → **III.** Engineering Relative Stability in 4 Dimensions

Navigating phase diagram complexity to design more efficient solid-state syntheses

Jiadong Chen, Sam Cross, Lincoln Miara, Eric Yan Wang, **Wenhao Sun**, *Nature Synthesis* (2024)

Efficient *ab initio* estimation of the high-temperature liquidus curve

Shibo Tan, Joshua Willwerth, Abrar Rauf, **Wenhao Sun**, *In preparation*

Optimal thermodynamic conditions to minimize kinetic by-products in aqueous materials synthesis

Zheren Wang, **Wenhao Sun***, Gerbrand Ceder*, *et al., Nature Synthesis* (2024)

DOE Early Career Award
Synthesis and Processing Science

A NEXT GENERATION SYNTHESIS CENTER

NSF U.S. National Science Foundation

What does "synthesizable" *mean*?

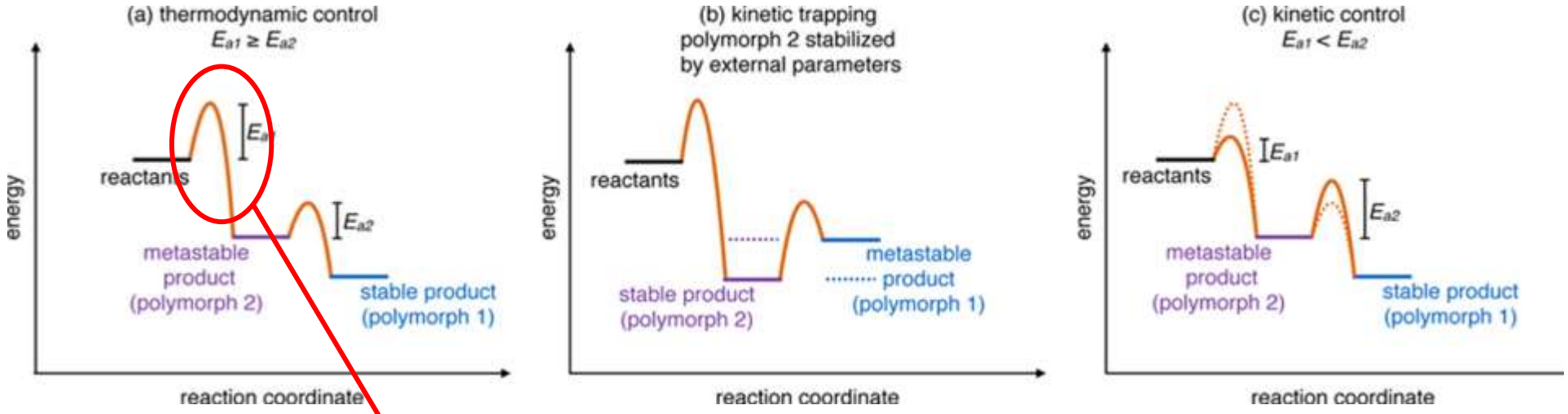
- Is it even **possible** to make this material?
- What experimental **method** would be best to synthesize it? (Solid-State, Hydrothermal, Flux?)
- Within my method, what **recipe** should I use? (Precursors, Temp., Time*, etc…*)
- Can I make my material in the desired ***form***? (Powder, Thin-film, Bulk Single Crystal)
- Can I synthesize it with high ***quality*****?** (No killer defects)
- Can I synthesize it ***reliably*** *and* ***reproducibly***?
- Can I synthesize it ***efficiently***? (Time, Electricity, $$ Cost, Labor)
- Can I synthesize it ***at scale*** for manufacturing?

- Is my material operationally stable?

→Can I **avoid the synthesis** of undesired phases during operation?

Interfacial phases
Corrosion byproducts
Decomposition products

Progressing along the energy landscape



Martinolich, Neilson *Chemistry of Materials* (2017)

Jamie Neilson
Colorado State Uni.

What is the nature of the first barrier? (Rate limiting step?)

Diffusionless

Ion-exchange, topotaxy, *chemie douce*

Nucleation

Surface energy versus Driving force, ***Structure Selection***

Diffusion and Growth

Pathway dependent (bulk, dislocation, surface, liquid flux)