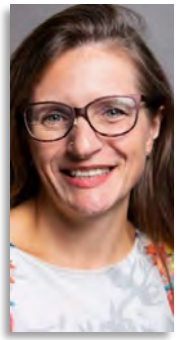
University at Buffalo The State University of New York

PXRD-Assisted Crystal Structure Predictions

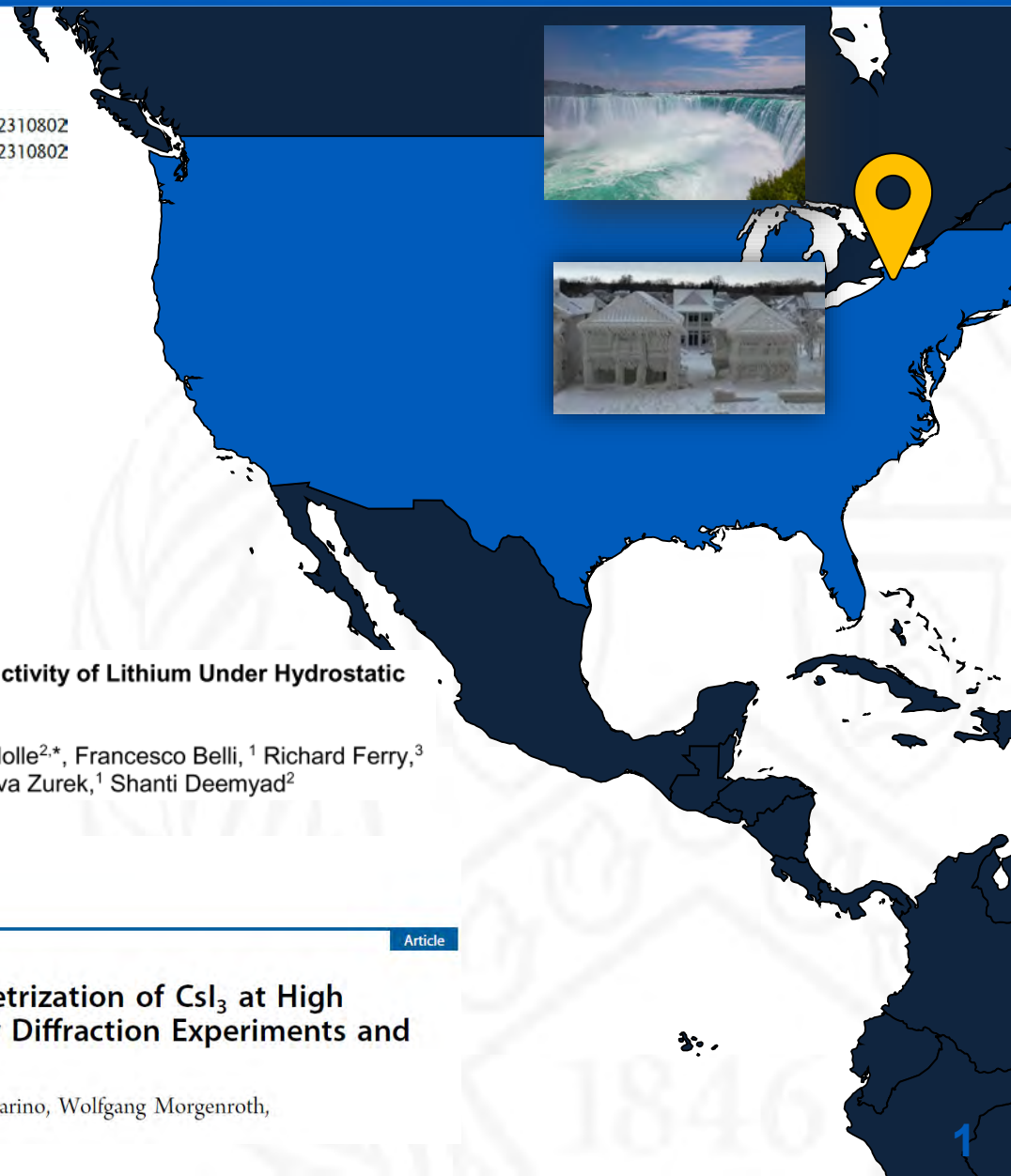
Dr. Stefano Racioppi

University at Buffalo The State University of New York

2021 – to date



Prof. Zurek



Solid-State Chemistry Hot Paper

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doi.org/10.1002/anie.202310802

On the Electride Nature of Na-hP4

Stefano Racioppi, Christian V. Storm, Malcolm I. McMahon, and Eva Zurek**

In memory of Neil Ashcroft († March 15, 2021)

CHEMISTRY OF MATERIALS
pubs.acs.org/cm Article

Intercalating Helium into A-Site Vacant Perovskites

Stefano Racioppi, Maosheng Miao, and Eva Zurek*

Phase Boundaries, Isotope Effect and Superconductivity of Lithium Under Hydrostatic Conditions

Stefano Racioppi,[1] Iren Saffarian-Deemyad,[2,*] William Holle[2,*], Francesco Belli, [1] Richard Ferry,[3] Curtis Kenney-Benson,[3] Jesse S. Smith,[3] Eva Zurek,[1] Shanti Deemyad[2]

J|A|C|S JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
pubs.acs.org/JACS Communication

Hydrazonyl Sultones as Stable Tautomers of Highly Reactive Nitrile Imines for Fast Bioorthogonal Ligation Reaction

Ming Fang, Gangam Srikanth Kumar, Stefano Racioppi, Heyang Zhang, Johnathan D. Rabb, Eva Zurek, and Qing Lin*

J|A|C|S JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
pubs.acs.org/JACS Communication

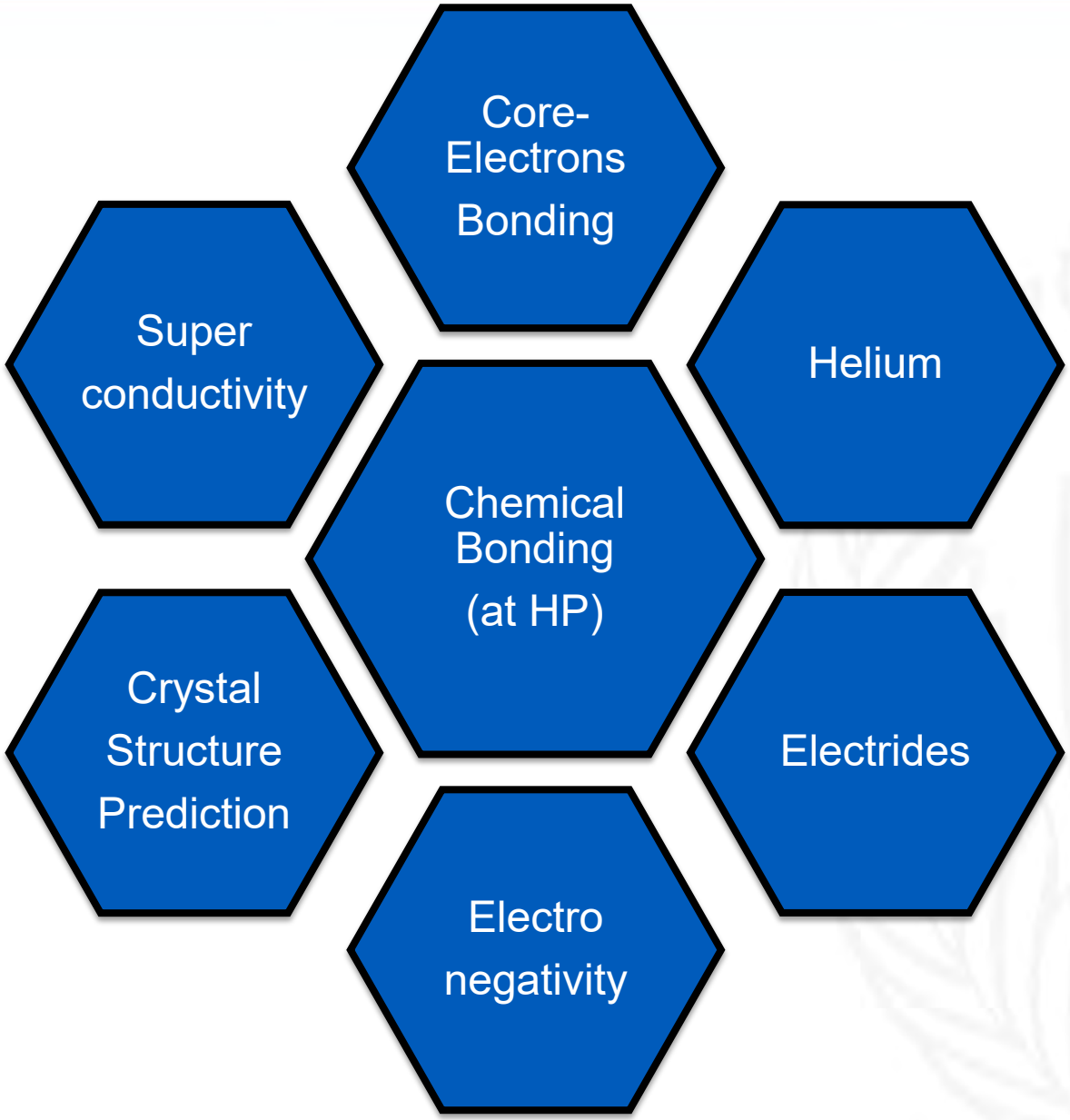
Superfast Tetrazole–BCN Cycloaddition Reaction for Bioorthogonal Protein Labeling on Live Cells

Gangam Srikanth Kumar, Stefano Racioppi, Eva Zurek, and Qing Lin*

Inorganic Chemistry
pubs.acs.org/IC Article

Investigating the Structural Symmetrization of CsI_3 at High Pressures through Combined X-ray Diffraction Experiments and Theoretical Analysis

Tomasz Poręba,[*,#] Stefano Racioppi,[*,#] Gaston Garbarino, Wolfgang Morgenroth, and Mohamed Mezouar


Core-Electrons Bonding
Super conductivity
Helium
Chemical Bonding (at HP)
Crystal Structure Prediction
Electrides
Electro negativity

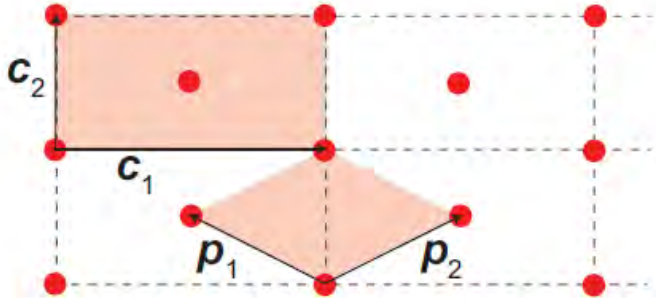
ONE of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition. Who, for example, would guess that graphite, not diamond, is the thermodynamically stable allotrope of carbon at ordinary temperature and pressure? Solids such as crystalline water (ice) are still thought to lie beyond mortals' ken.

Yet one would have thought that, by now, it should be possible to equip a sufficiently large computer with a sufficiently large program, type in the formula of the chemical and obtain, as output, the atomic coordinates of the atoms in a unit cell.

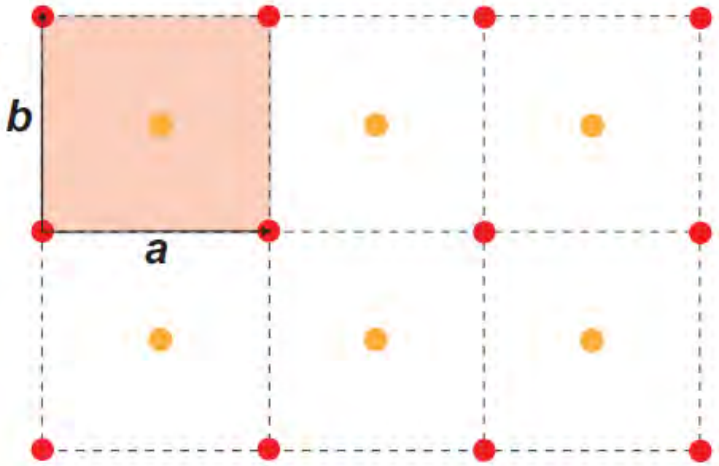
John Maddox, 1988, Nature

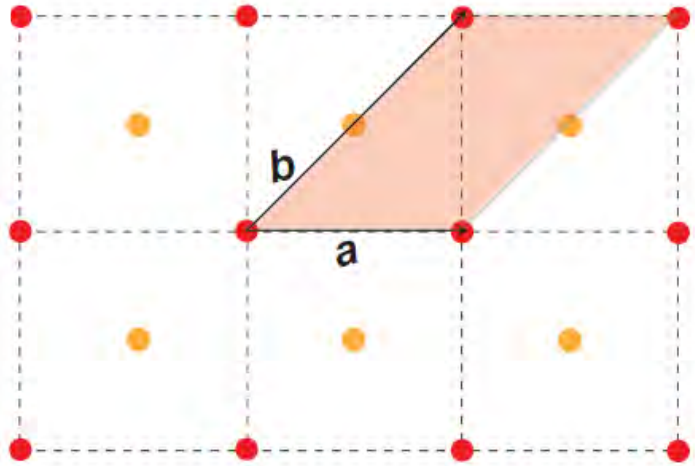
We want an **algorithm** that tells us where the **low-line region** is.

Minimum of the **PES**



Primitive vs.
conventional unit cell



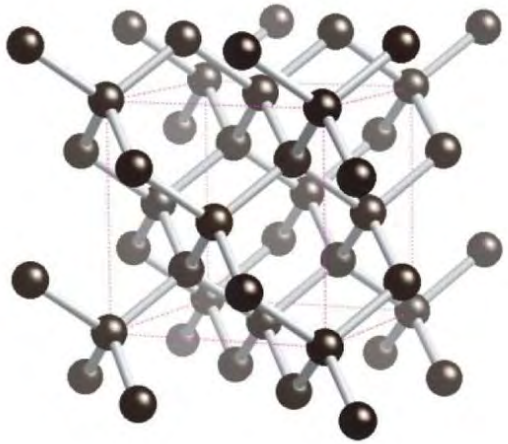


Two different unit cells describing the same lattice
3 x 2 supercells

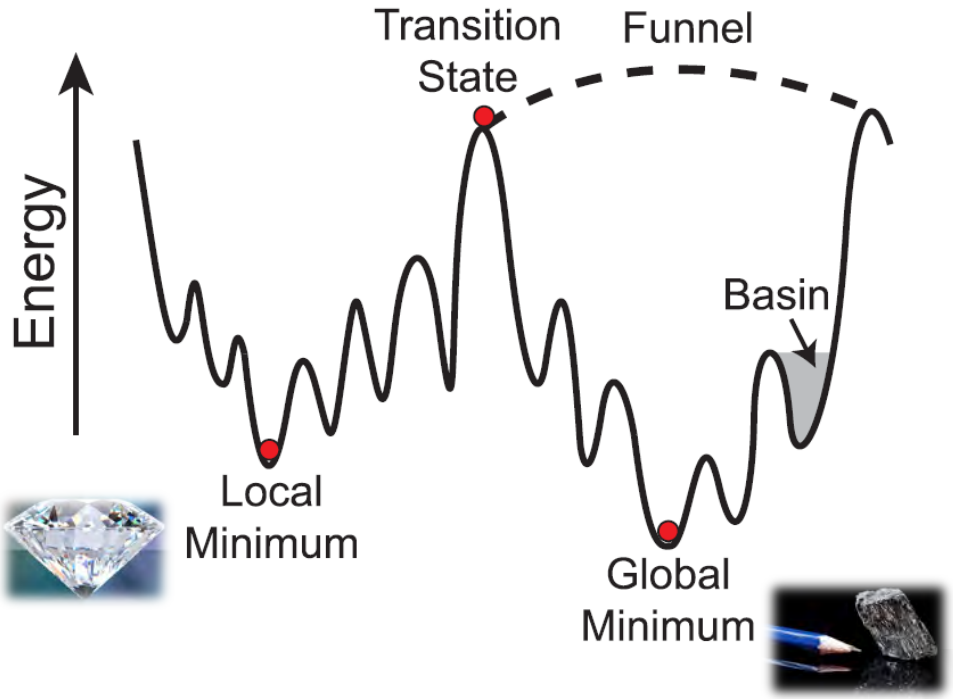
3*N* + 6 (3*N* atomic coordinates, 3 angles, 3 lattice vectors) degrees of freedom

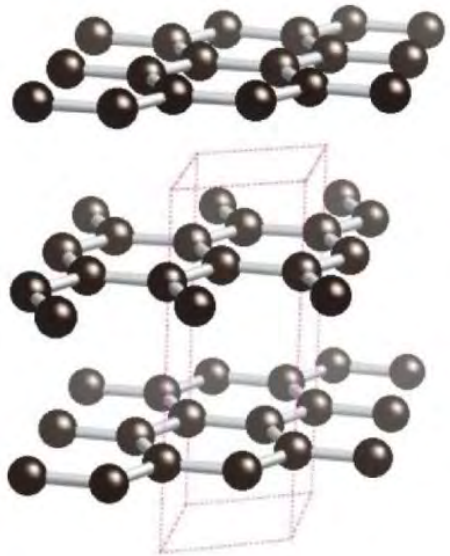
Number of **formula units** (FU) in the unit cell is generally **unknown**

230 Space Groups that can describe all possible 3D crystal structures



(Diamond)





(Graphite)

3N+6 F.U.? 230 S.P. Unit cell?

Basin of attraction: all configurations that will optimize to same minimum

Funnel: super-basin contains number of neighboring basins

Global minimum: thermodynamically stable

Local minimum: metastable if transition state is sufficiently high

We **do not know the shape of the PES**, but we want to find the global and local minima.

- The **number of local minima** in a PES scales exponentially with the number of atoms

$$n_s(N) = \exp(\alpha N)$$

- As the number of atom-types increases, so does the number of local minima because different atom-types are not invariant to permutations.

- Finding global minimum is an **non-deterministic polynomial-time-hard (NP-hard) problem**. No algorithm that scales as a polynomial in # DoF.

- **No Free Lunch Theorem**: any searching and optimization algorithm that performs well on one class of problems will perform poorly on another class. All algorithms will give equivalent success rates when averaged over all PES.

- No way to confirm the global minimum has been found unless all local minima have been explored.

We need to **bias** our algorithm using chemistry and physics knowledge in order to be able to find the local minima and global minimum in an effective way.

Only certain regions of the PES are chemically relevant.

- No need to explore chemically unreasonable regions.

Low energy basins occupy the largest amount of “space” within the PES.

- A randomly generated structure has a high probability to fall in this basin.

Bell Evans Polanyi principle: barriers between low-lying minima in a PES are expected to be small. Low-energy basins are likely to be close to one another.

- Once the search has landed in a low-energy basin small structural changes sampling the surrounding PES should find the most stable configuration within the funnel to which the basin belongs.

Simplest Method

- Following Soft Phonon Modes

When a good guess of the structure is known

- Simulated Annealing
- Minima Hopping
- Metadynamics

If you know nothing (or something) about the structure

- Random Search (*e.g.*, AIRSS)
- Particle Swarm Optimization (*e.g.*, CALYPSO)
- Genetic/Evolutionary Algorithms (*e.g.*, USPEX and XtalOpt)

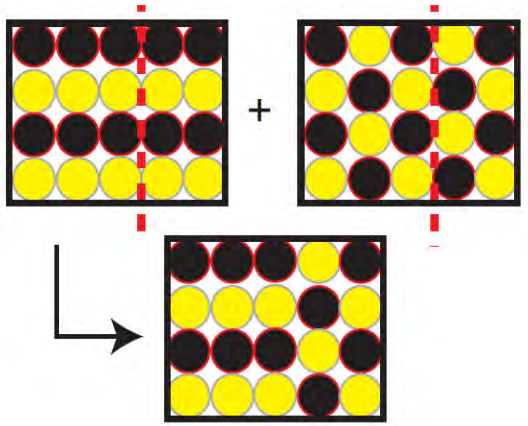
AIRSS

CALYPSO

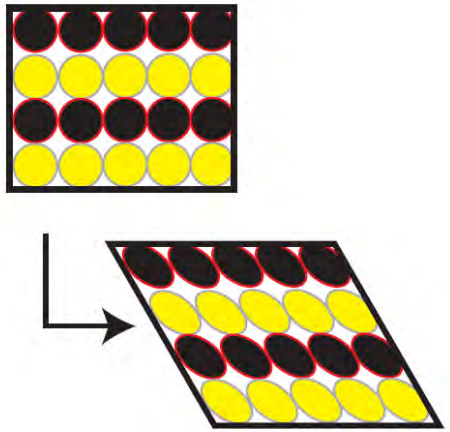
USPEX Computational Materials Discovery

XtalOpt Evolutionary Crystal Structure Prediction

1. Crossover (Breeding)



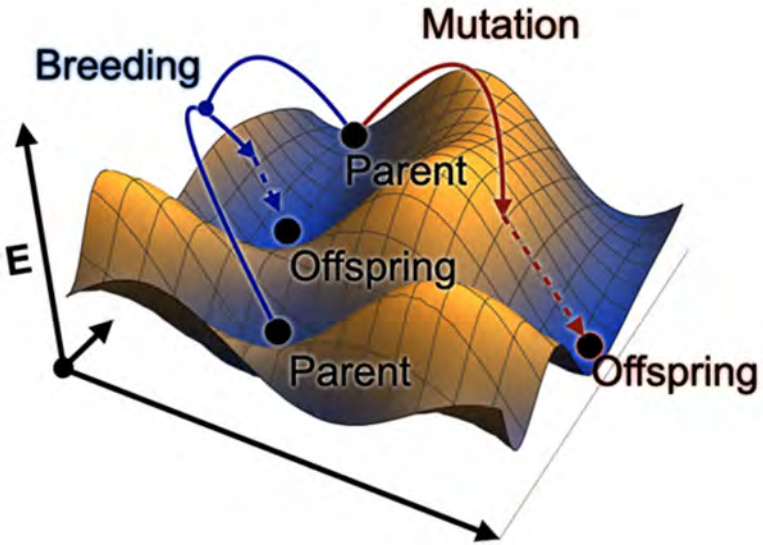
2. Strain



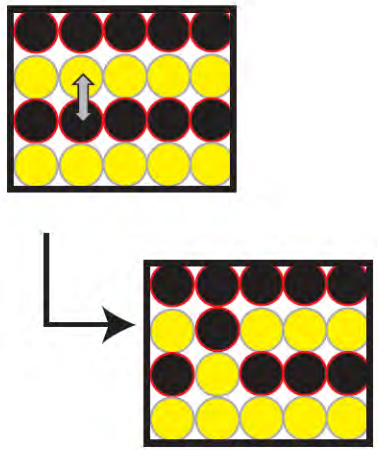
XtalOpt Evolutionary Crystal Structure Prediction

Even more effective when multiple operations are combined

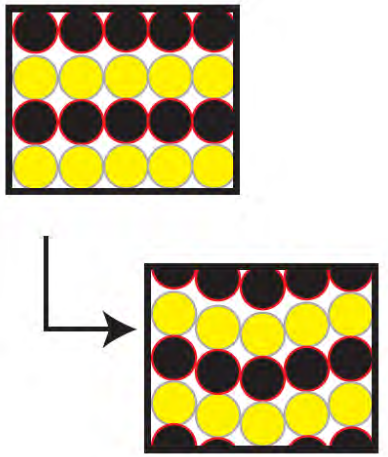
Stripple = (2) + (4)
Permustrain = (2) + (3)



3. Exchange



4. Ripple



Fitness

$$f_s = \left(\frac{H_{max} - H_s}{H_{max} - H_{min}}\right)$$

H_s = enthalpy of structure s
H_{max} = max enthalpy
H_{min} = min enthalpy

"Useful to explore **metastable** phases"

Multi-objective Search

$$f_s = w\left(\frac{S_{max} - S_s}{S_{max} - S_{min}}\right) + (1 - w)\left(\frac{H_{max} - H_s}{H_{max} - H_{min}}\right)$$

S = Second objective
w = Weight

The *Second objective* can ideally be anything that can be quantified.

Optimization type

minimization, maximization, filtration

XTALOPT Version 13: Multi-Objective Evolutionary Search for Novel Functional Materials

Samad Hajinazar[a] and Eva Zurek[a,*]

[a] *Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14260-3000, United States*
[*] *Corresponding author: ezurek@buffalo.edu*

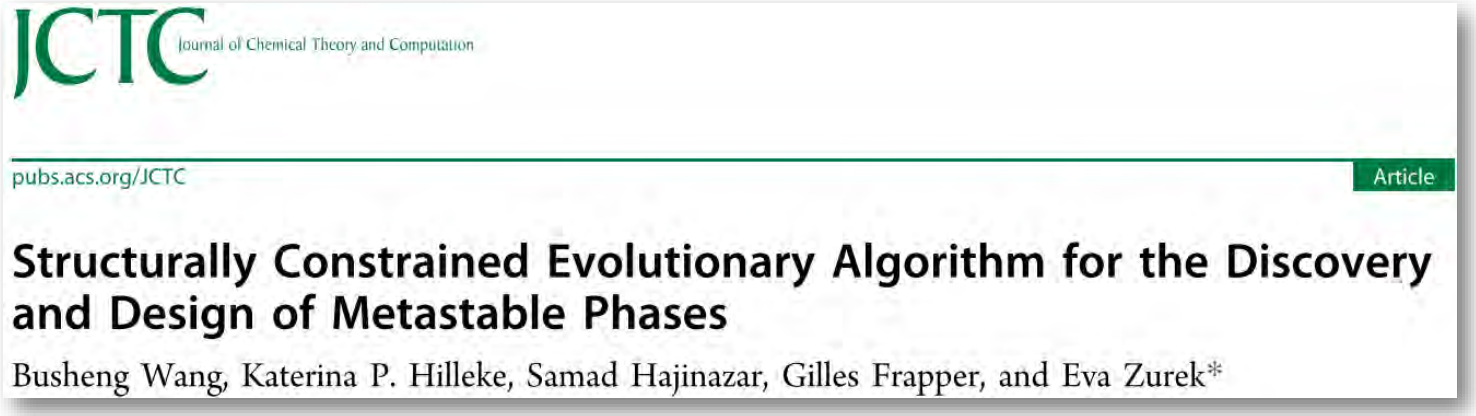
Constraints Criteria

Criteria

- *Local crystalline order* (coordination number, chemical environment)
- *Symmetry* (Bravais lattice, space group)

These criteria are used to **constrain the parent pool**

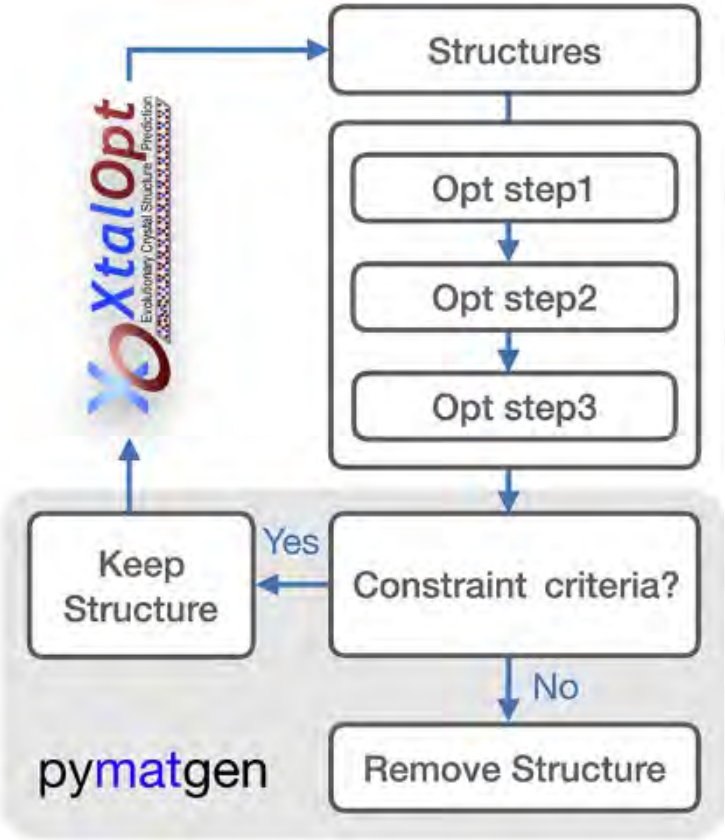
This allows to **focus on local minima** (metastable structures)


JCTC Journal of Chemical Theory and Computation

pubs.acs.org/JCTC Article

Structurally Constrained Evolutionary Algorithm for the Discovery and Design of Metastable Phases

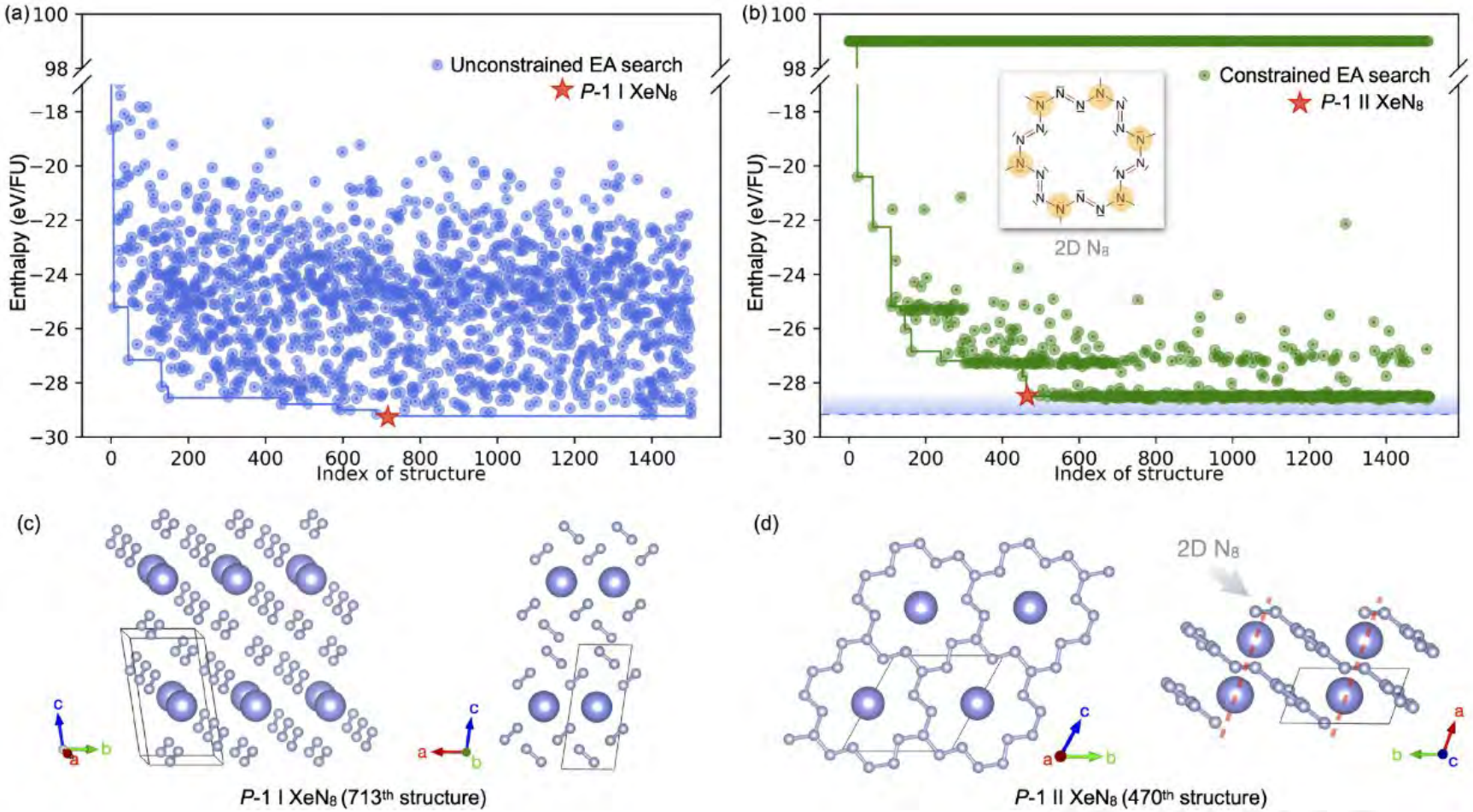
Busheng Wang, Katerina P. Hilleke, Samad Hajinazar, Gilles Frapper, and Eva Zurek*



Criteria

- Local crystalline order (coordination number, chemical environment)

@50 GPa



Unconstrained
Tends to promote N≡N triple bonds

Constrained
Highlights structures with N-N single and N=N double bonds (increased coordination)

Global minimum

Local minimum (polymeric structure)

Criteria

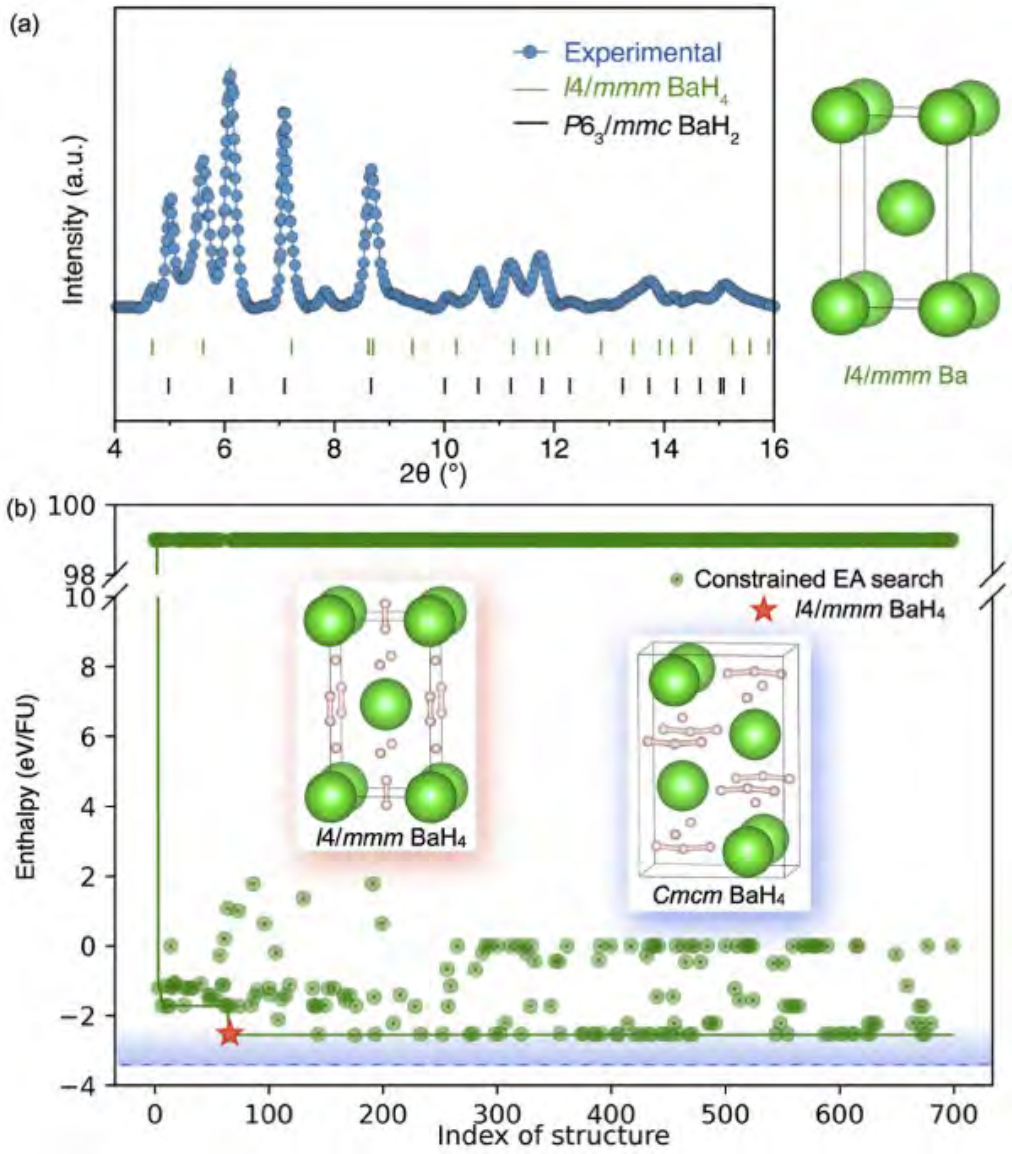
- Symmetry (Bravais lattice, space group)

A mixture of BaH_2 ($P6_3/mmc$) and an unknown BaH_4 phase was synthesized in DAC.

The BH_4 phase was proposed to be I4/mmm, based on the Ba position, but the position of the hydrogen atoms could not be resolved

The ground state found via CSP is assigned to a Cmcm structure

The constraint search (fixed space group) helped to find the most probable metastable phase (ranked as the 354th lowest enthalpy candidate from the unconstrained CSP).

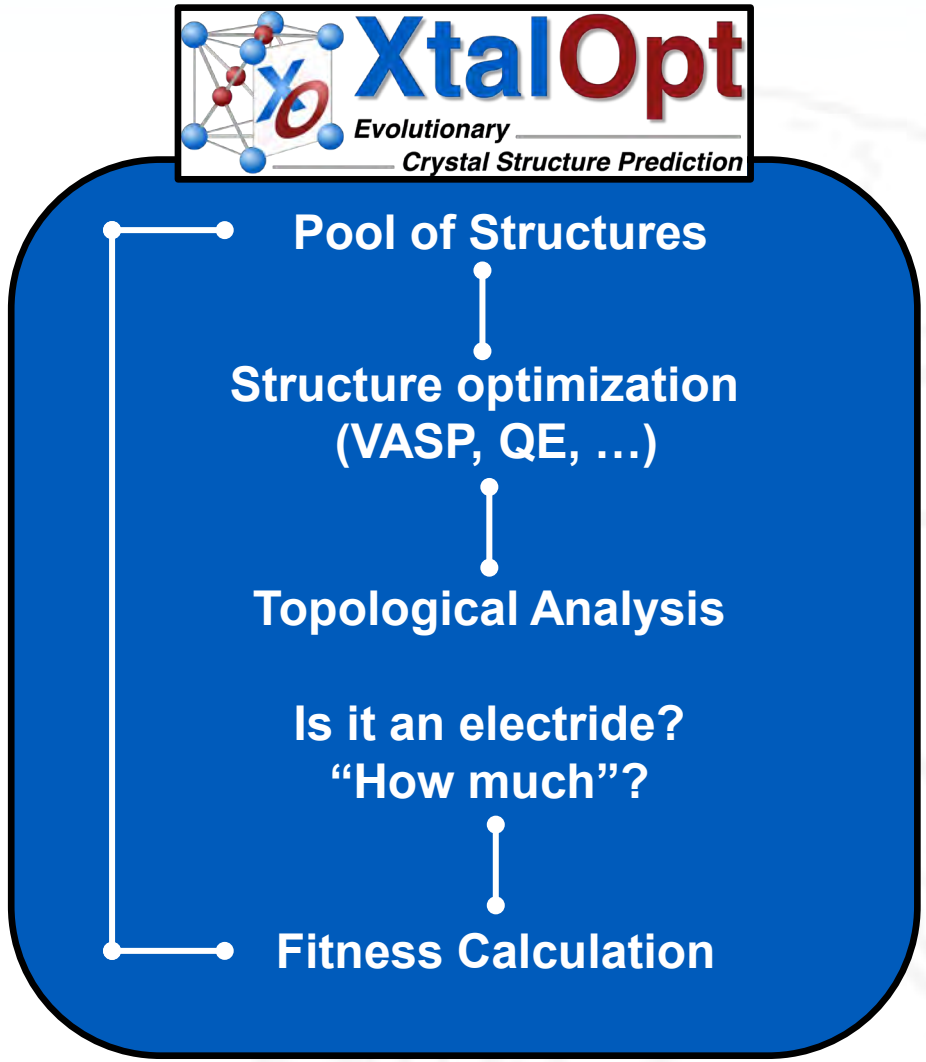


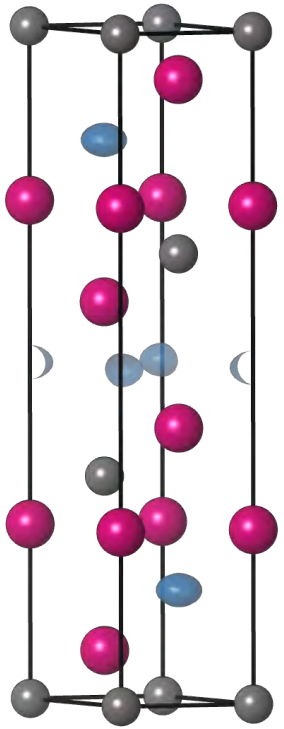
Key Features in "Electrides"

- Nuclear-maxima of the electron density ρ(r)
- $\nabla^2\rho(r) < 0$ (charge accumulation)
- Electron Localization Function (ELF) basin (~1)

Topology-based method

- No needs of pre-set parameters
- Usable at high-pressure



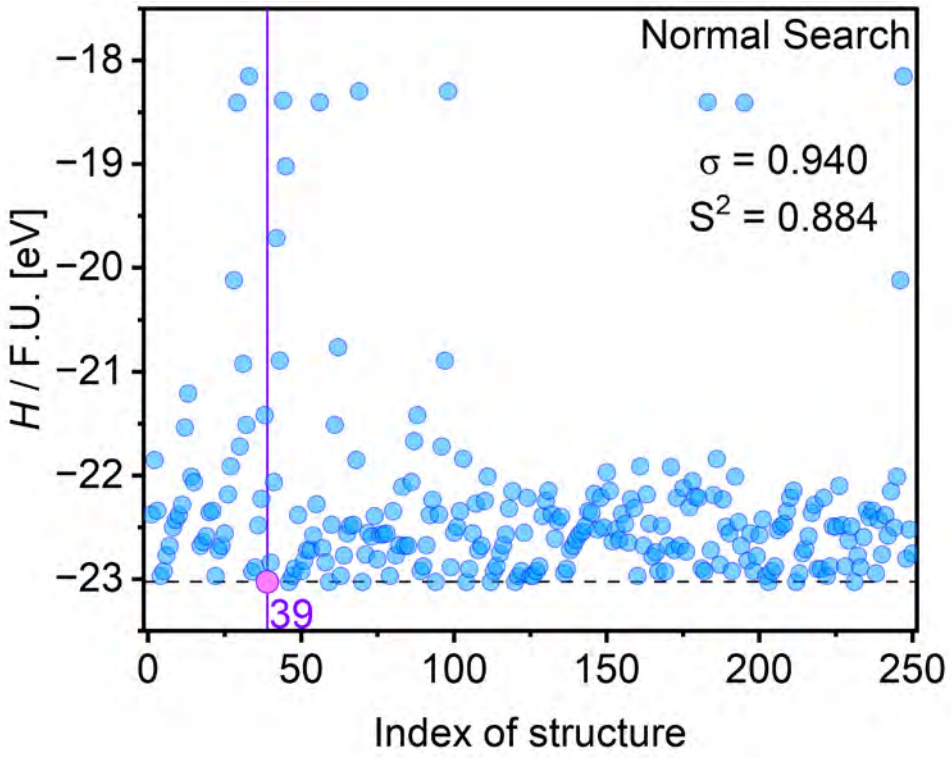


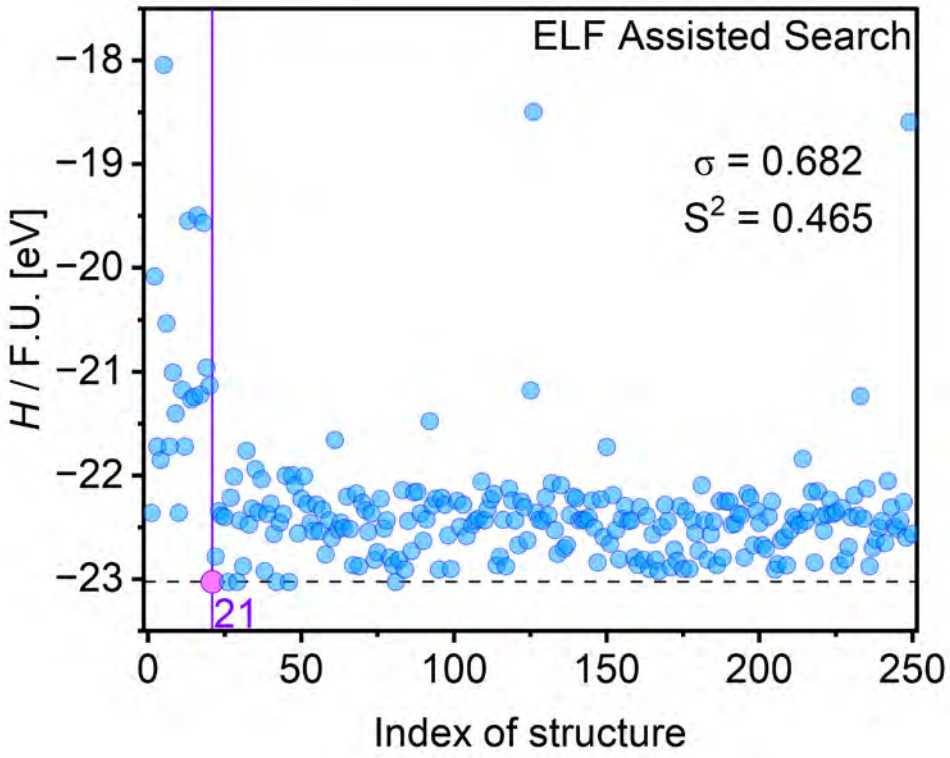
Sc_2C *
R-3m
(ground state)

Advantages

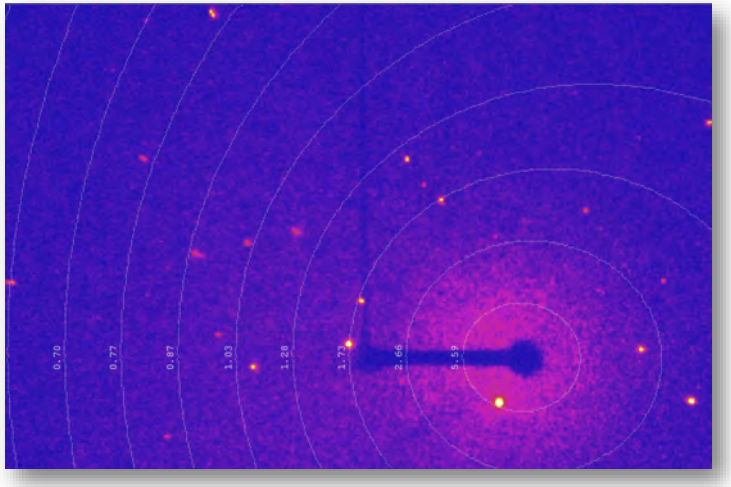
Accelerated predictions of electrides
(more electrides found with fewer structures)

Instant recognition of electrides



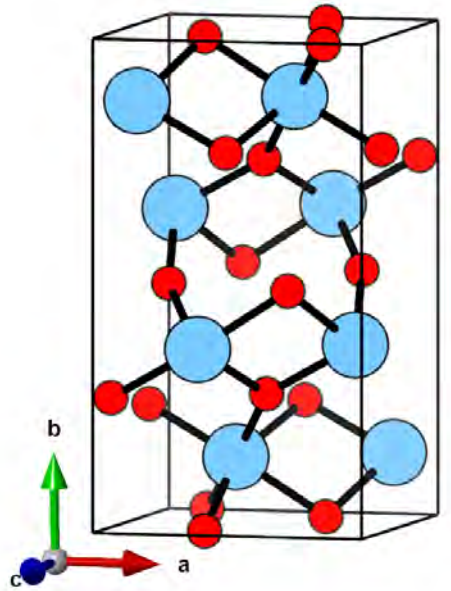


Single Crystal

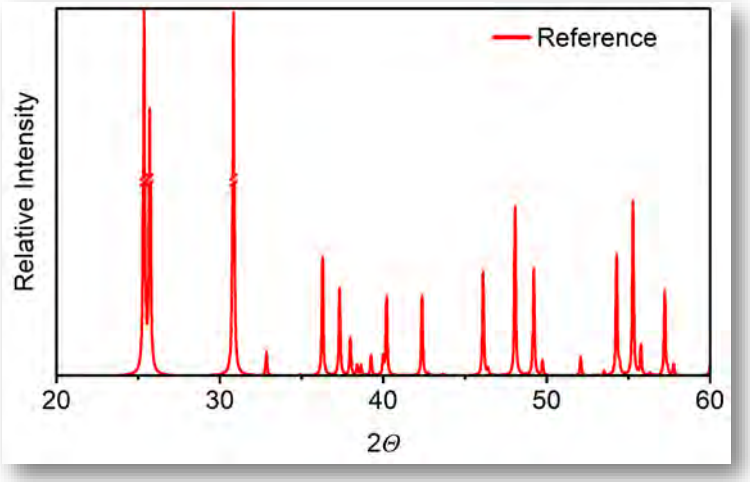


Relatively Easy

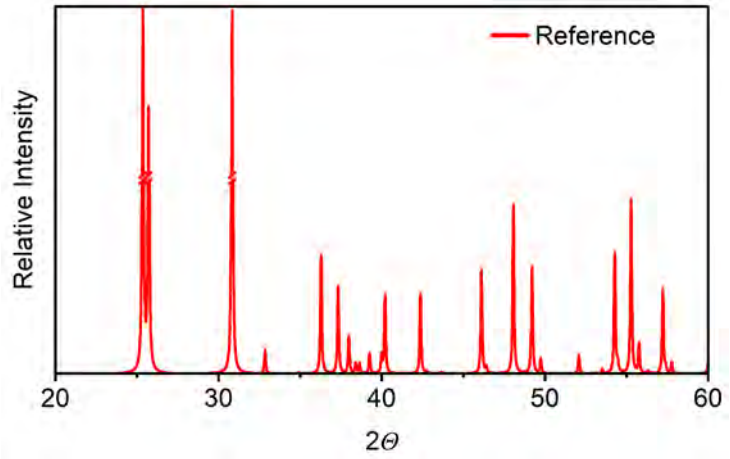
Structure Solution



Powder

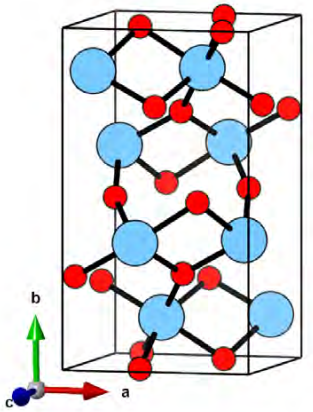


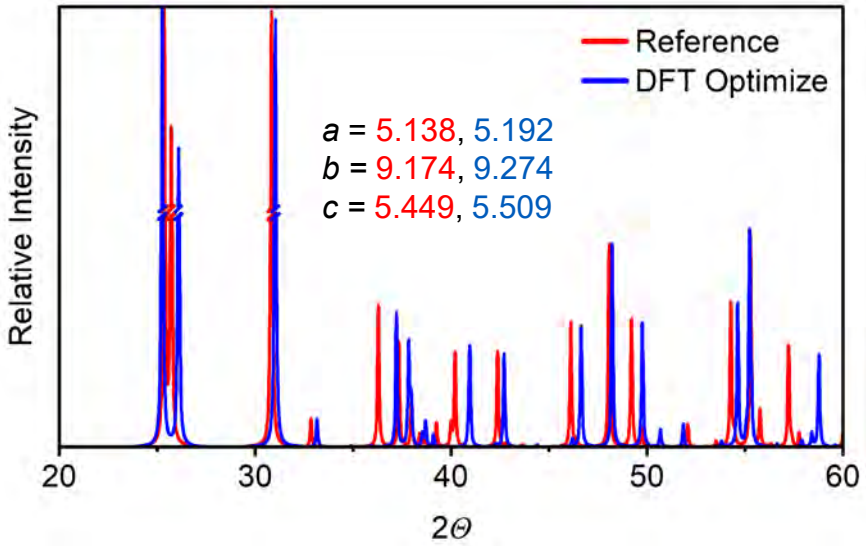
Challenging

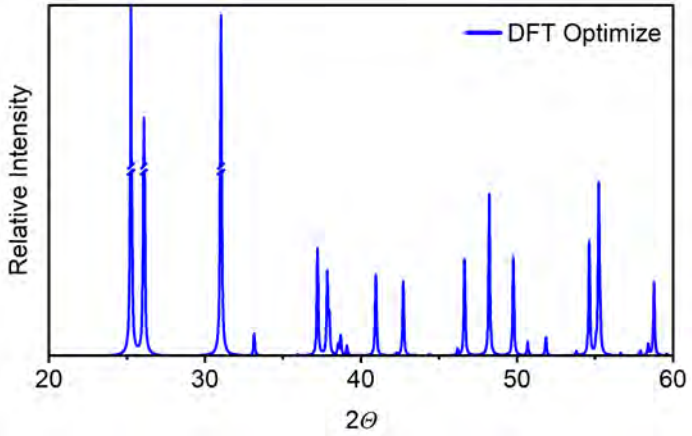


XtalOpt
Evolutionary
Crystal Structure Prediction

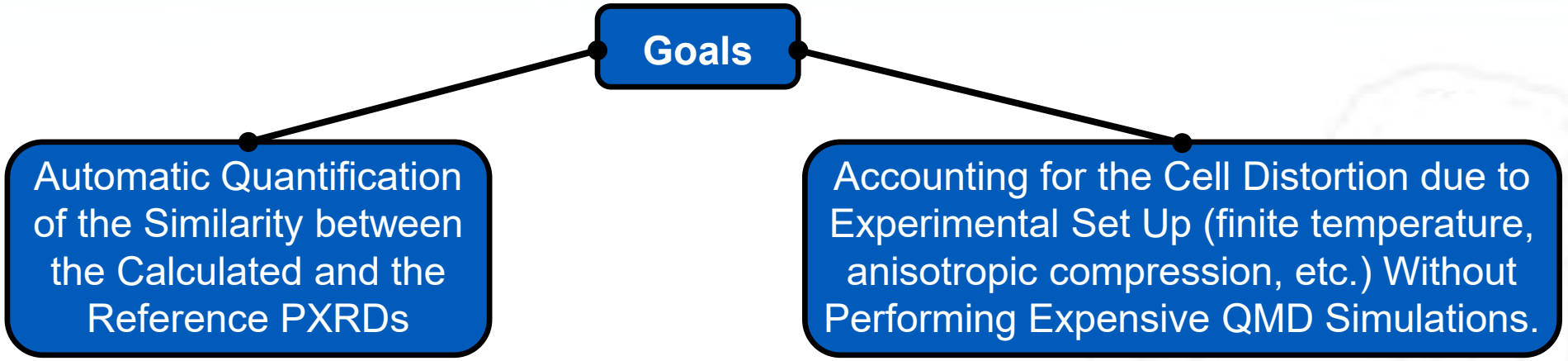
***H* Ranking**

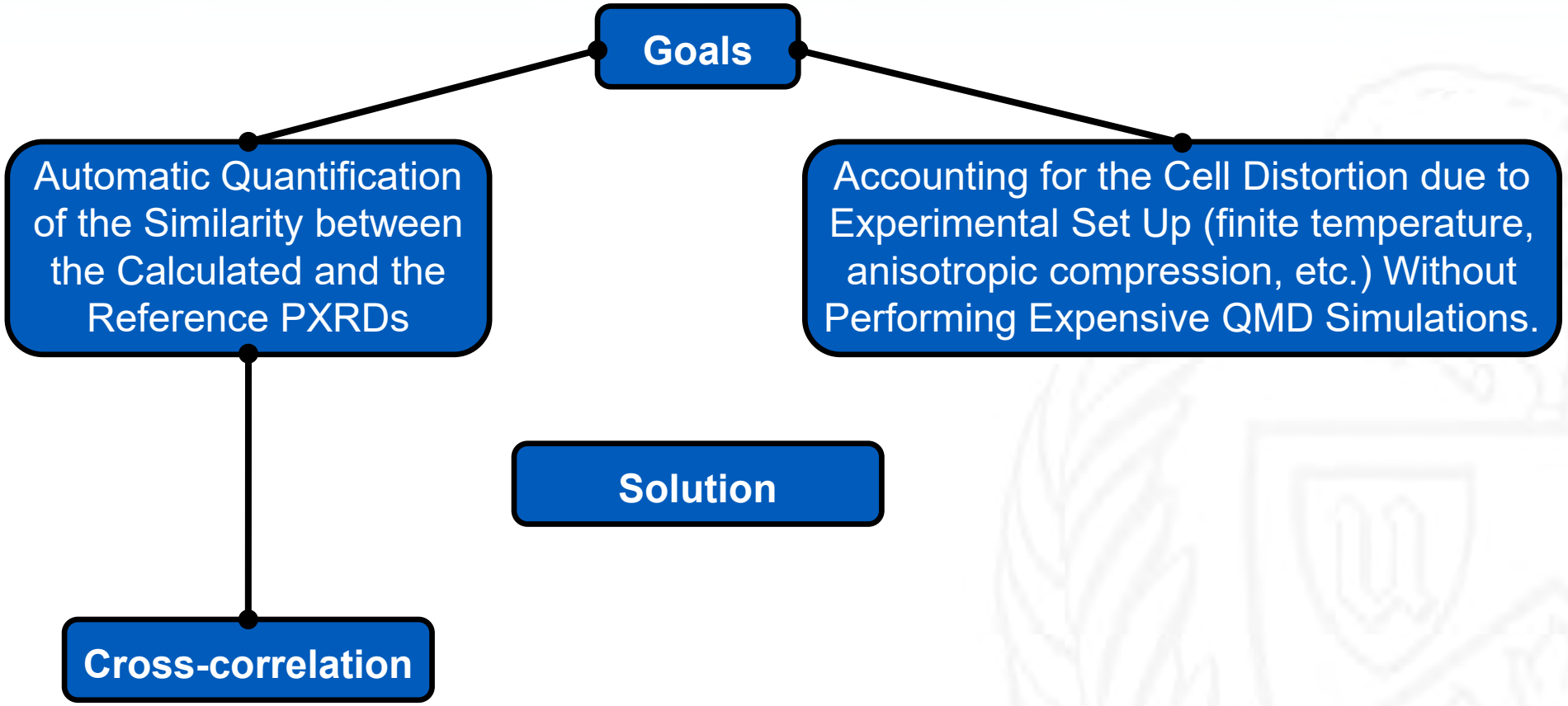






Assuming that the experimental data correspond to the ground state phase


Goals
Automatic Quantification of the Similarity between the Calculated and the Reference PXRDs
Accounting for the Cell Distortion due to Experimental Set Up (finite temperature, anisotropic compression, etc.) Without Performing Expensive QMD Simulations.



De Gelder, J. Comp. Chem. 2001

$$S_{AB}(r) = \int p_A(x) p_B(x + r)\, dx$$

0 = Perfect match

Goals

- Automatic Quantification of the Similarity between the Calculated and the Reference PXRDs
- Accounting for the Cell Distortion due to Experimental Set Up (finite temperature, anisotropic compression, etc.) Without Performing Expensive QMD Simulations.

Solution

Cross-correlation

De Gelder, J .Comp. Chem. 2001

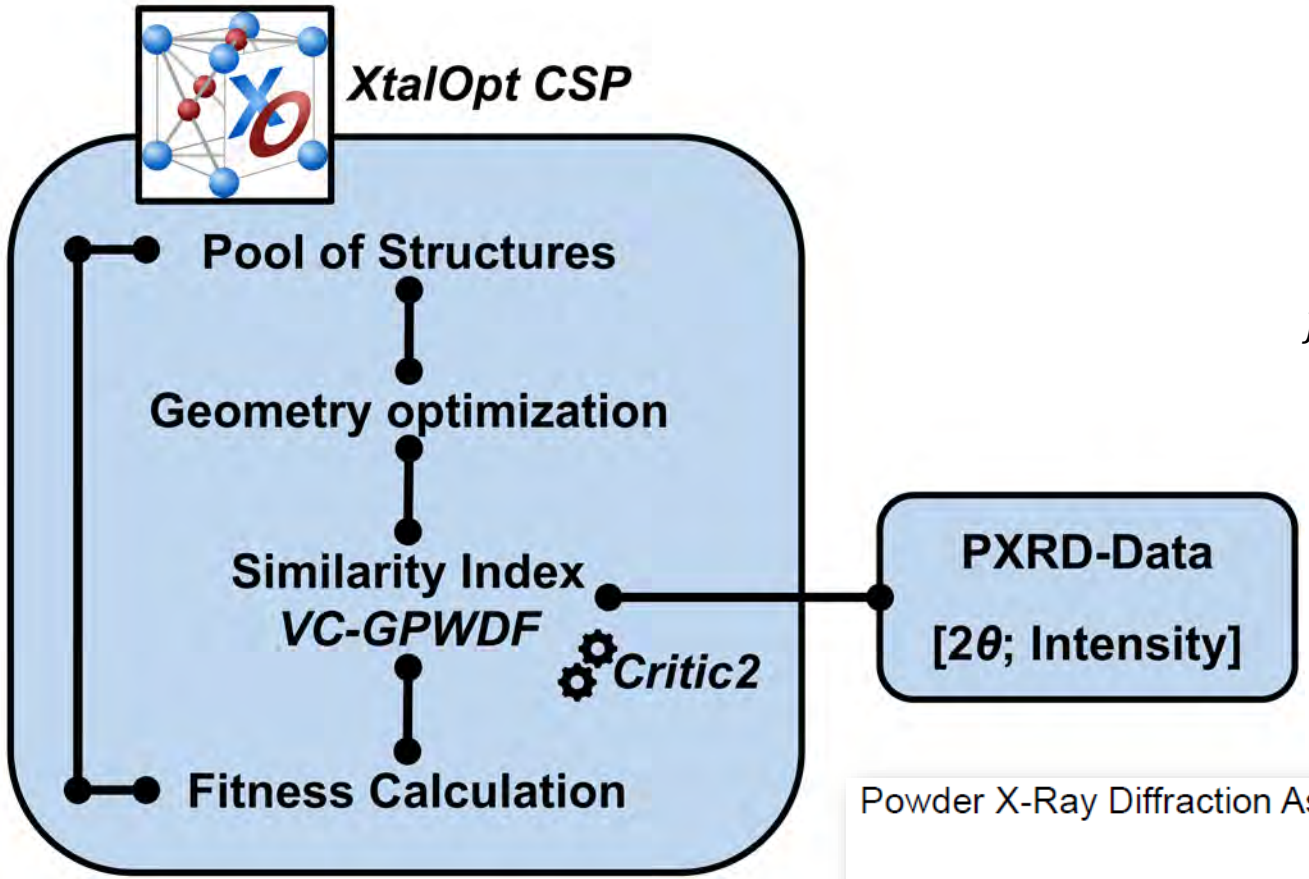
$$S_{AB}(r) = \int p_A(x) p_B(x+r)\, dx$$

0 = Perfect match

Variable-cell Gaussian powder-based similarity index (*VC-GPWDF*)

1) Does not need the PXRD to be indexed.
2) Performs iterative distortions of the DFT (Niggli) cell, looking for the best match with the reference.

doi:10.26434/chemrxiv-2024-hdt4m



$$f_s = w\left(\frac{S_{max} - S_s}{S_{max} - S_{min}}\right) + (1 - w)\left(\frac{H_{max} - H_s}{H_{max} - H_{min}}\right)$$

S = Similarity index
w = Weight

Powder X-Ray Diffraction Assisted Evolutionary Algorithm for Crystal Structure Prediction

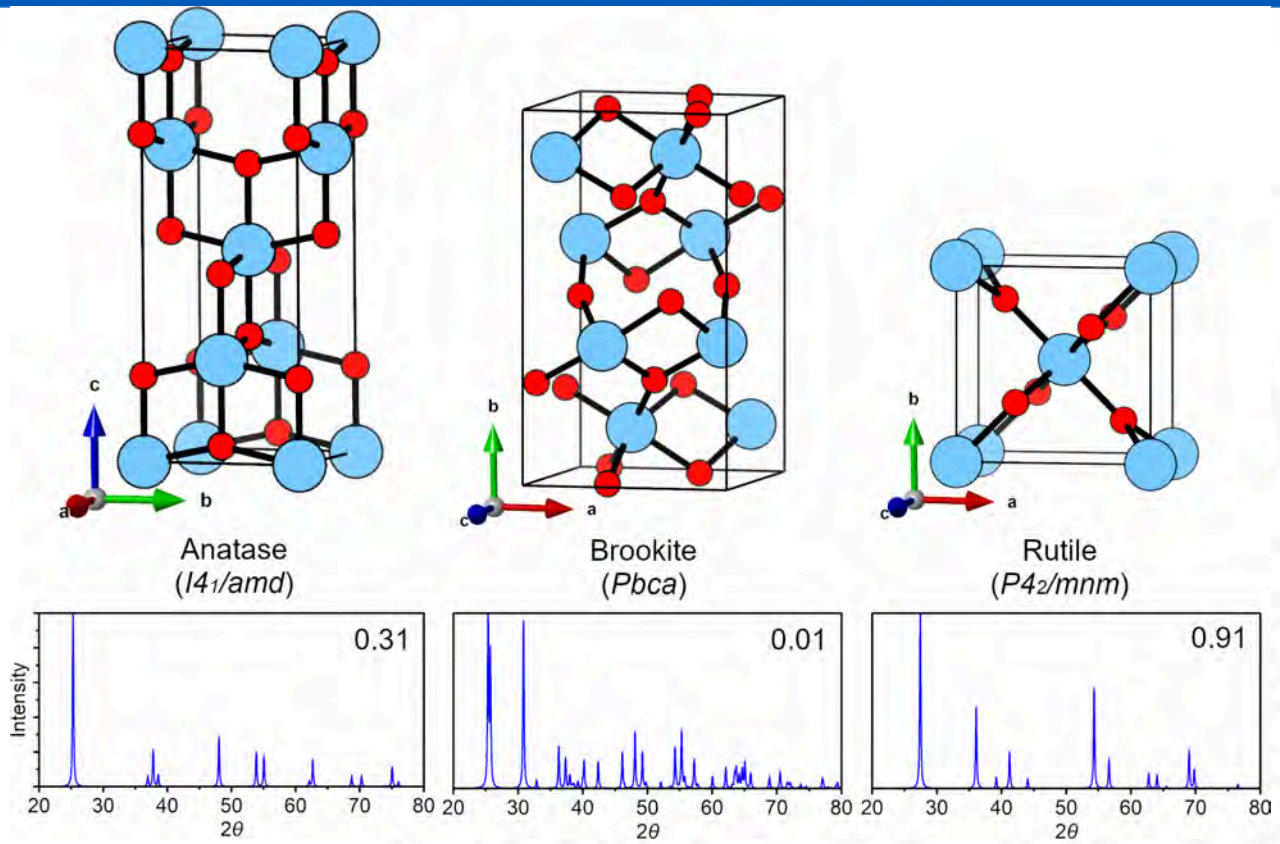
Stefano Racioppi[a], Alberto Otero de la Roza[b], Samad Hajinazar[a], Eva Zurek[a*]

https://arxiv.org/abs/2407.05394

Metastable Phases of TiO_2

	$\Delta H_{Anatase}$
Anatase (*$I4_1/amd$*, FU =4)	0.0 meV/atom
Rutile (*$P4_2/mnm$*, FU =2)	26.8 meV/atom
Brookite (*Pbca*, FU =8)	13.5 meV/atom

	single-objective		*multi-objective*		
Run	**1**	**2**	**1**	**2**	**3**
# Structures	1000	1000	500	500	500
w	0.0	0.0	0.3	0.6	0.9
Brookite	*No*	*No*	*No*	*Yes*	*Yes*



Without Refinement

(A) = 0.43 (B) = 0.17 (R) = 0.93

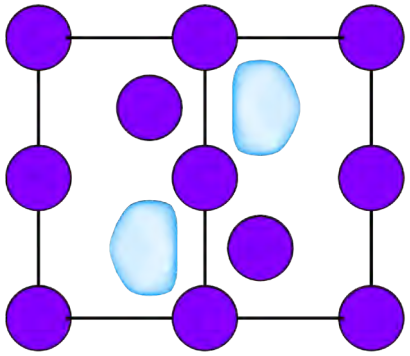
Brookite

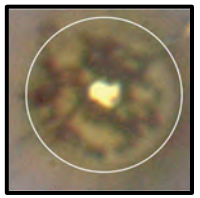
Exp. a = 5.138 ; b = 9.174 ; c = 5.449

DFT a = 5.192; b = 9.274; c = 5.509

DFT-refined a = 5.140 ; b = 9.171 ; c = 5.447

Na in Ramp Compression



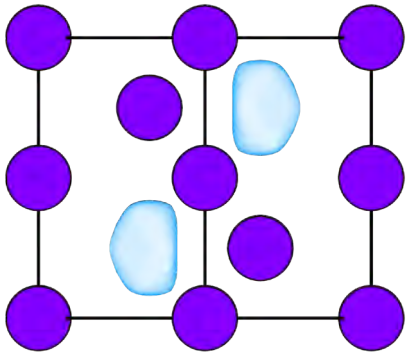


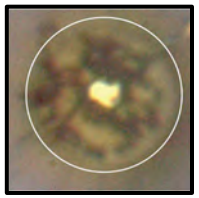
NiAs type of structure
Space Group = $P6_3/mmc$
a* = *b = 2.92
c = 4.27
V = 31.53
P = 190 GPa

Na(1) – Na(1) = 2.720 Å
Na(2) – Na(2) = 2.135 Å
Na(1) – Na(2) = 1.995 Å

Transparent at 190 GPa

Na in Ramp Compression





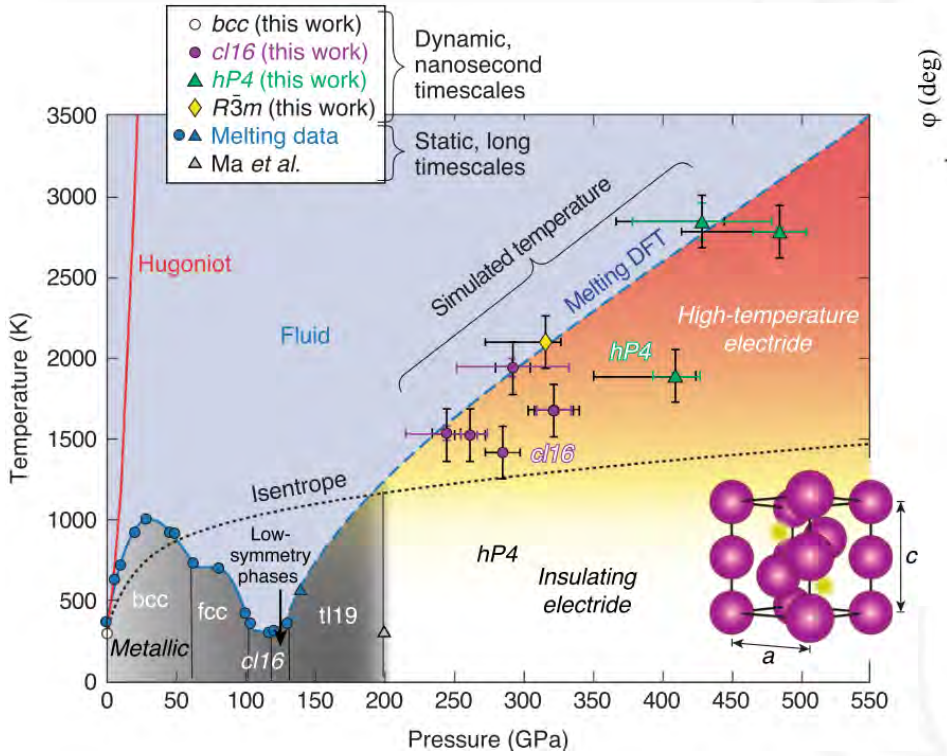
NiAs type of structure
Space Group = $P6_3/mmc$
a* = *b = 2.92
c = 4.27
V = 31.53
P = 190 GPa

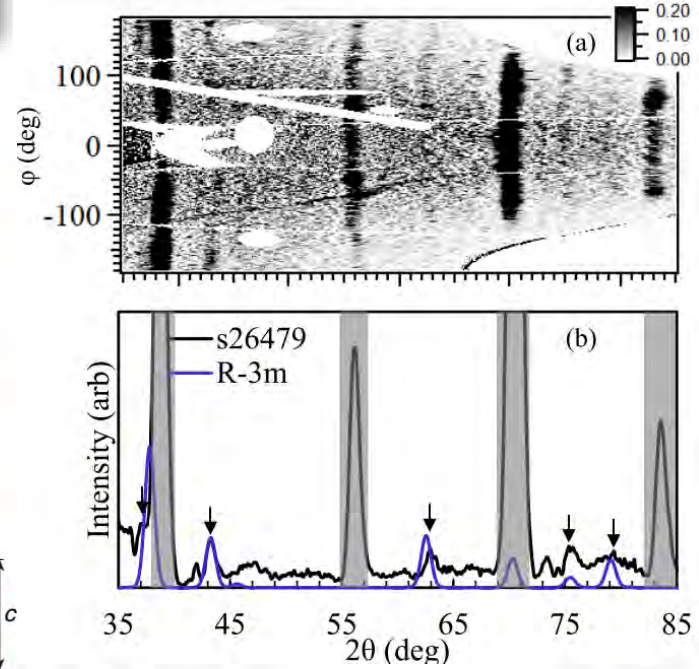
Na(1) – Na(1) = 2.720 Å
Na(2) – Na(2) = 2.135 Å
Na(1) – Na(2) = 1.995 Å

Transparent at 190 GPa

Structural complexity in ramp-compressed sodium to 480 GPa

Danae N. Polsin[1,2✉], Amy Lazicki[3], Xuchen Gong[1,2], Stephen J. Burns[2], Federica Coppari[3], Linda E. Hansen[1,4], Brian J. Henderson[1,4], Margaret F. Huff[1,4], Malcolm I. McMahon[5], Marius Millot[3], Reetam Paul[1,2], Raymond F. Smith[3], Jon H. Eggert[3], Gilbert W. Collins[1,2,4] & J. Ryan Rygg[1,2,4]





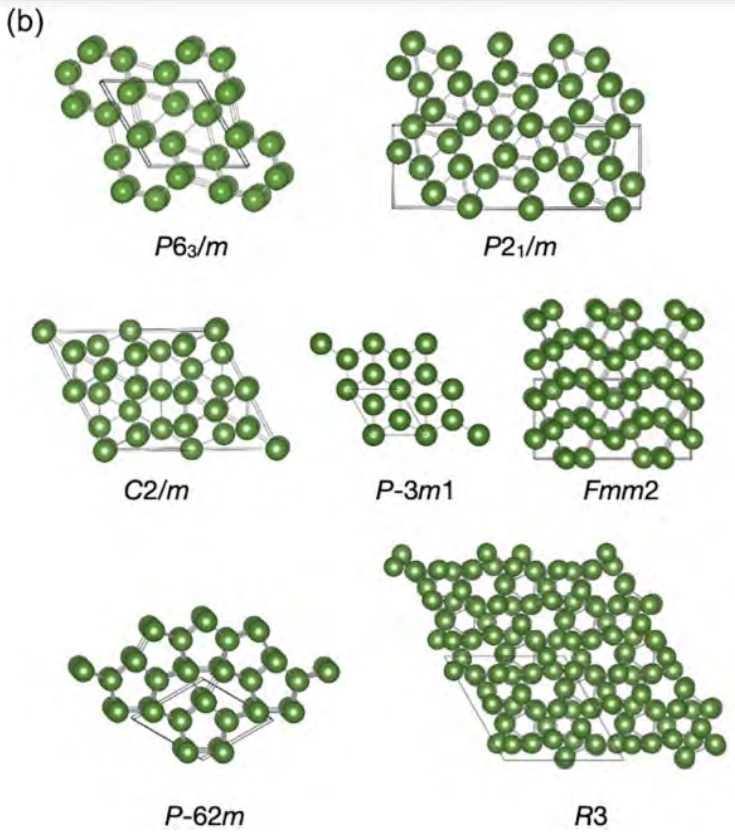
P = 315 GPa

Na in Ramp Compression

PHYSICAL REVIEW B 107, 184101 (2023)

Topological electride phase of sodium at high pressures and temperatures

Busheng Wang,[1] Katerina P. Hilleke,[1] Xiaoyu Wang,[1] Danae N. Polsin,[2,3] and Eva Zurek[1,4,5,*]



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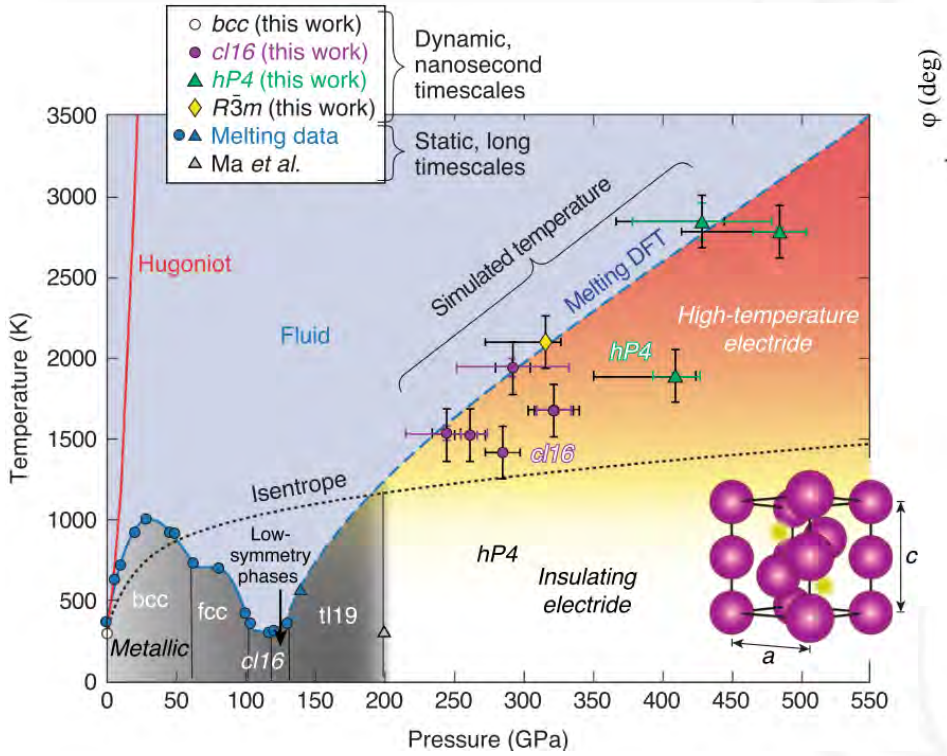
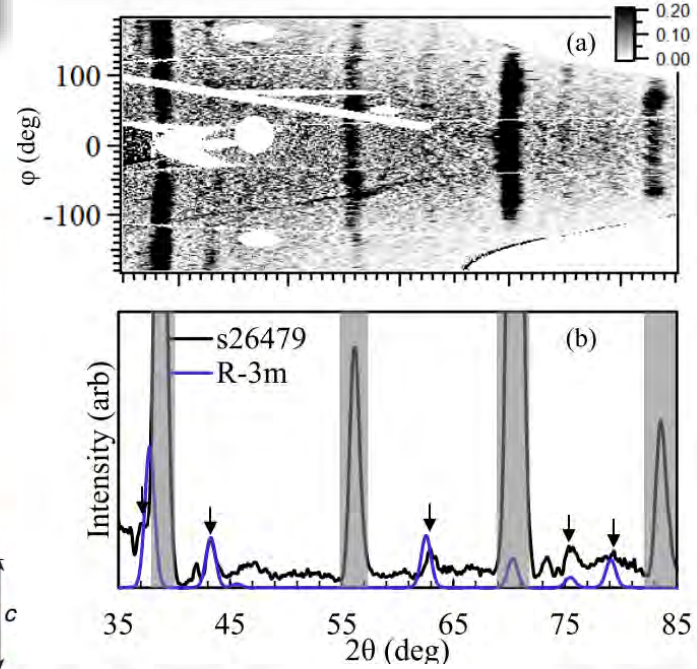
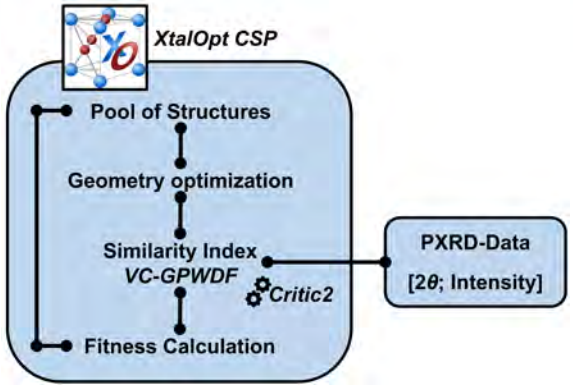


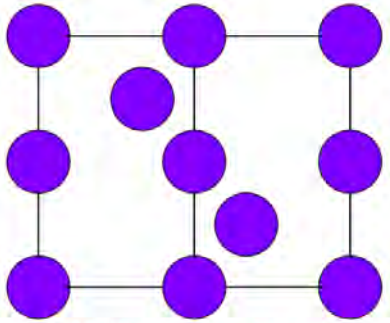


P = 315 GPa



P = 315 GPa

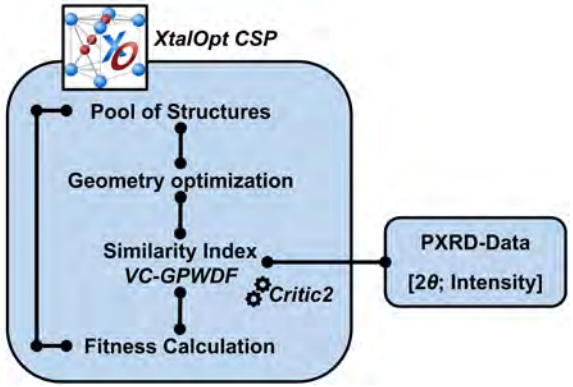
Na-hP4



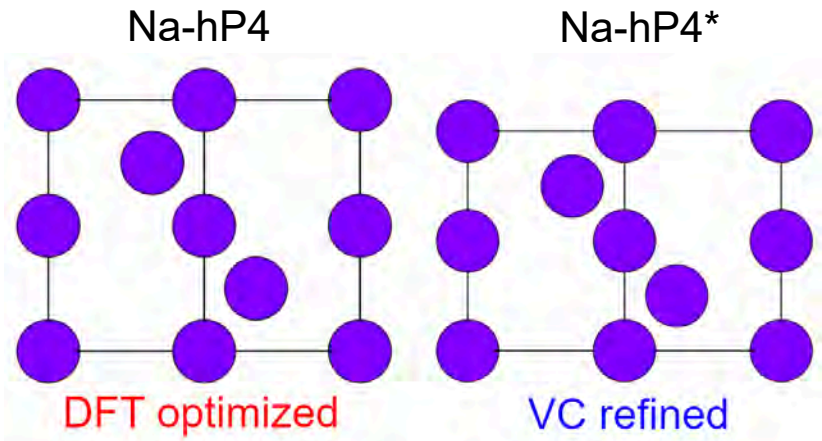
DFT optimized

c/a = 1.393

d = 5.817 g/cm^3

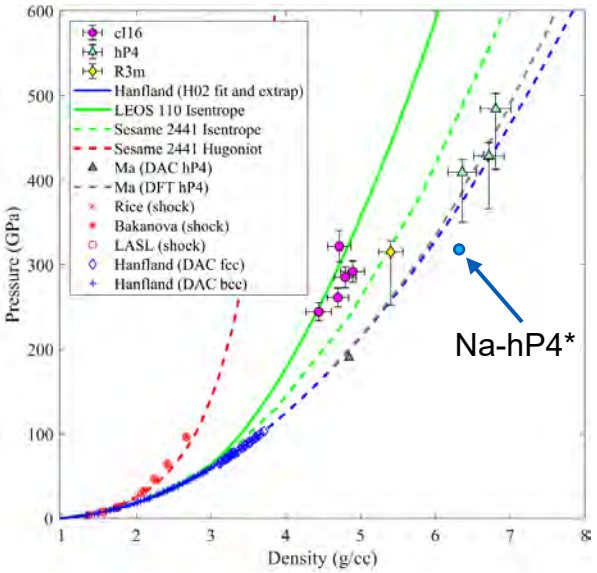


P = 315 GPa



c/a = 1.393
d = 5.817 g/cm^3

c/a = 1.212
d = 6.361 g/cm^3



ΔH =199 meV/atom

Similarity index

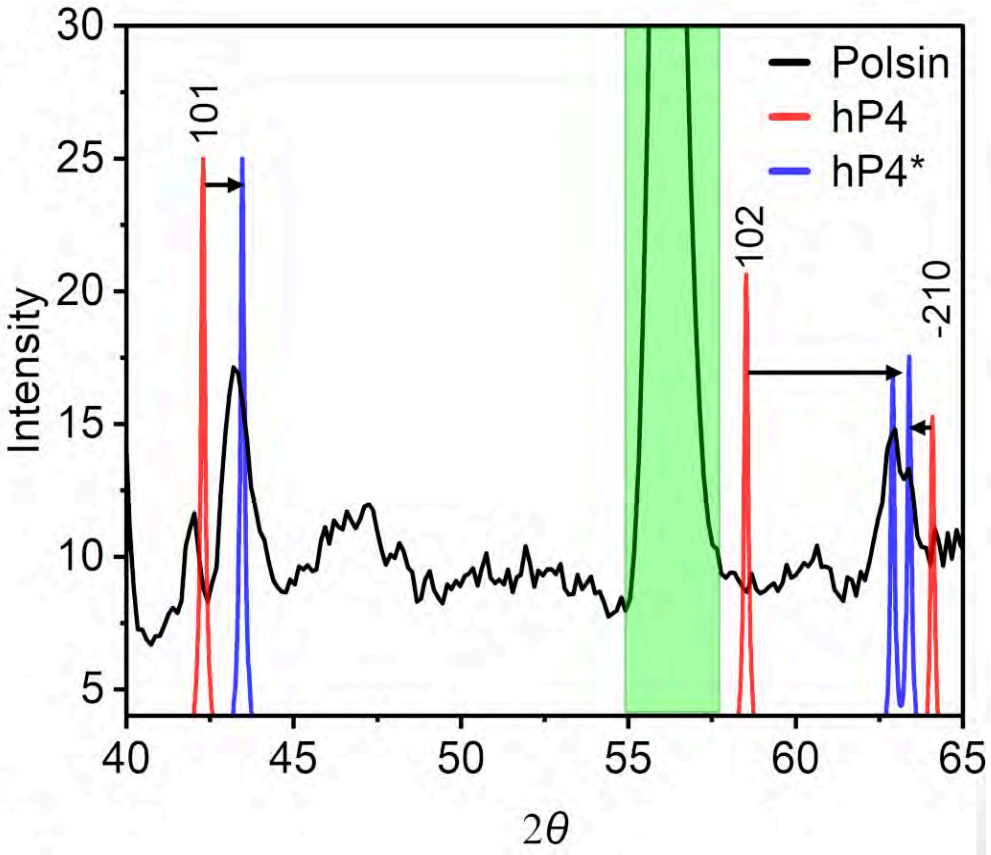
Pre-refinement = 0.991

Post-refinement = 0.086

Calculated Stress (hP4*)

Along a, b = ~370 GPa

Along c = ~425 GPa



Vaterite, $CaCO_3$

Natural polymorphs of $CaCO_3$
calcite, aragonite and vaterite

Past Proposed Structures

Meyer, 1959 – *Pnma* FU = 4
Kamhi, 1963 – *$P6_3/mmc$* FU = 2 (disordered)
Wang, 2009 (DFT) – *$P6_522$*
Le Bail, 2011 – *Ama2* FU = 4
DeMichels (DFT), 2012 – *$P6_522$*, *$P3_221$*
Mugnaioli, *2012 – Triclinic + Monoclinic*
DeMichels (DFT), 2013 – *$P6_5$*, *Cc*, *C2*

Vaterite, $CaCO_3$

Vaterite Crystals Contain Two Interspersed Crystal Structures 2013

Lee Kabalah-Amitai,[1,2] Boaz Mayzel,[3] Yaron Kauffmann,[1] Andrew N. Fitch,[4] Leonid Bloch,[1] Pupa U. P. A. Gilbert,[5] Boaz Pokroy[1,2*]

Unlocking the mysterious polytypic features within vaterite $CaCO_3$

Received: 15 June 2023
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Xingyuan San[1,6], Junwei Hu[2,6], Mingyi Chen[2], Haiyang Niu[2], Paul J. M. Smeets[3], Christos D. Malliakas[4], Jie Deng[5], Kunmo Koo[3], Roberto dos Reis[3], Vinayak P. Dravid[3] & Xiaobing Hu[3]

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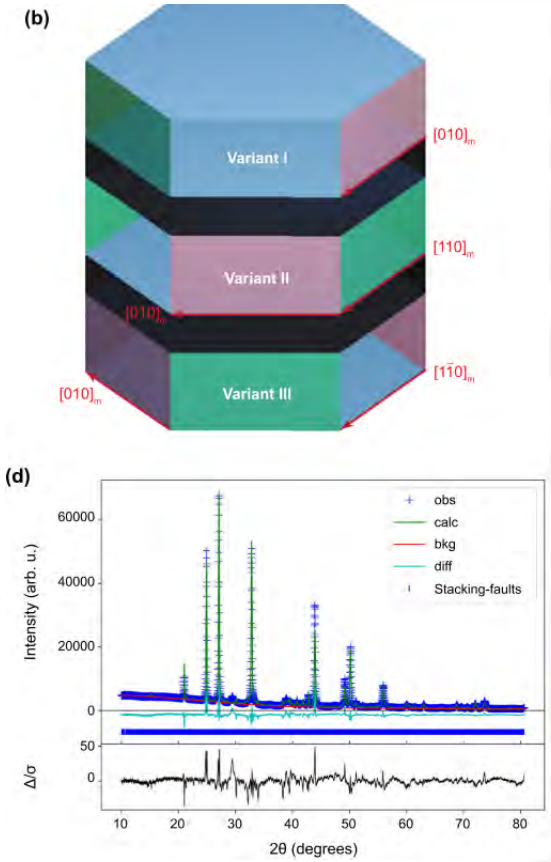

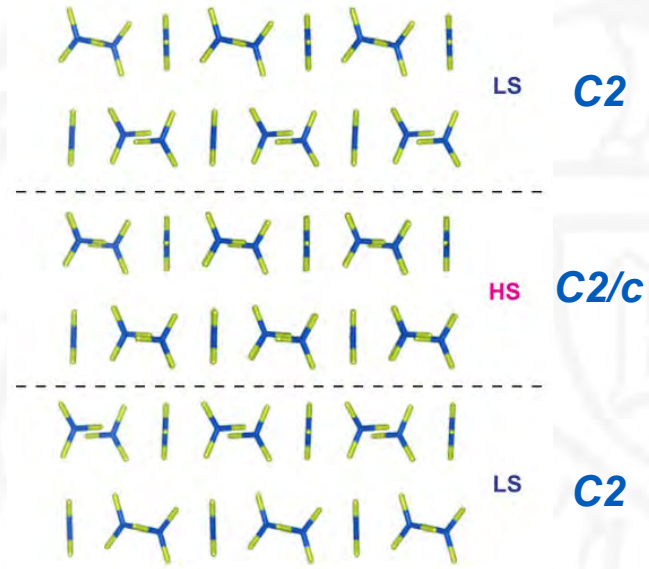

Composed by ***C2*** and ***C2/c*** monoclinic building blocks (predicted by Demichelis in 2012 and 2012)

Vaterite, $CaCO_3$

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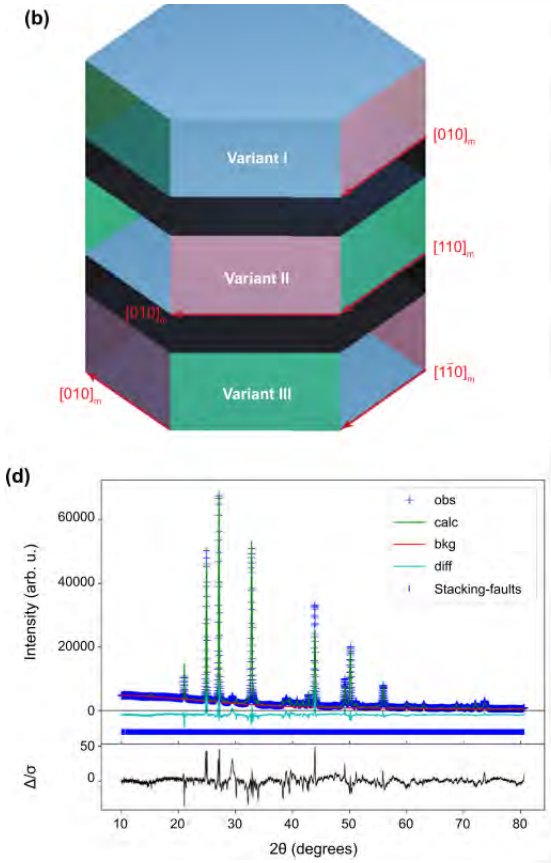
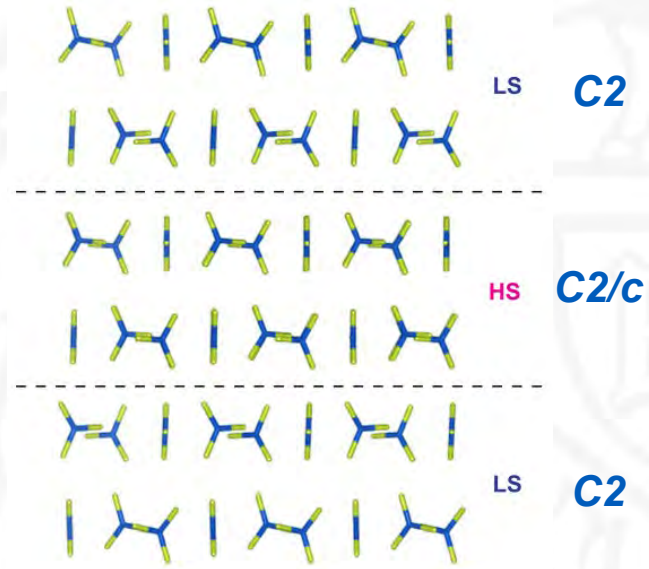
Vaterite **could not be solved by CSP** methods only.
Can our method **support the solutions** of such tricky systems?

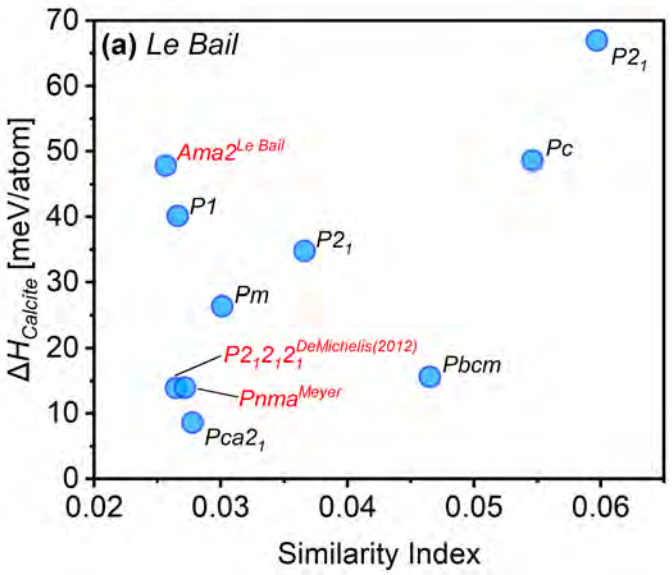


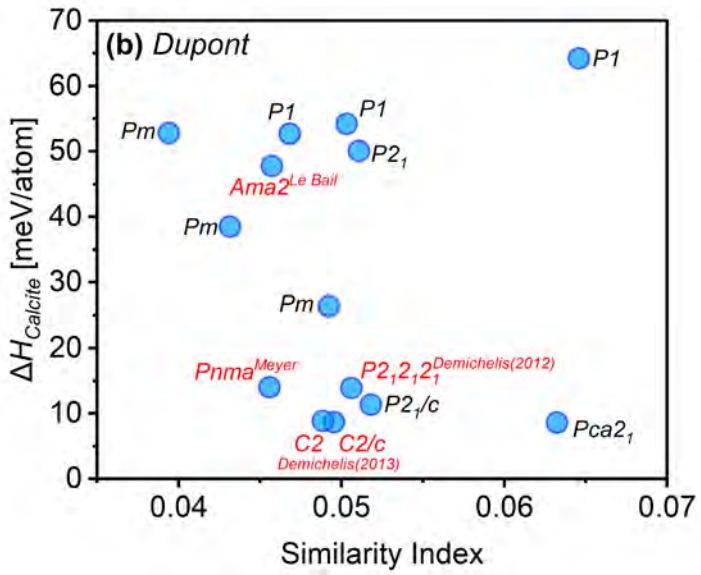


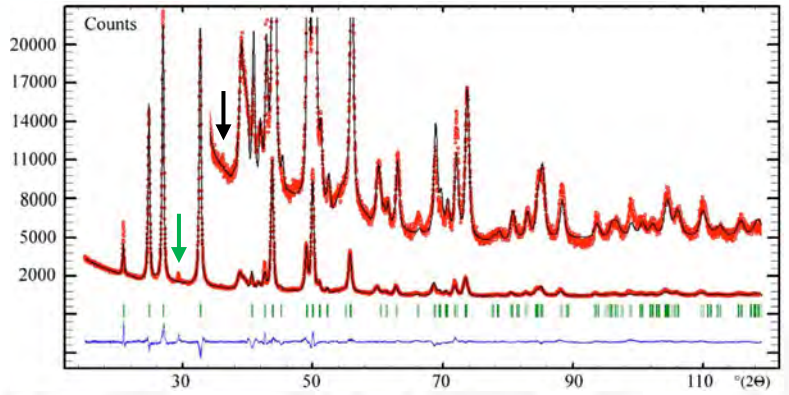
Composed by ***C2*** and ***C2/c*** monoclinic building blocks (predicted by Demichelis in 2012 and 2012)

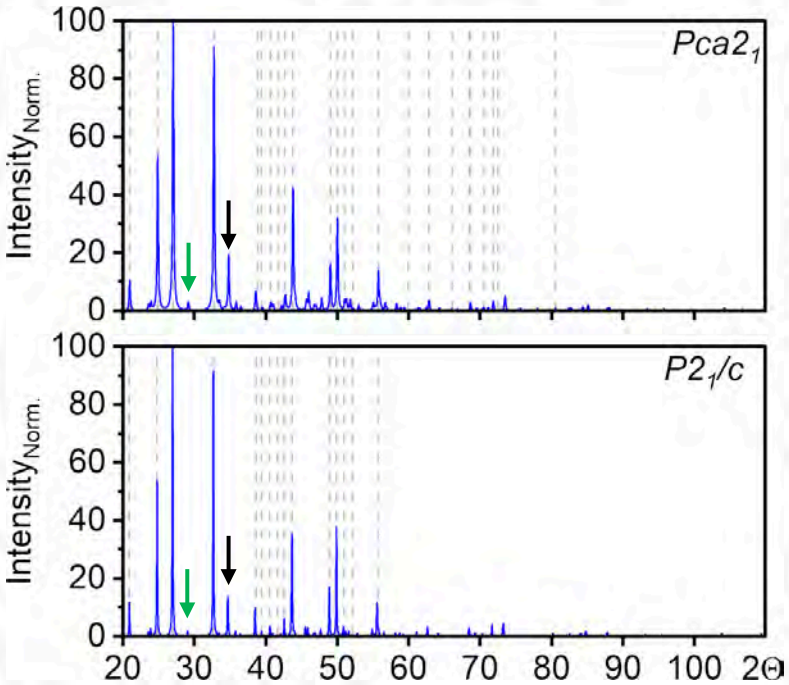
Available Data
Dupont, 1997
Le Bail, 2011

XtalOpt
Evolutionary Crystal Structure Prediction





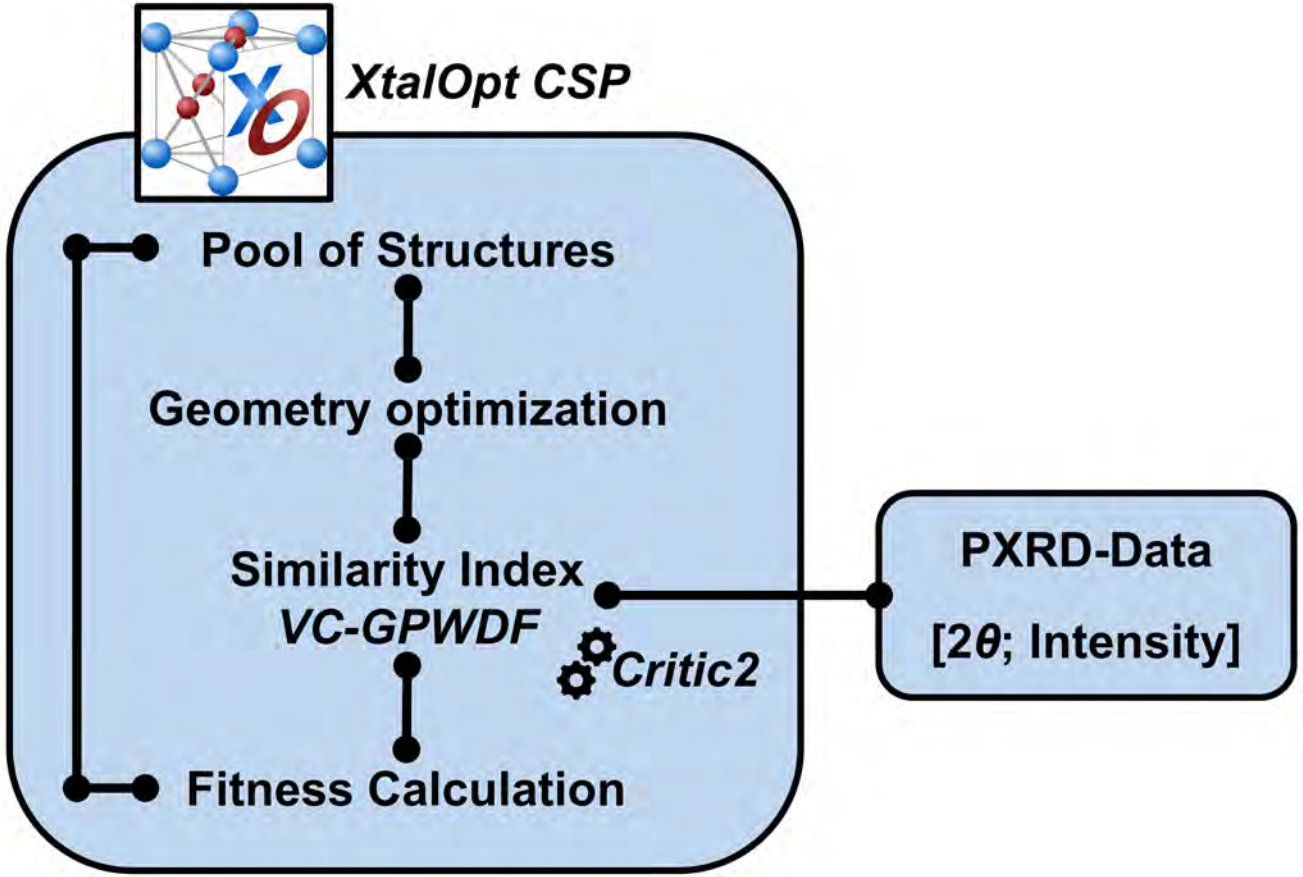




XtalOpt- VC-GPWDF
could **generate on-the-fly** all the phases necessary to achieve the solution of the polytypic model of vaterite

Implementation

1) Easy input of the PXRD data
2) Choice of the wavelenght
3) Broadening of the peaks
4) Type of optimization



Powder X-Ray Diffraction Assisted Evolutionary Algorithm for Crystal Structure Prediction

Stefano Racioppi[a], Alberto Otero de la Roza[b], Samad Hajinazar[a], Eva Zurek[a*]

Thank you

University at Buffalo
The State University of New York

Center for Matter at Atomic Pressure

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University at Buffalo The State University of New York