An Automated Ab Initio Search for Ferroelectrics

Qualifying Exam for PhD Candidacy

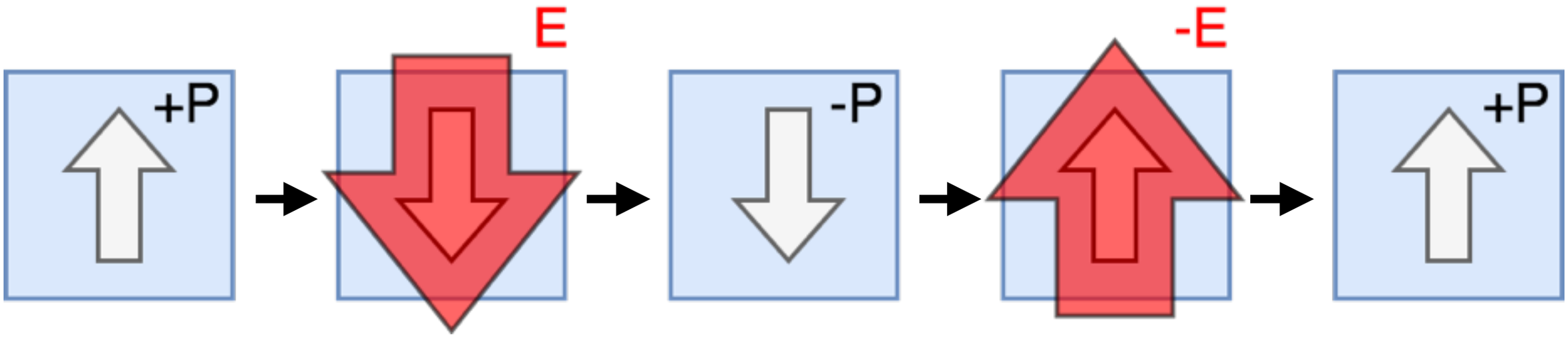
Tess E. Smidt

Outline

Introductions to Ferroelectrics
Search Overview
Search Details
Candidates
Future Work
Conclusions

Other projects from my research

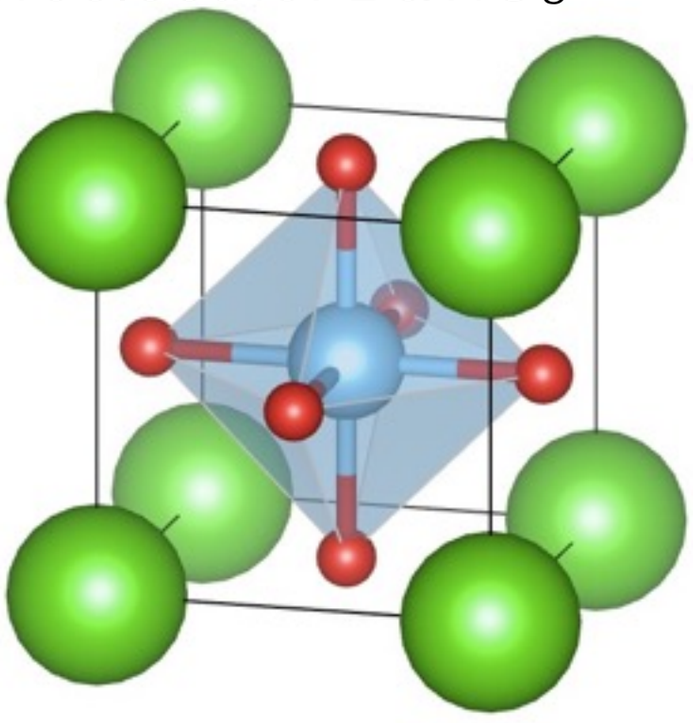
Ferroelectrics are materials with a spontaneous polarization switchable by an applied electric field.

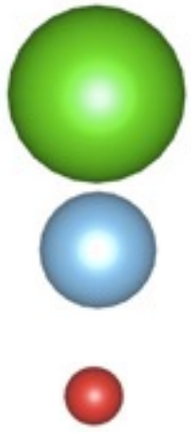


Ferroelectrics are a product of symmetry breaking.

Example ferroelectric: $BaTiO_3$

Cubic Perovskite Structure





Ba (A site)

Ti (B site)

O

Known ferroelectric since mid-1940s.
(von Hippel et al in 1944 and Wul in 1946)

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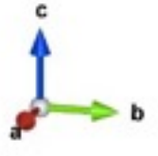

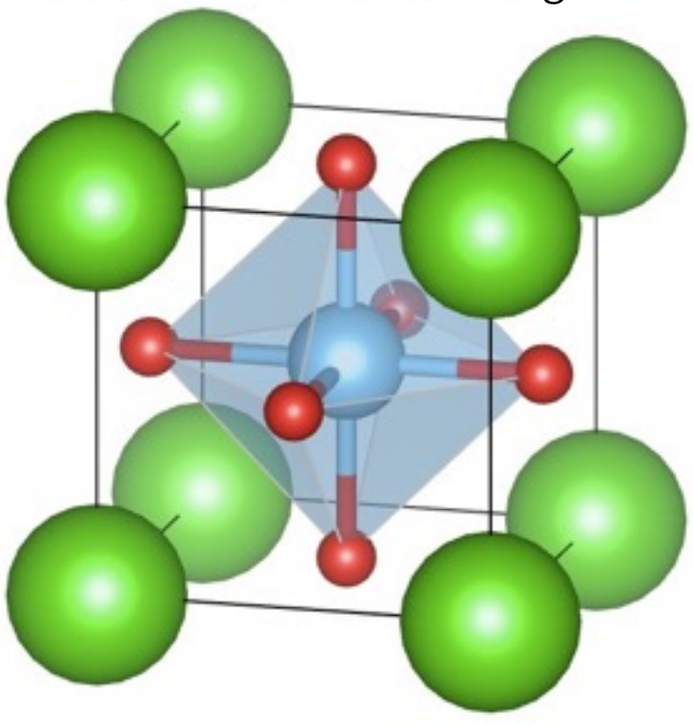

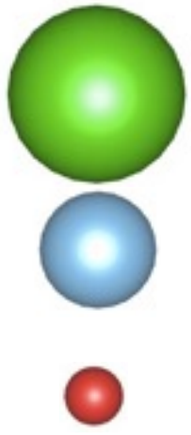

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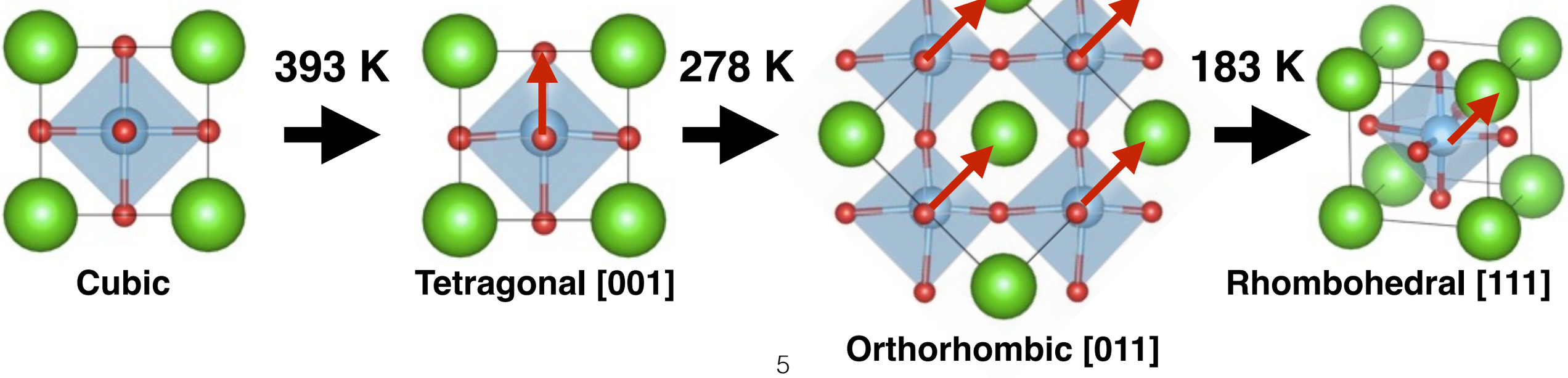
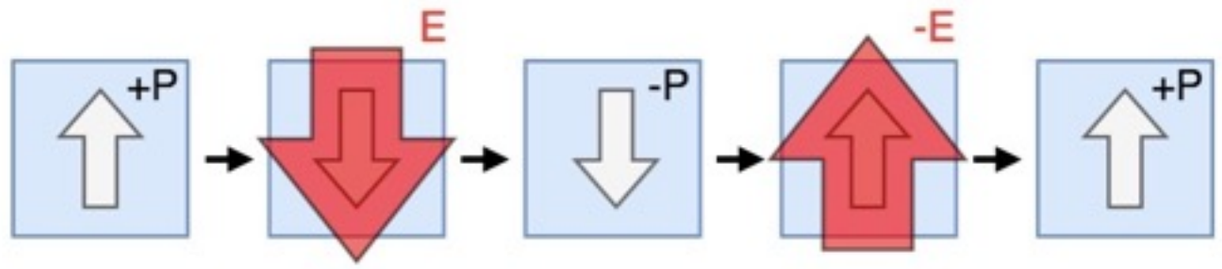
$$P_{s(20°C)} = 26\ \mu C/\mathrm{cm}^2$$

Wemple, S. H., et al. Journal of Physics and Chemistry of Solids 29.10 (1968): 1797-1803.

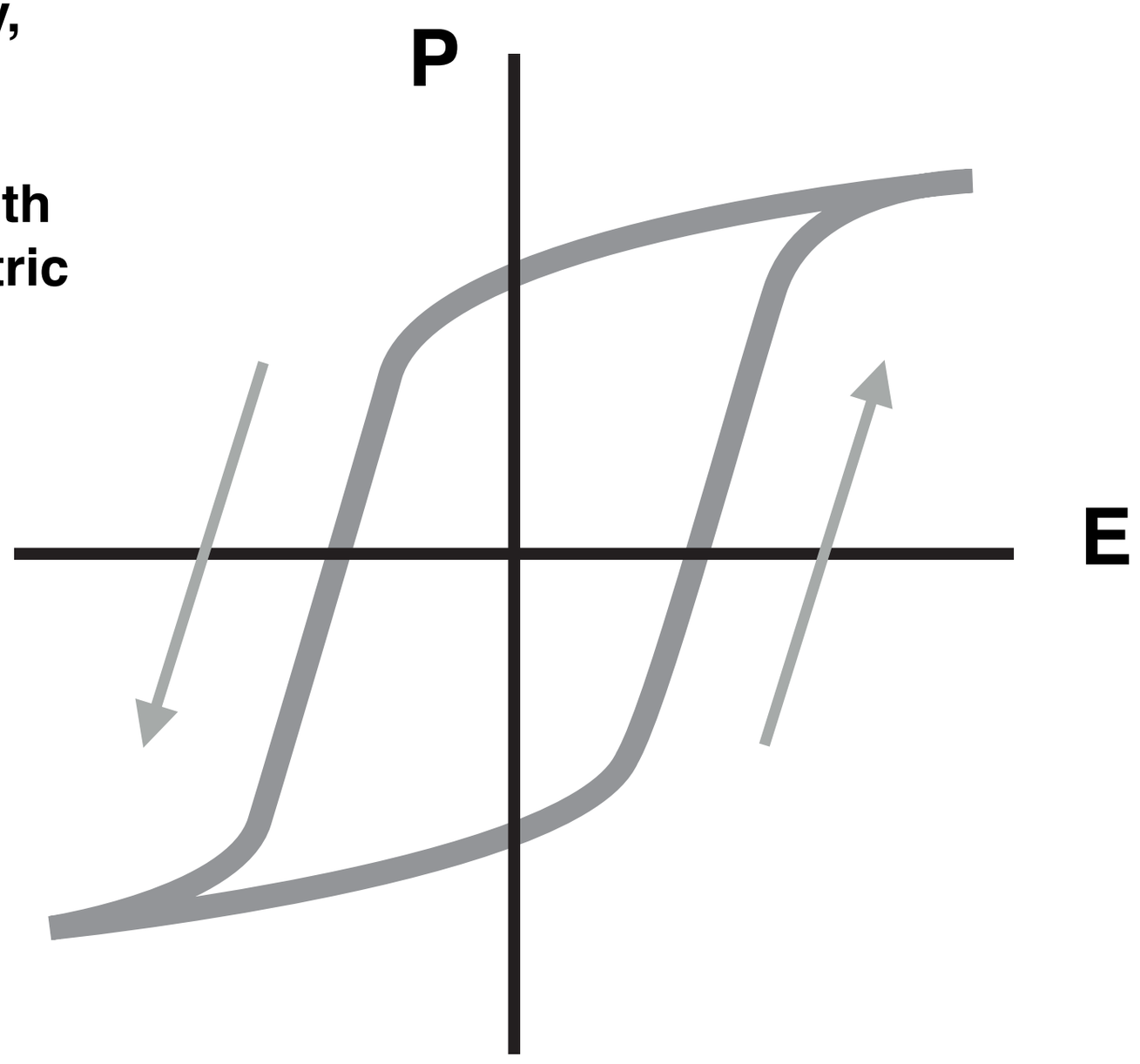
Phase transitions lead to different polarization directions.



Ferroelectrics are materials with a spontaneous polarization switchable by an applied electric field.



Experimentally, hysteresis is observed in polarization with changing electric field.



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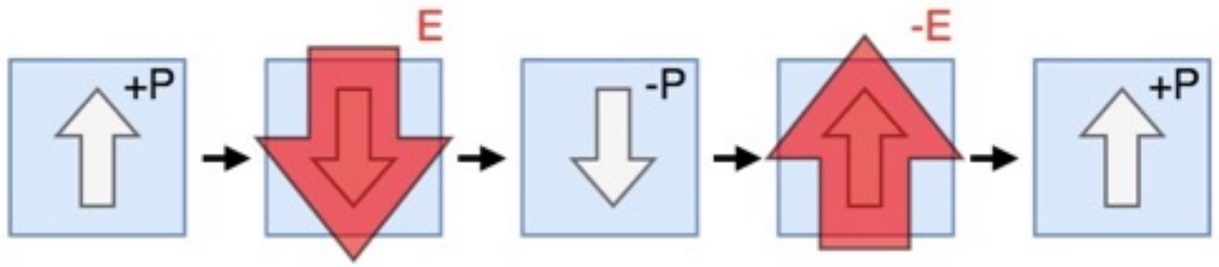
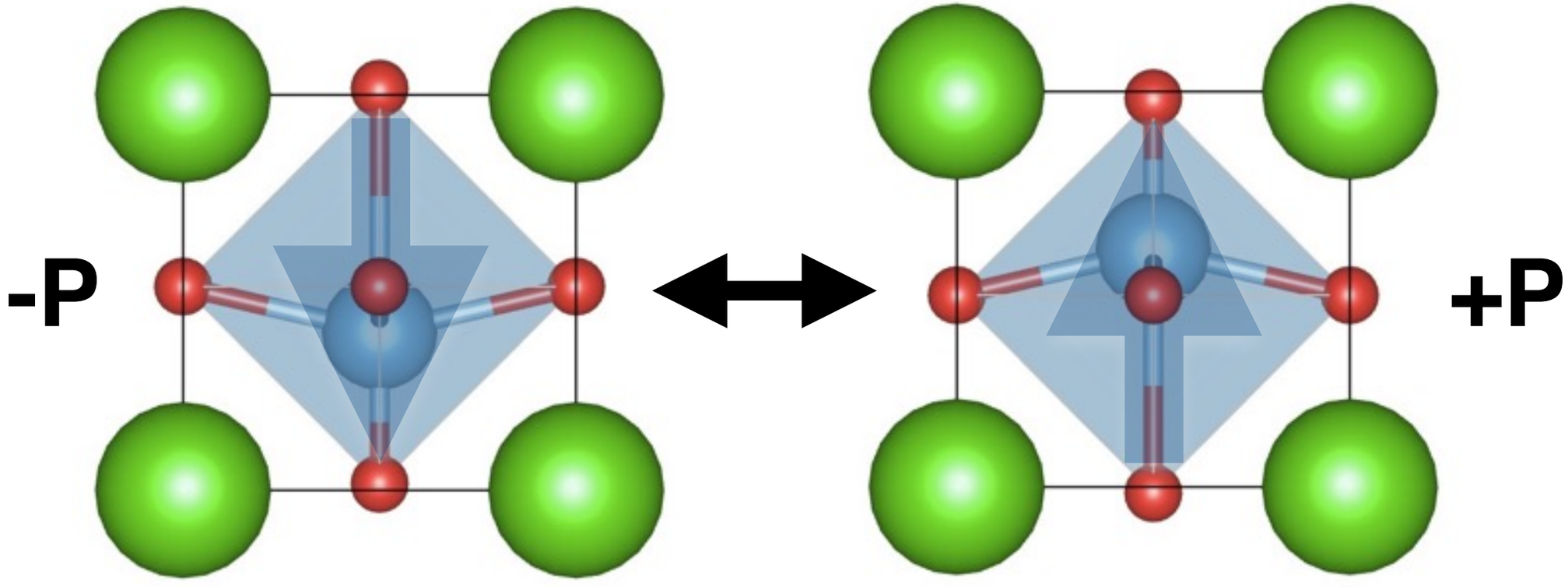


Atomically, this corresponds to switching between two stable structures.

$BaTiO_3$



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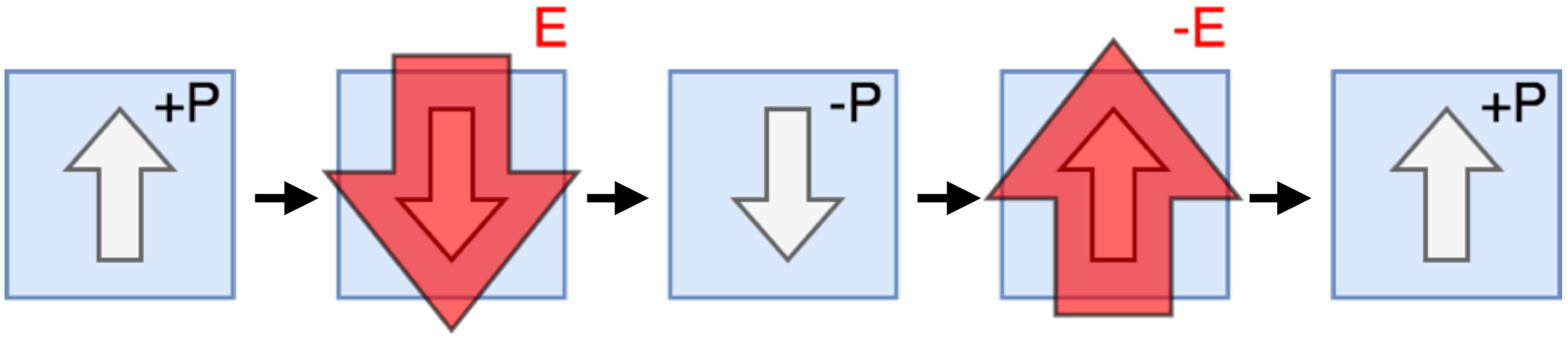
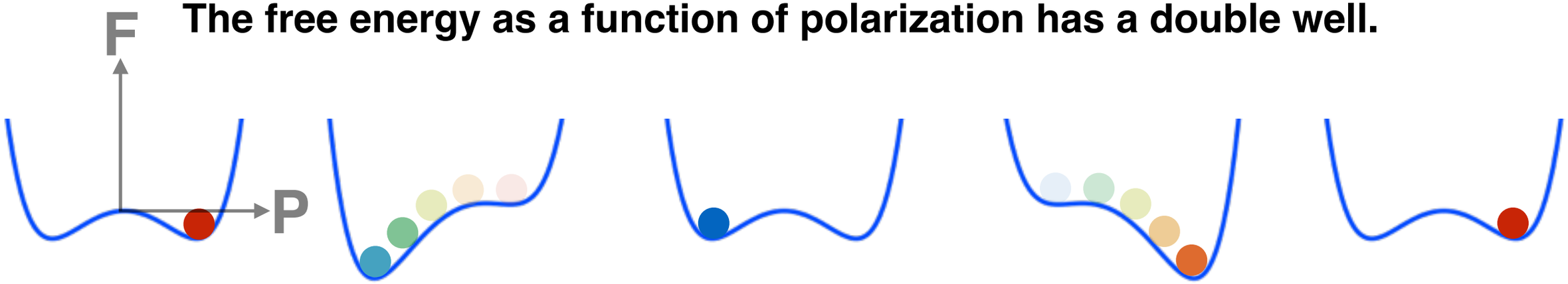


The free energy as a function of polarization has a double well.



We automate a first-principles computational ferroelectric search.

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Why?

Fundamental physics.
Technologically useful.

Still many materials out there that we don't know are ferroelectric!

Might find something surprising!

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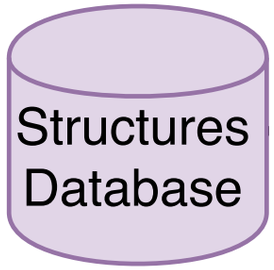

+

= **Ferroelectric candidates**

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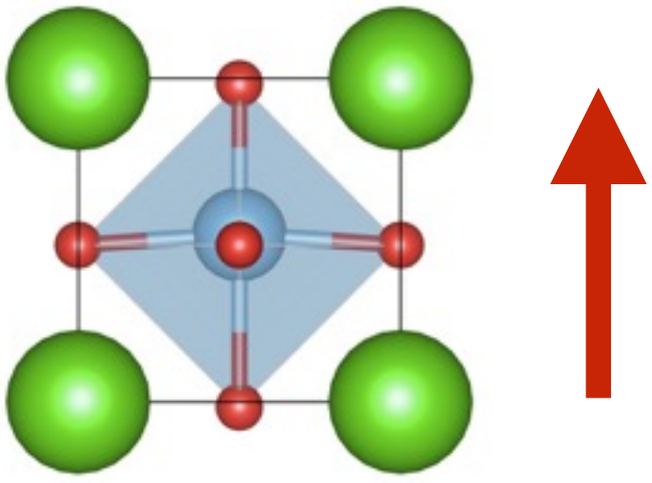
Proof of principle:

Materials Project database.

(~ 67K structures)

Our dataset is the first large dataset (100s of candidates) of known and new ferroelectrics calculated with a standardized method that permits straightforward comparison.

Ferroelectrics belong to polar space groups because polarization vector is compatible with the crystal symmetry.



$BaTiO_3$

Polar space groups have polar point groups.

Out of the 32 point groups, there are 10 polar points groups:
(1, 2, m, mm2, 4, 4mm, 3, 3m, 6, 6m)

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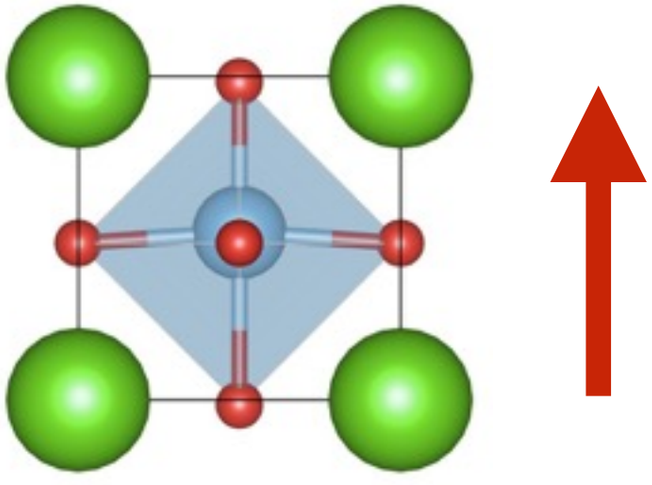

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Previous work has used these symmetry requirements but in total only suggest ~50 candidates. Only some have DFT calculations.

Our first automated search has already yielded ~100 diverse new candidates.

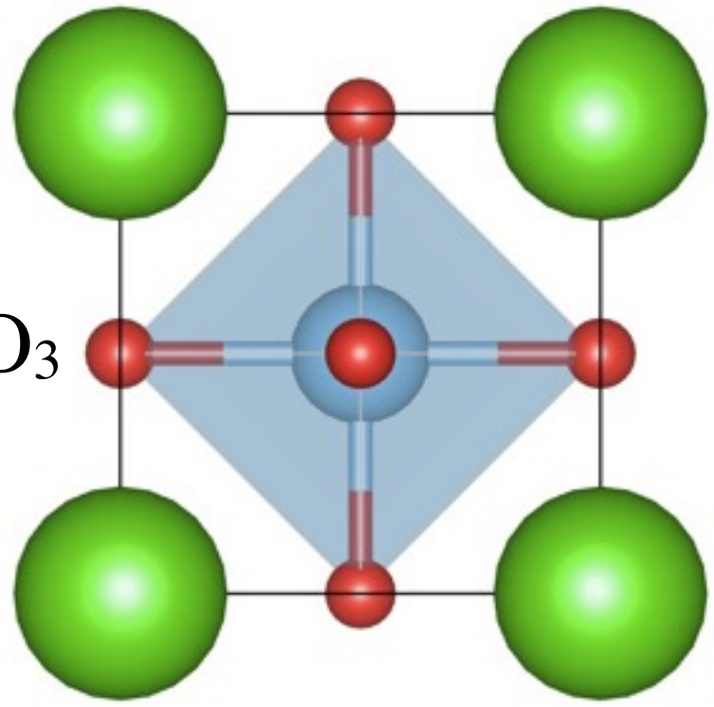
- S. C. Abrahams, Structurally Based Prediction of Ferroelectricity in Inorganic Materials with Point Group 6mm, Acta Cryst. B44, 585-595 **(1988).**
- E. Kroumova, M.I. Aroyo, and J.M. Perez-Mato, Prediction of new displacive ferroelectrics through systematic pseudosymmetry search, Acta Cryst. Sect. B Struct. Sci. 58, 921 **(2002).**
- J.W. Bennett and K.M. Rabe, Integration of first-principles methods and crystallographic database searches for new ferroelectrics, J. Solid State Chem. 195, 21 **(2012).**
- K. Garrity, High-throughput first principles search for new ferroelectrics, arXiv:1610.04279 **(2016)** [searching for soft phonons modes]

Predicting ferroelectrics from first-principles:
Calculate polarization along continuous path from a nonpolar reference phase to ferroelectric polar phase.

Nonpolar reference phase

$P_s=0$

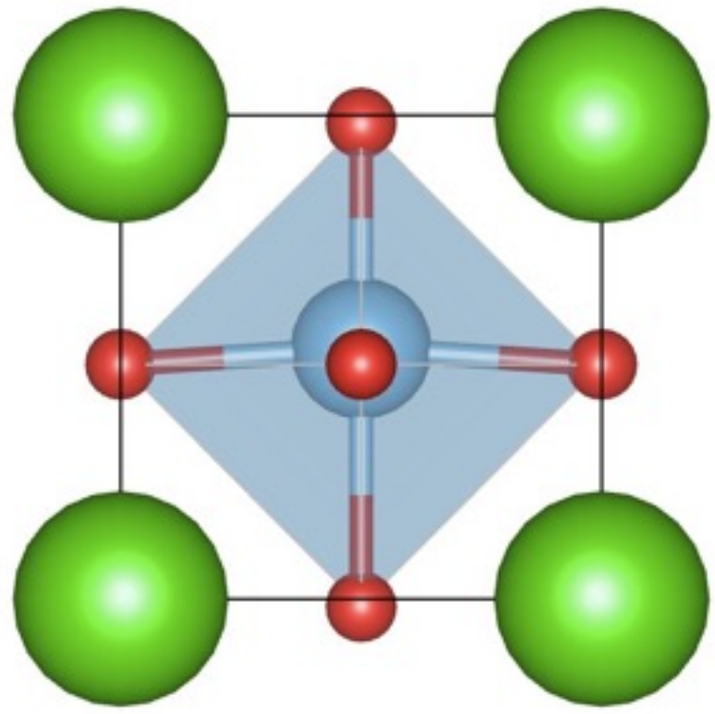
$BaTiO_3$



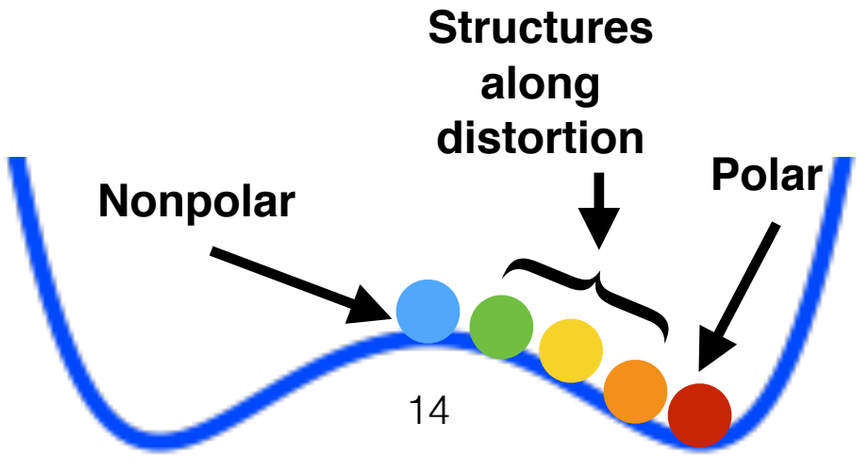
Space group 221
(P**m-3m**)

Polar ferroelectric structure

$P_s=P$



Space group 99
(P**4mm**)



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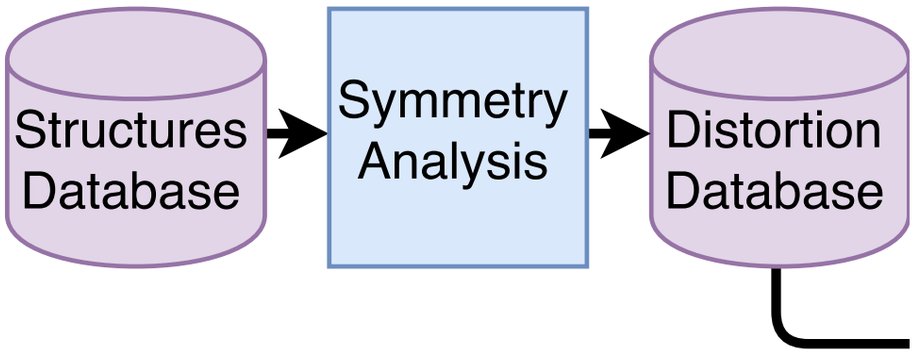

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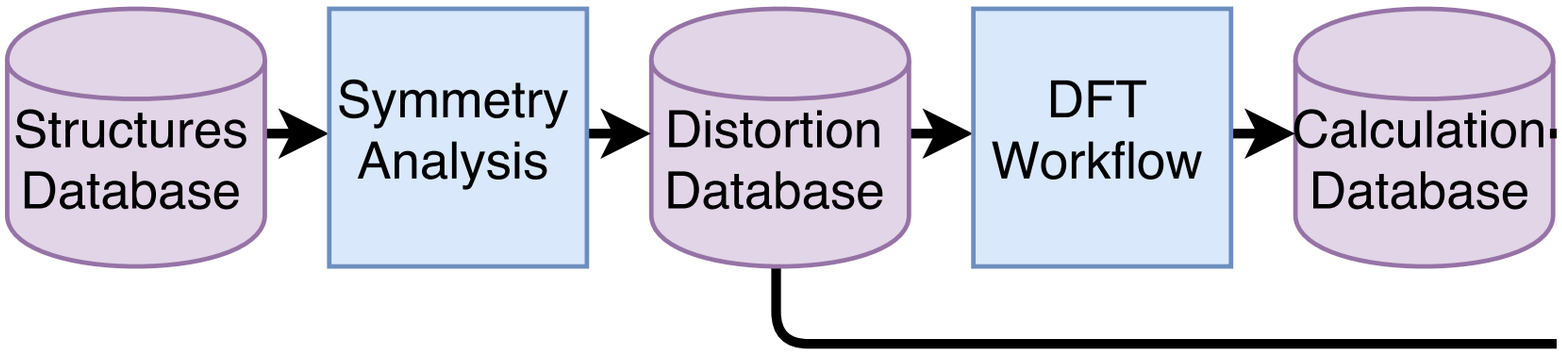
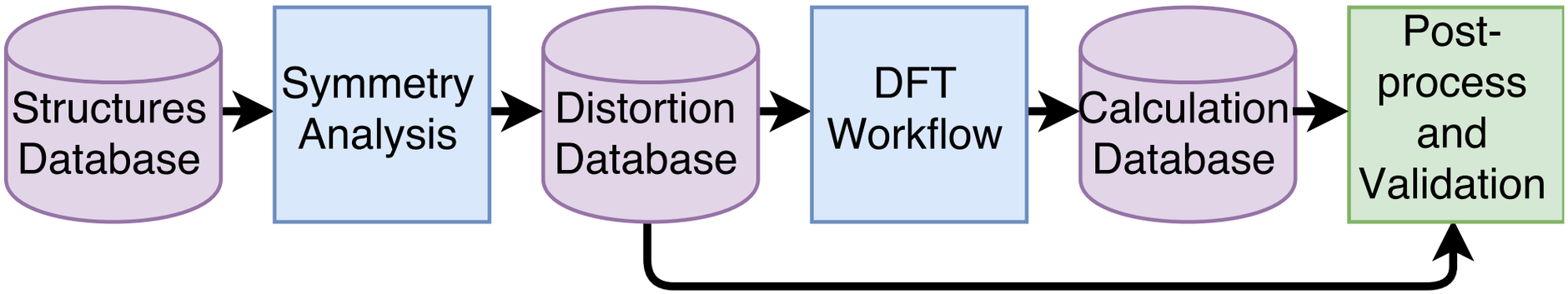
We've created an automated framework for identifying ferroelectrics using nonpolar - polar structure pairs.



<u>We've automated the following:</u>

1. Identifying candidate nonpolar-polar structure pairs and checking their symmetry relations.
2. **Performing density functional theory (DFT) calculations of total energy and polarization across the distortion.**

We've created an automated framework for identifying ferroelectrics using nonpolar - polar structure pairs.



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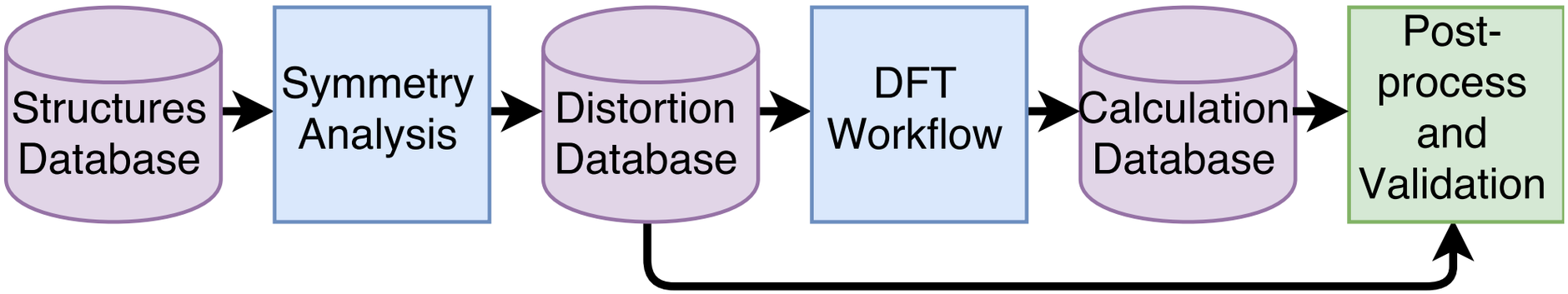

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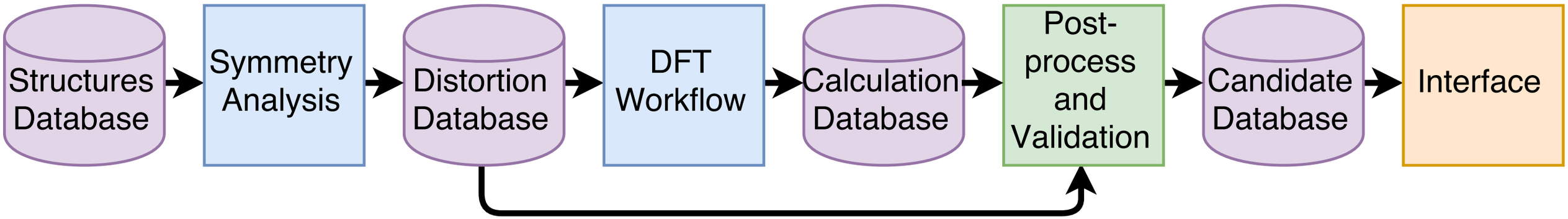

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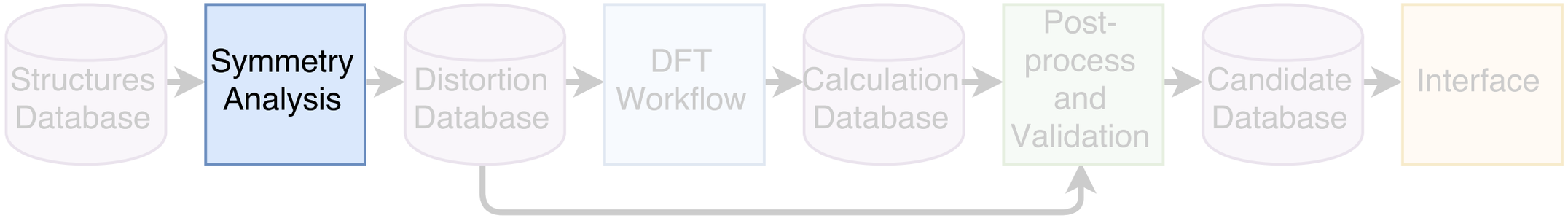
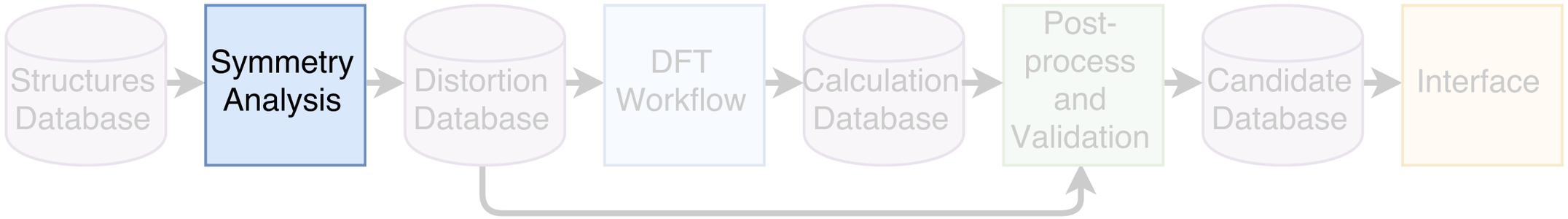
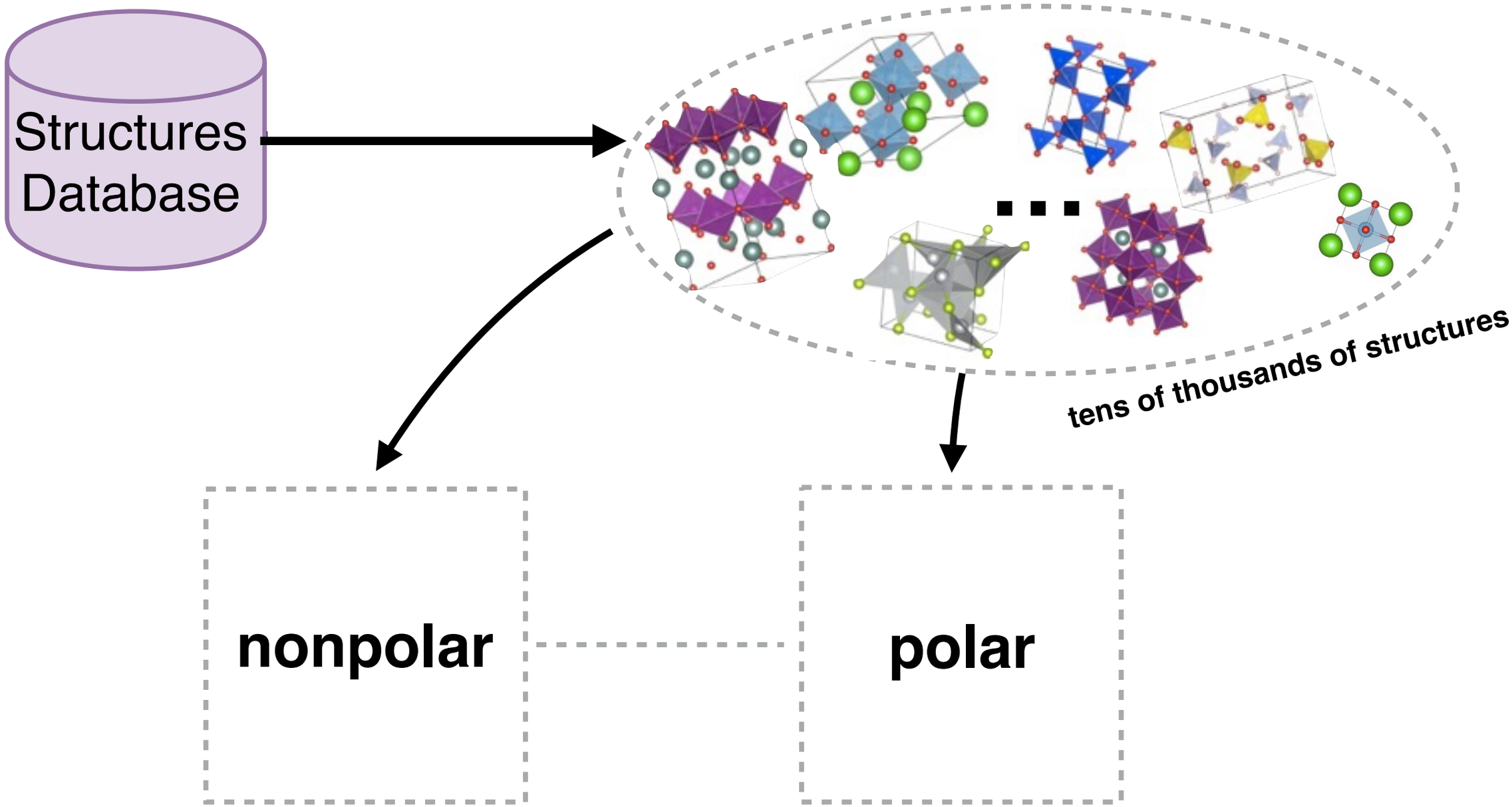
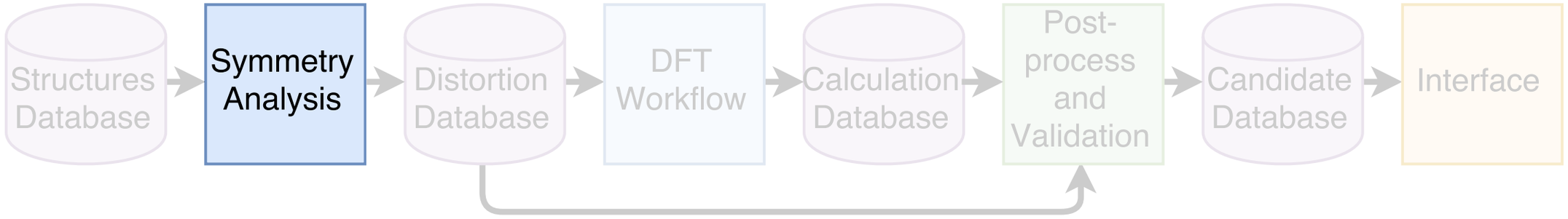
4. Validating the quality of each ferroelectric candidate.
5. **Creating an interface for viewing the results for all candidates.**


Structures Database
Symmetry Analysis
Distortion Database
DFT Workflow
Calculation Database
Post-process and Validation
Candidate Database
Interface



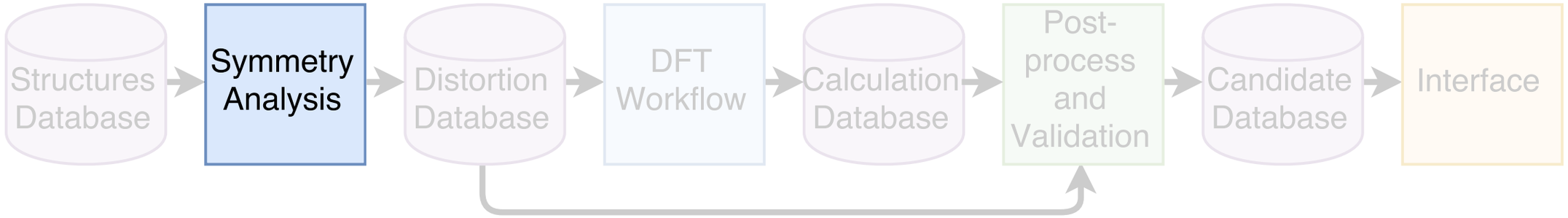
How do we find nonpolar-polar structure pairs that can be distorted into one another?





Step 0: Find nonpolar-polar group-subgroup pairs of same composition. ***(pymatgen)***

All symmetry operations in the polar space group are in the nonpolar space group.



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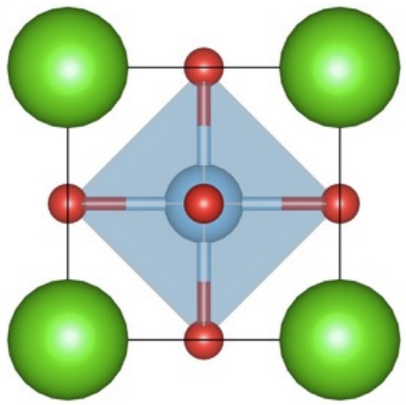
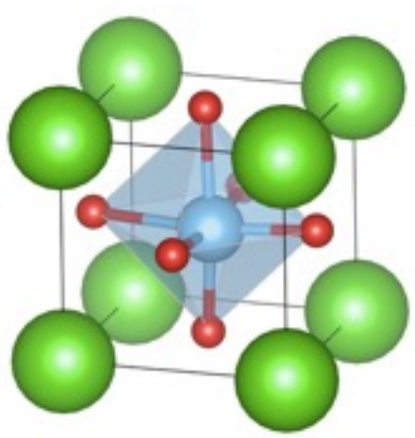
$BaTiO_3$

cubic
Pm-3m

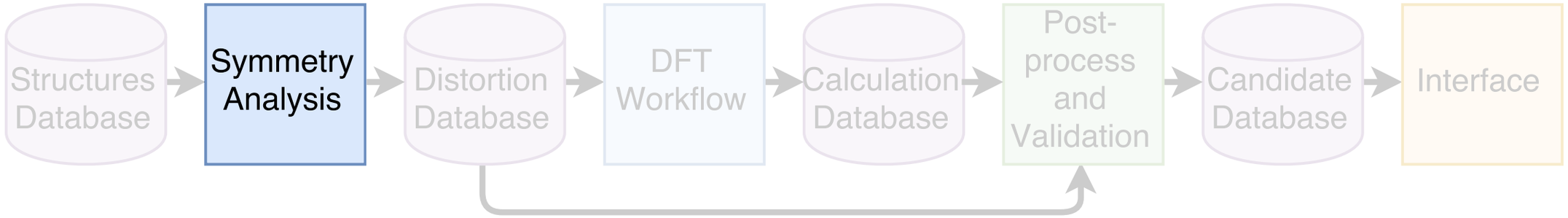


rhomb.
R3m



No change in translation symmetry.

Change in point group symmetry. Must check that 3m is subgroup of m-3m.



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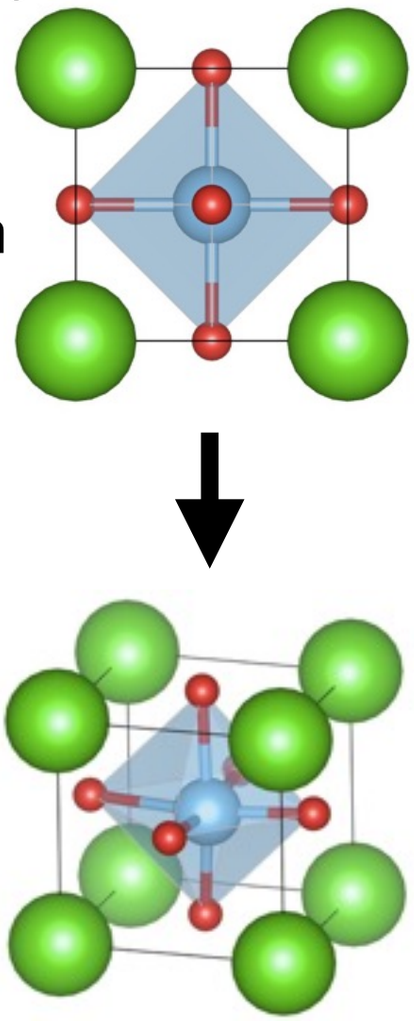
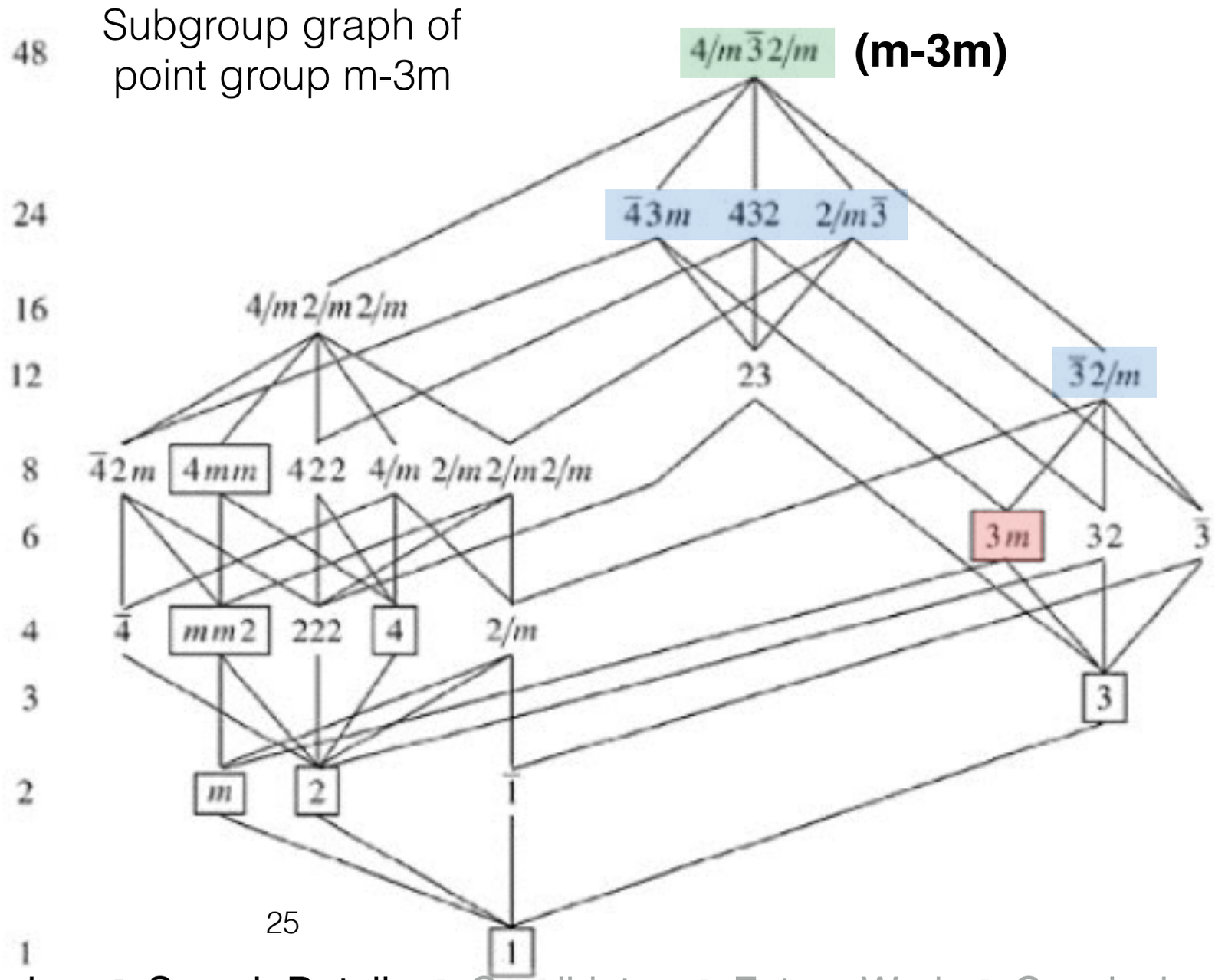
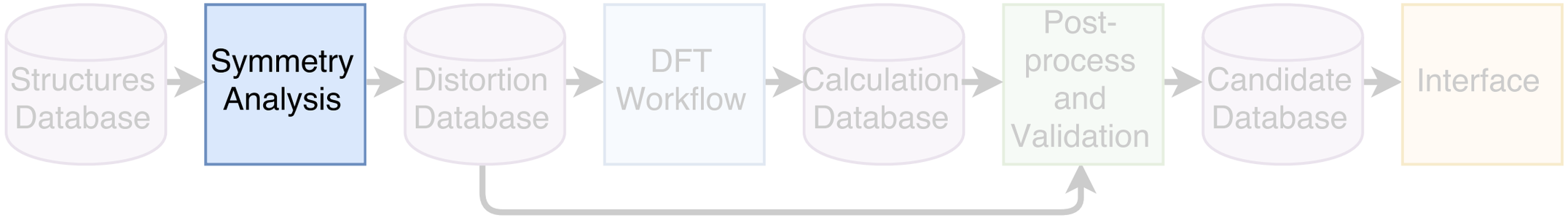


cubic
Pm-3m

rhomb.
R3m

Subgroup graph of point group m-3m





Once we have a pair, we check whether the pair of structures found in the database can be distorted into one another.

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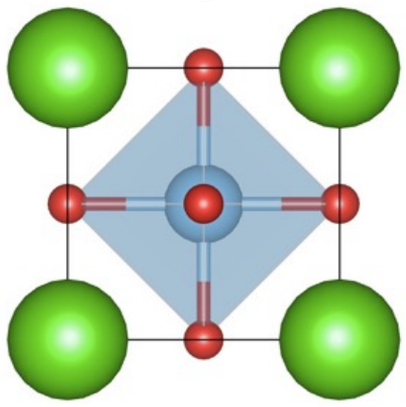
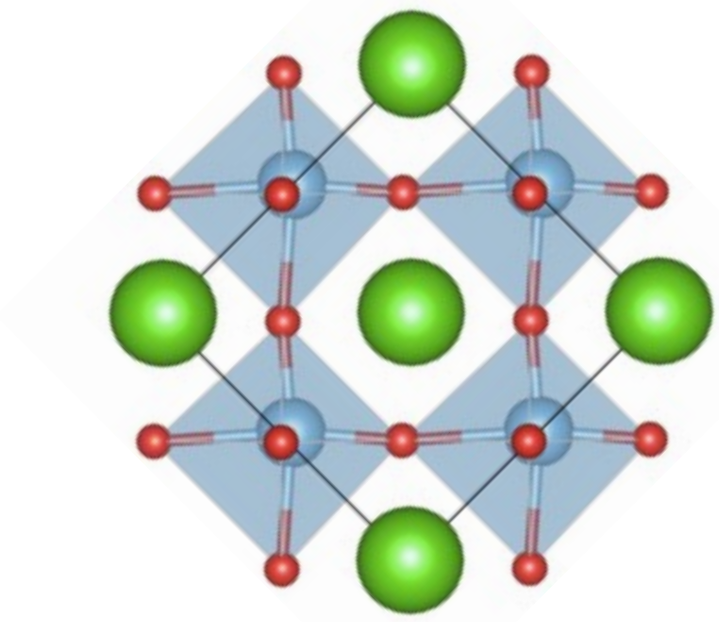
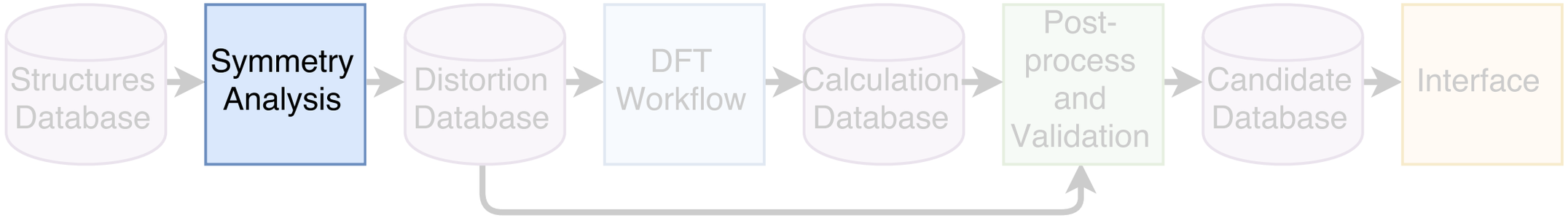


cubic



orthorhombic structure



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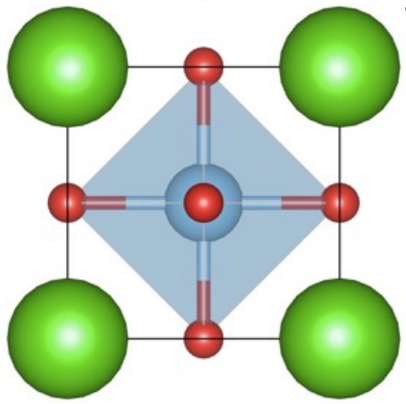
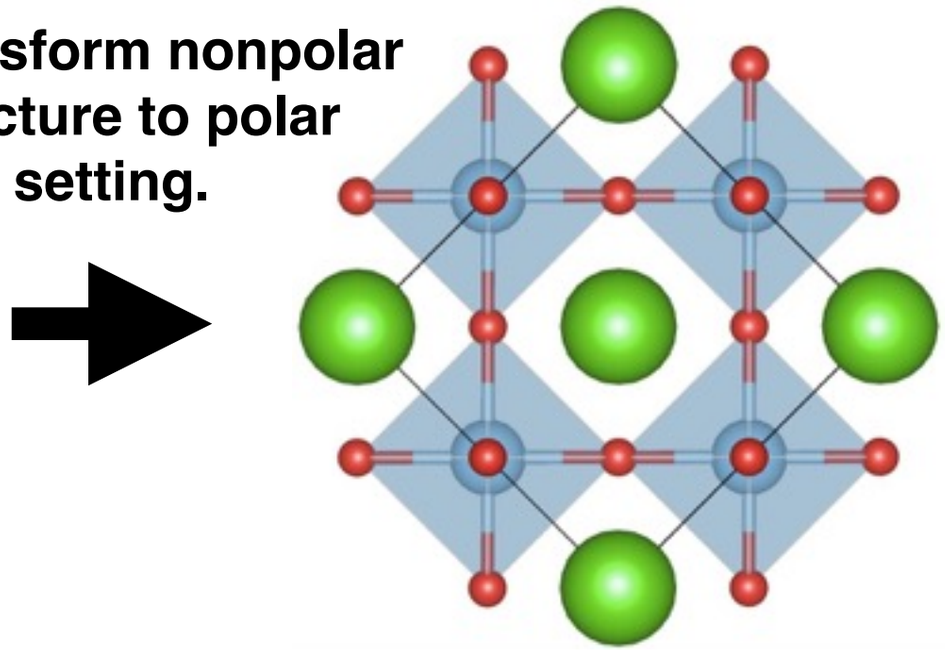
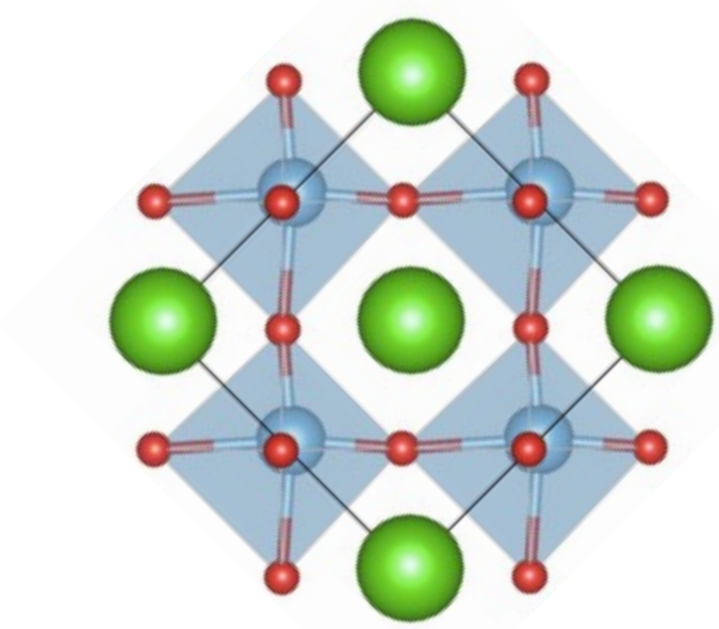


cubic

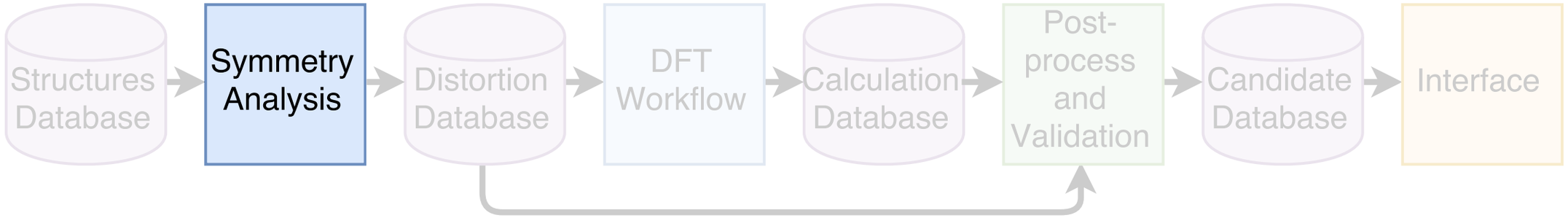
1. Transform nonpolar structure to polar setting.



cubic structure in orthorhombic setting



orthorhombic structure



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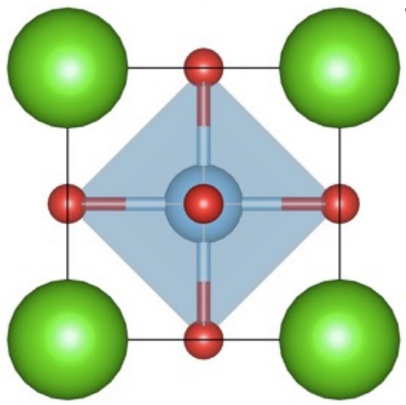

cubic

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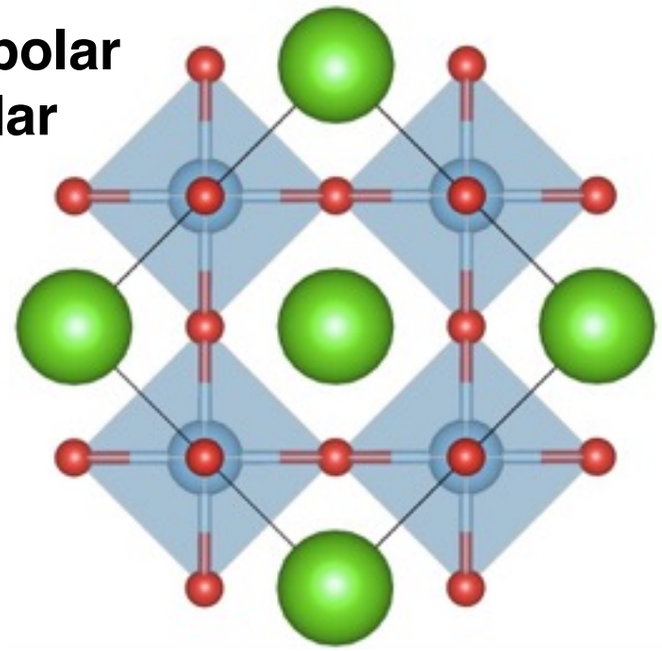
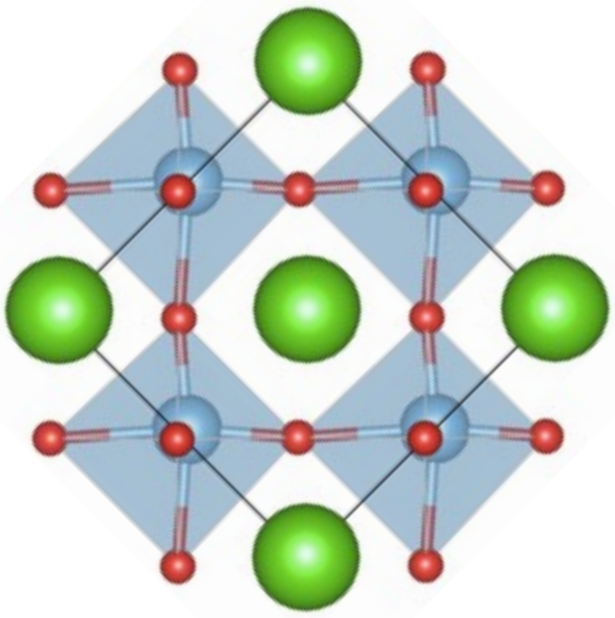


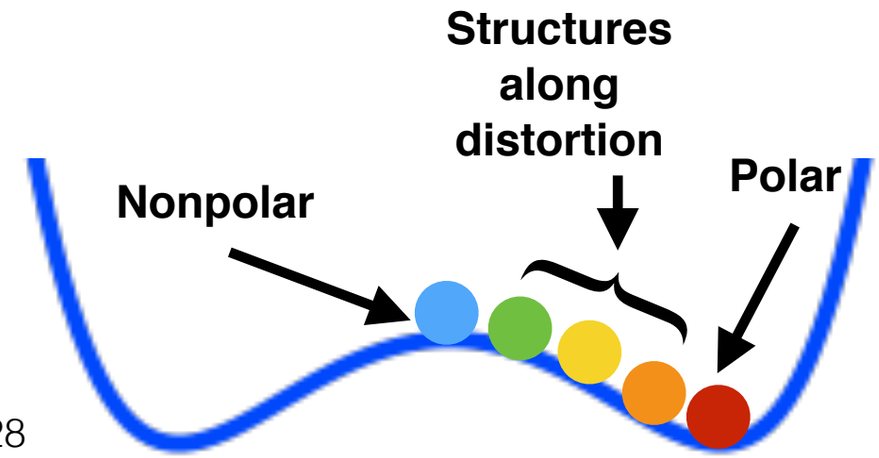
cubic structure in orthorhombic setting

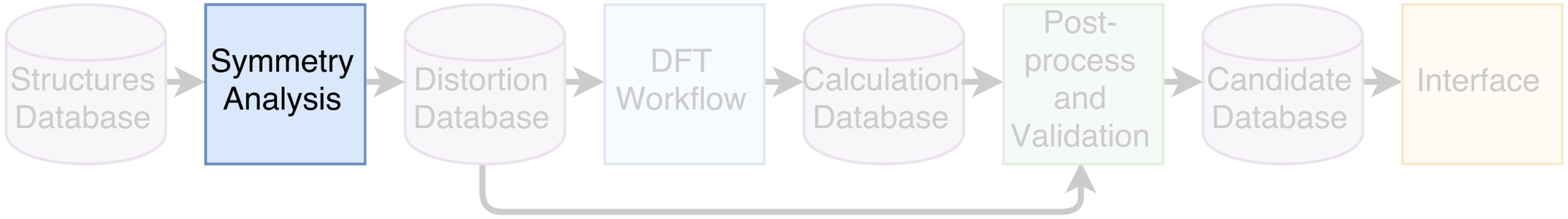
2. Check that distortion is physical.



orthorhombic structure

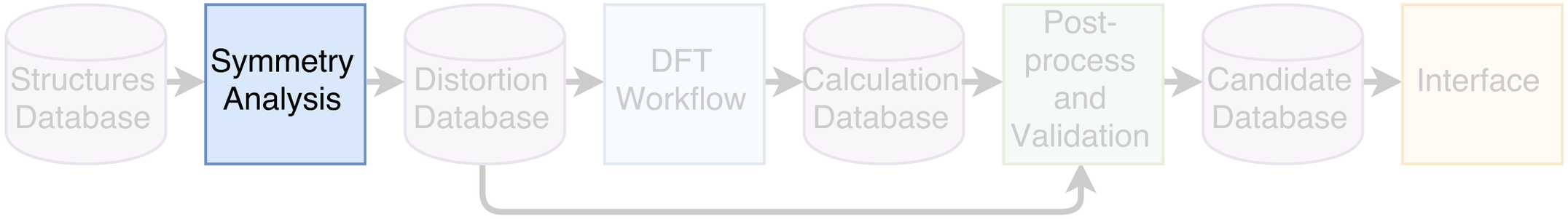
Create structures along distortion using linear interpolations of nonpolar and polar structure.





Step 1: Transform nonpolar structure to polar setting.

(python scripts that interact with the Bilbao Crystallographic Server)



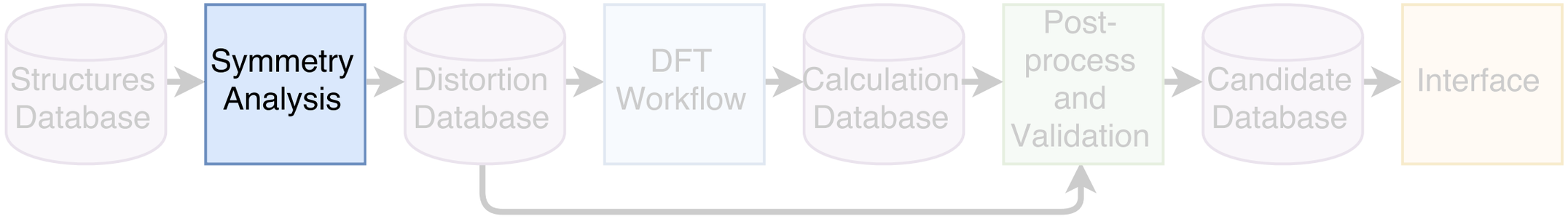
Step 1: Transform nonpolar structure to polar setting.

(python scripts that interact with the Bilbao Crystallographic Server)

1a. Compute index of group-subgroup relation.

$$i = i_k \cdot i_t = \begin{pmatrix} \text{ratio of number of} \\ \text{formula units in primitive} \\ \text{cell polar to nonpolar} \end{pmatrix} \mathbf{x} \begin{pmatrix} \text{ratio of point} \\ \text{group operations} \\ \text{nonpolar to polar} \end{pmatrix}$$

i, i_k, i_t are always positive integers.



Step 1: Transform nonpolar structure to polar setting.

(python scripts that interact with the Bilbao Crystallographic Server)

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i, i_k, i_t are always positive integers.

$BaTiO_3$

subgroups of cubic Pm-3m

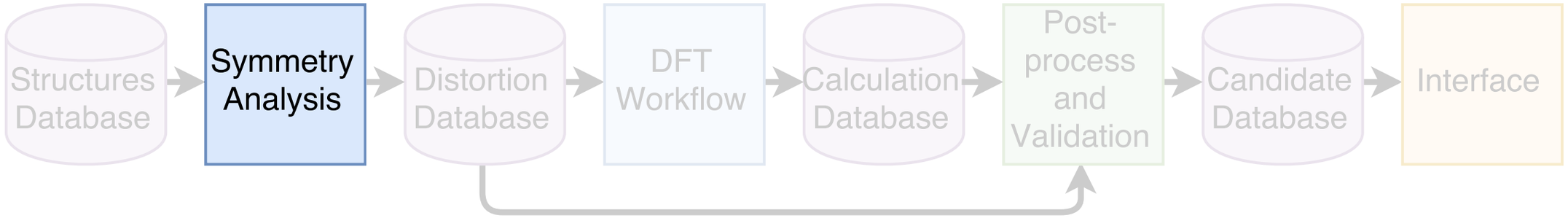
rhombohedral

tetragonal

orthorhombic

N	HM Symbol	ITA	index	t-index	k-index	More info
1	*R3m*	160	8	8	1	show...
2	*R3*	146	16	16	1	show...
3	*P4mm*	099	6	6	1	show...
4	*P4*	075	12	12	1	show...
5	*Amm2*	038	12	12	1	show...
6	*Cmm2*	035	12	12	1	show...
7	*Pmm2*	025	12	12	1	show...
8	*Cm*	008	24	24	1	show...
9	*Pm*	006	24	24	1	show...
10	*C2*	005	24	24	1	show...
11	*P2*	003	24	24	1	show...
12	*P1*	001	48	48	1	show...

No change in number of formula units for subgroups with $i_k = 1$.

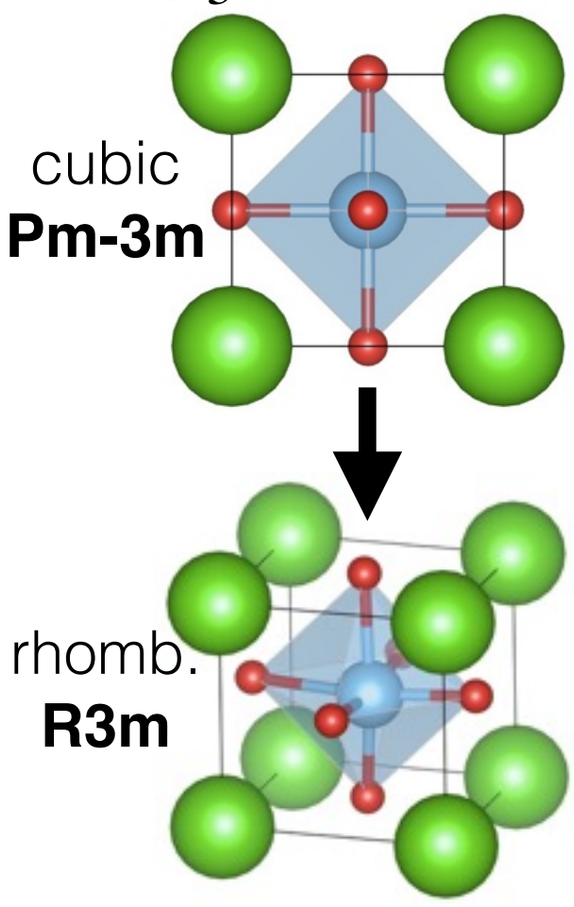


Step 1: Transform nonpolar structure to polar setting.

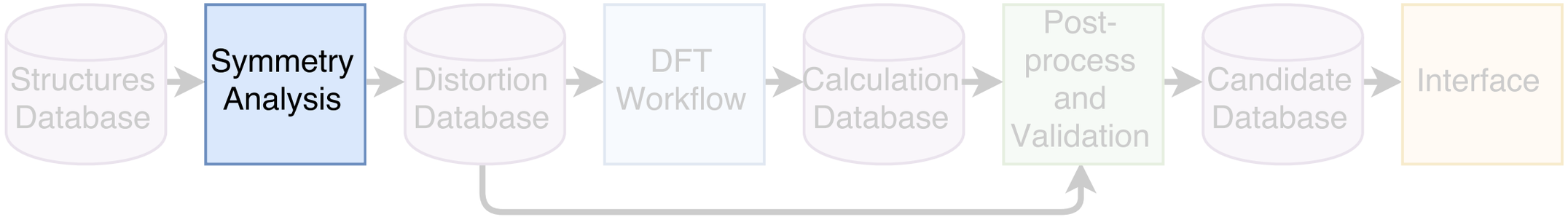
(python scripts that interact with the Bilbao Crystallographic Server)

1b. Get transformation for chains of compatible maximal subgroups.

$BaTiO_3$



Check		Chain [indices]	Chain with HM symbols	Transformation	Identical
◉	1	221 215 160 [2 4]	*Pm*-3*m* > *P*-43*m* > *R*3*m*	$\begin{pmatrix} -1 & 0 & -1 & 0 \\ 1 & -1 & -1 & 0 \\ 0 & -1 & 1 & 0 \end{pmatrix}$	to group 1
○	2	221 166 160 [4 2]	*Pm*-3*m* > *R*-3*m* > *R*3*m*	$\begin{pmatrix} 1 & 0 & 1 & 0 \\ -1 & 1 & 1 & 0 \\ 0 & -1 & 1 & 0 \end{pmatrix}$	to group 2
○	3	221 166 160 [4 2]	*Pm*-3*m* > *R*-3*m* > *R*3*m*	$\begin{pmatrix} -1 & 0 & -1 & 0 \\ -1 & 1 & 1 & 0 \\ 0 & 1 & -1 & 0 \end{pmatrix}$	to group 3
○	4	221 166 160 [4 2]	*Pm*-3*m* > *R*-3*m* > *R*3*m*	$\begin{pmatrix} 1 & 0 & 1 & 0 \\ 1 & -1 & -1 & 0 \\ 0 & 1 & -1 & 0 \end{pmatrix}$	to group 4



Step 2: Determine if transformation is physical.
(python scripts that interact with the Bilbao Crystallographic Server)

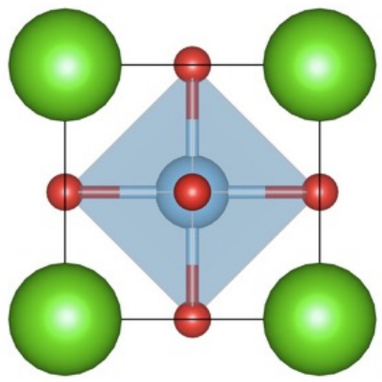
1c. Get atomic positions in transformed unit cell.

Use Wyckoff splitting.

Wyckoff positions

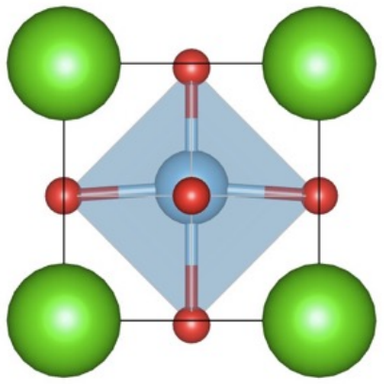
Pm-3m	P4mm
48n	8g 8g 8g 8g 8g 8g
24m	4d 4d 8g 8g
24l	4f 4f 4f 4f 8g
24k	4e 4e 4e 4e 8g
12j	4f 4f 4d
12i	4e 4e 4d
12h	4f 4e 2c 2c
8g	4d 4d
6f	4f 1b 1b
6e	4e 1a 1a
3d	2c 1a
3c	2c 1b
1b	1b
1a	1a

cubic

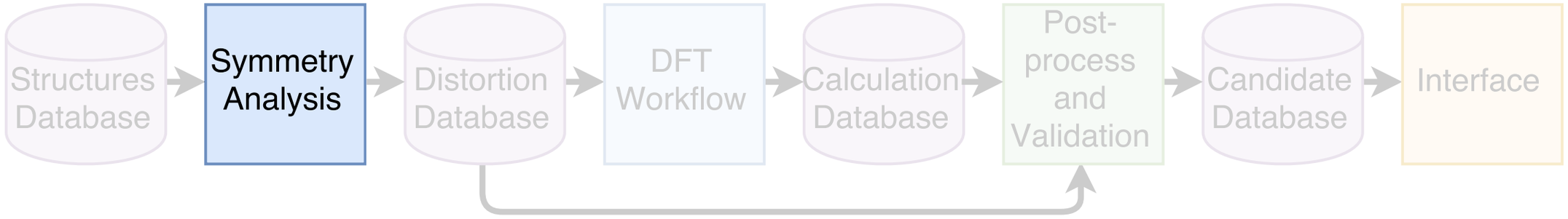


3 symmetrically unique positions

tetragonal



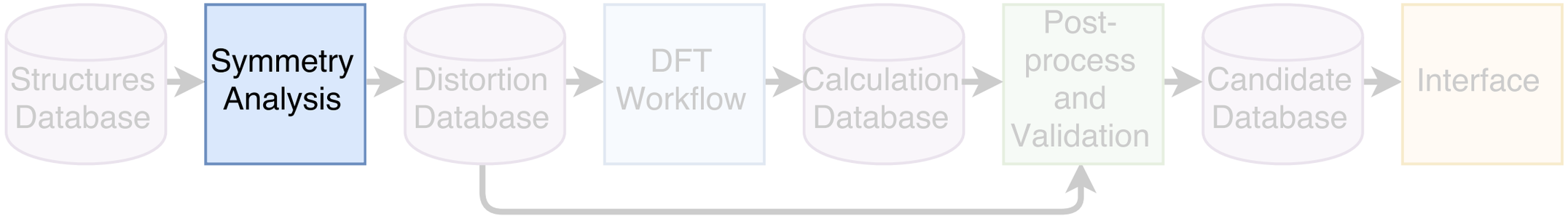
4 symmetrically unique positions



Step 2: Determine if transformation is physical.

(python scripts that interact with the Bilbao Crystallographic Server)

2a. Check that the transformed nonpolar lattice is similar to the polar lattice.



Step 2: Determine if transformation is physical.

(python scripts that interact with the Bilbao Crystallographic Server)

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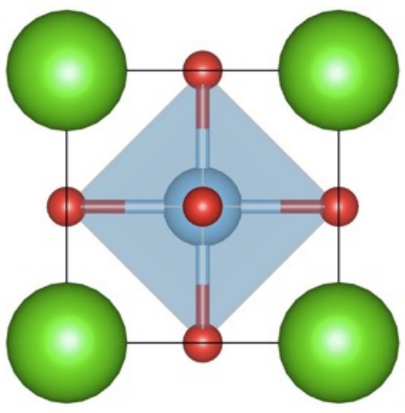
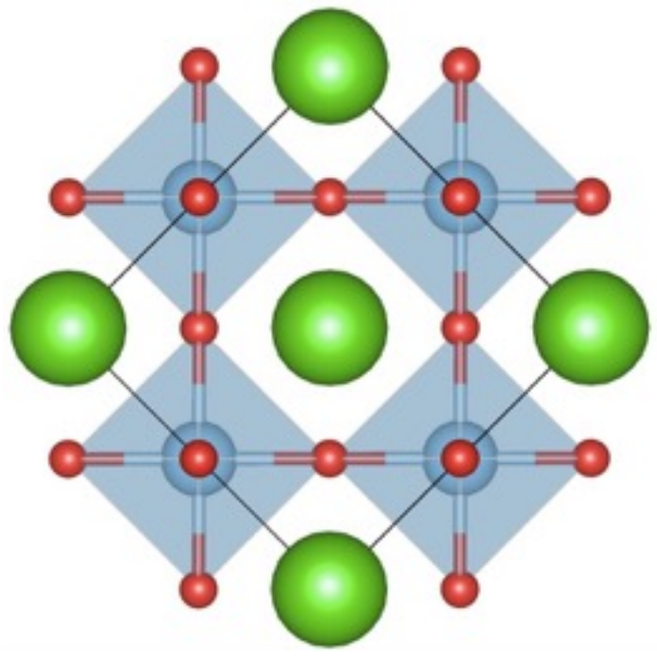
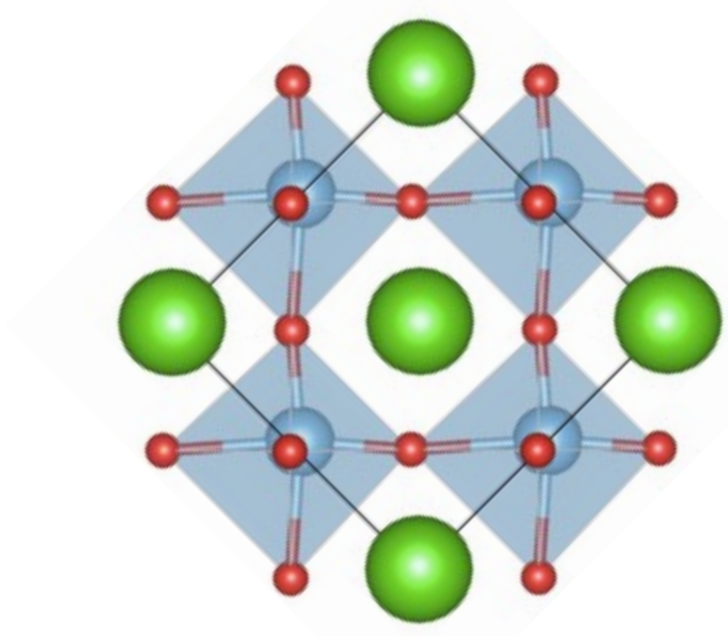
$BaTiO_3$





cubic structure in orthorhombic setting



orthorhombic structure in orthorhombic setting

Lattice length tolerance:
< 3 Å
Lattice angle tolerance:
< 10 °

nonpolar

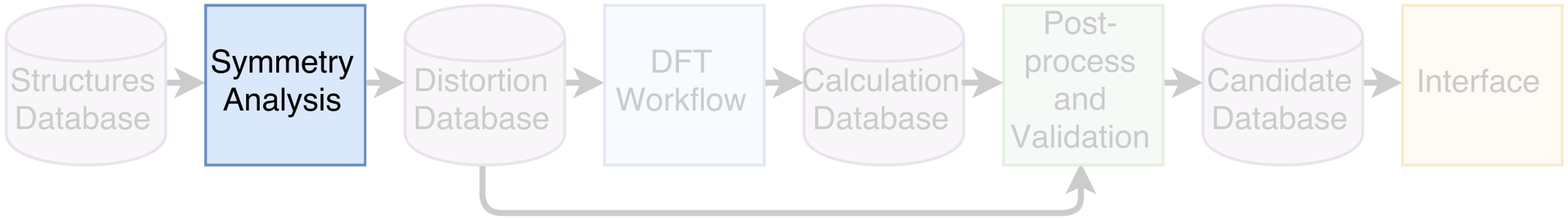
$a = 4.04, b = 5.71, c = 5.71$

$\alpha = \beta = \gamma = 90°$

polar

$a = 3.99, b = 5.81, c = 5.89$

$\alpha = \beta = \gamma = 90°$

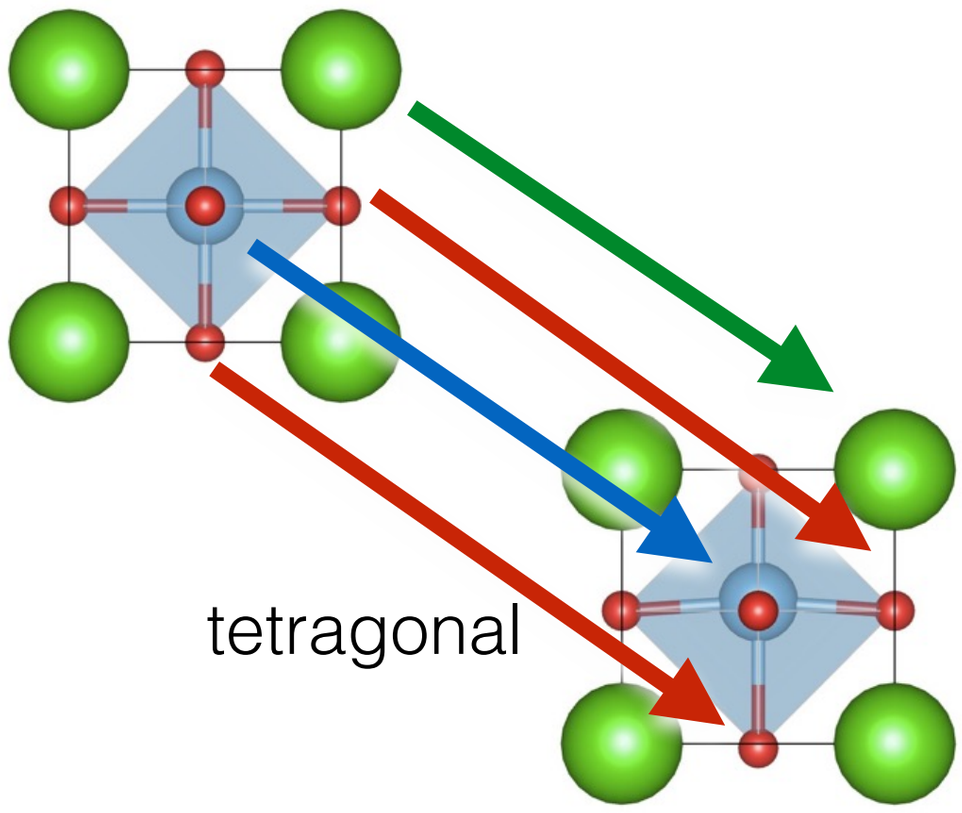


Step 2: Determine if transformation is physical.

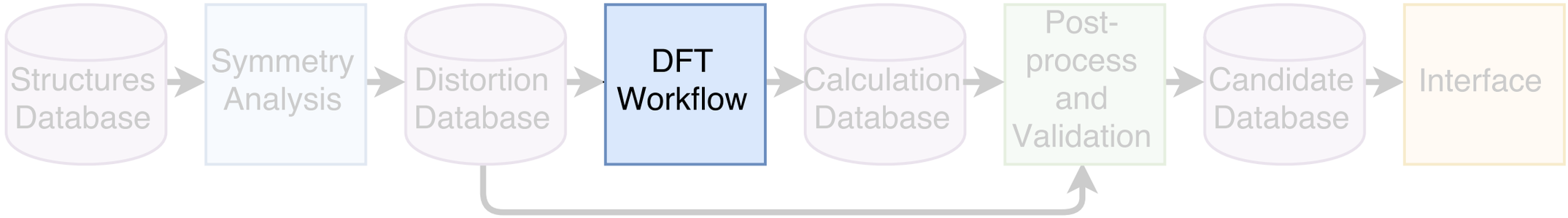
(python scripts that interact with the Bilbao Crystallographic Server)

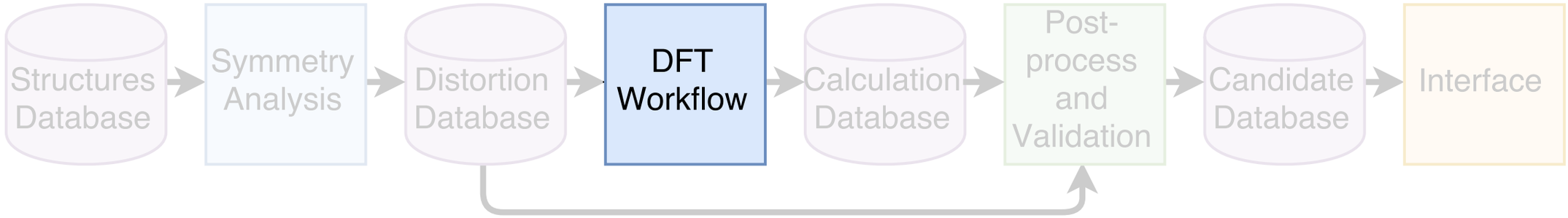
2c. Check that no atom moves more than 1.5 Å throughout the distortion.

$BaTiO_3$



Max displacement ~ 0.15 Å


Structures Database
Symmetry Analysis
Distortion Database
DFT Workflow
Calculation Database
Post-process and Validation
Candidate Database
Interface



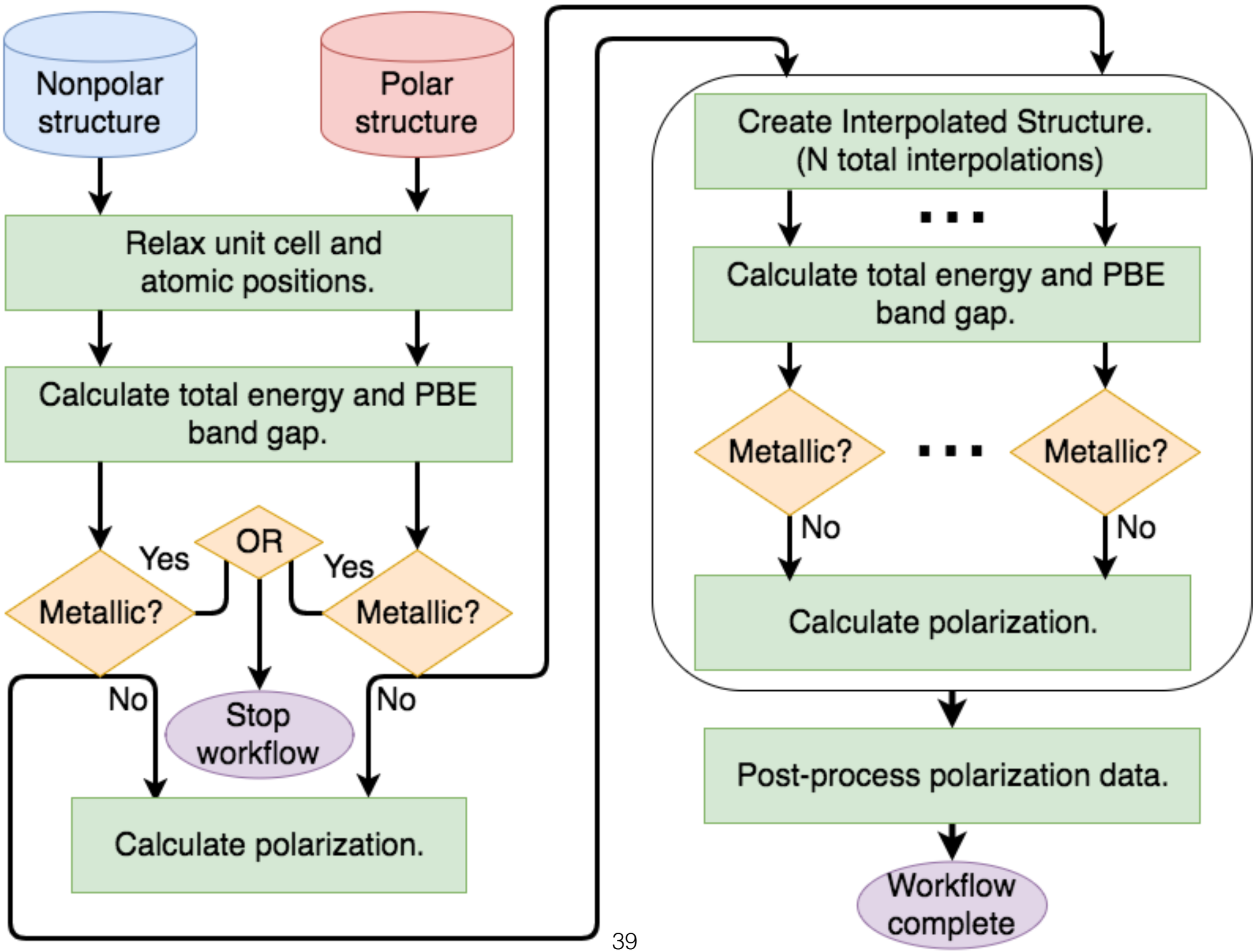
Using the Vienna Ab Initio Software Package (VASP) for density functional theory calculations.
(1000 / number of atoms) k-points.
PAW pseudopotentials
520 eV energy cutoff for plane wave basis.

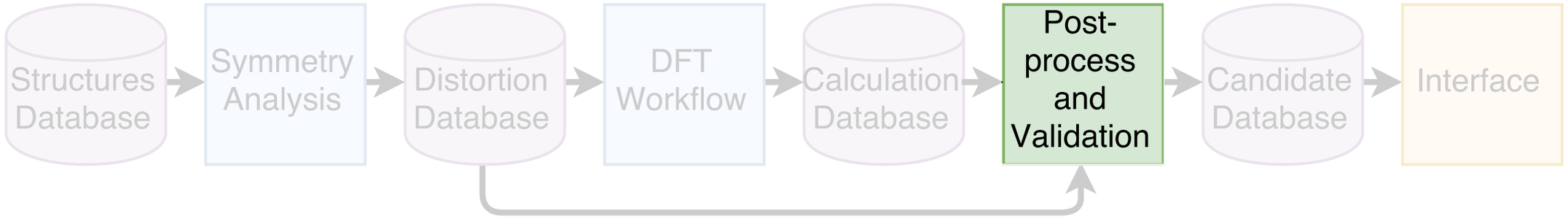
Using input parameter sets from pymatgen
MPRelaxSet and **MPStaticSet**

Using DFT PBE (GGA) functional to compare to Materials Project calculations.

We expect PBE to overestimate polarization due to larger calculated unit cell volumes.

DFT workflow used in proof-of-principle search. Many variations possible!

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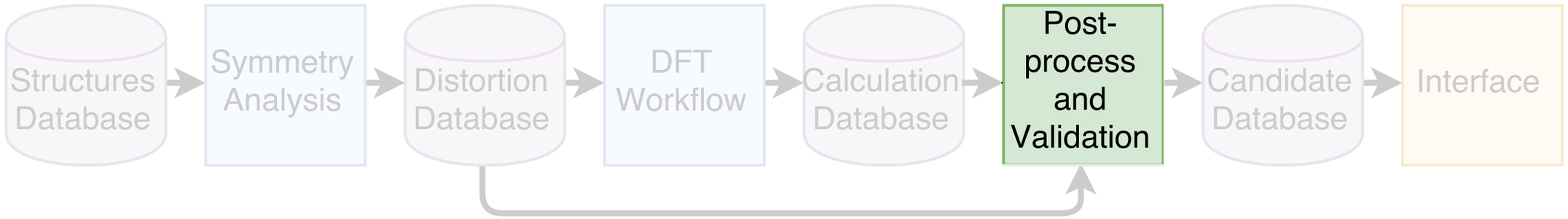
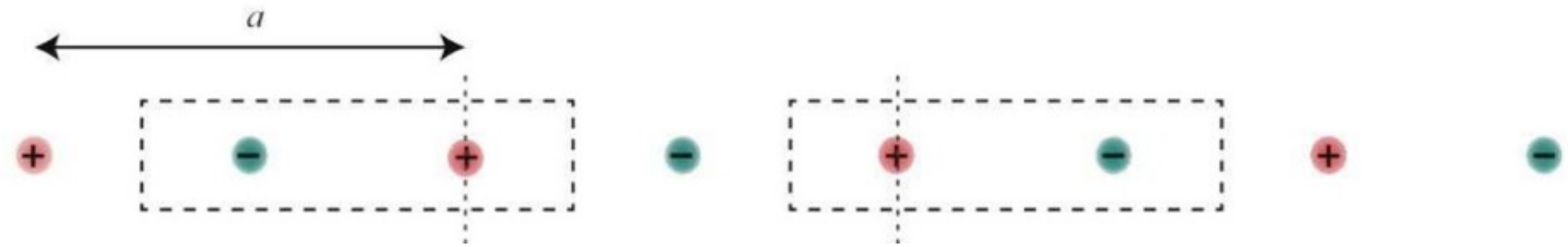
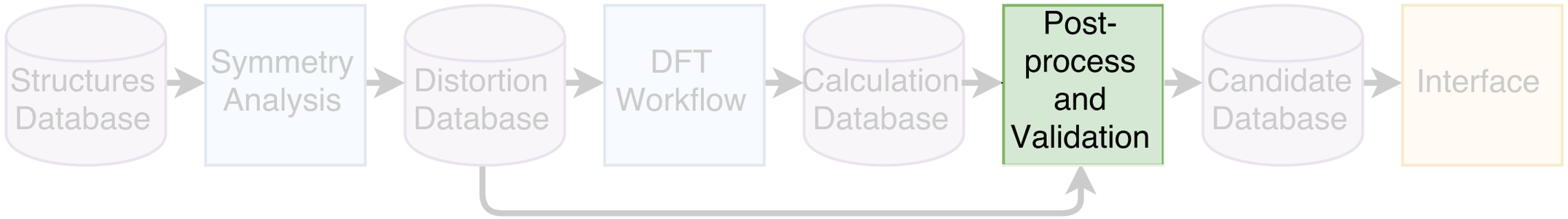


Let's define polarization to be the dipole moment per unit volume.

$$P = \sum_i \frac{q_i r_i}{\Omega}$$

For a 1D chain of alternating charges:





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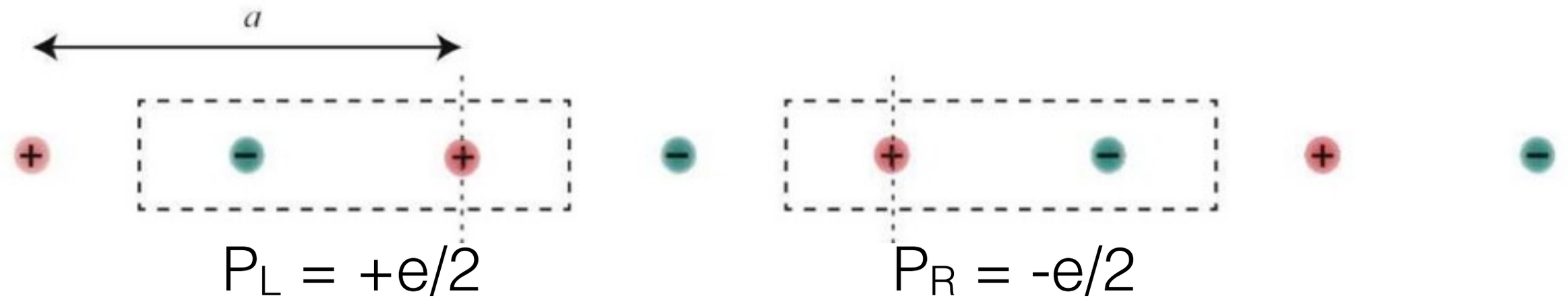

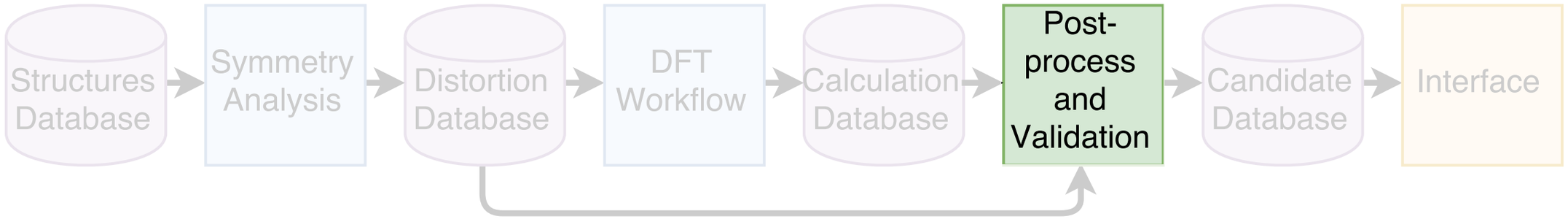

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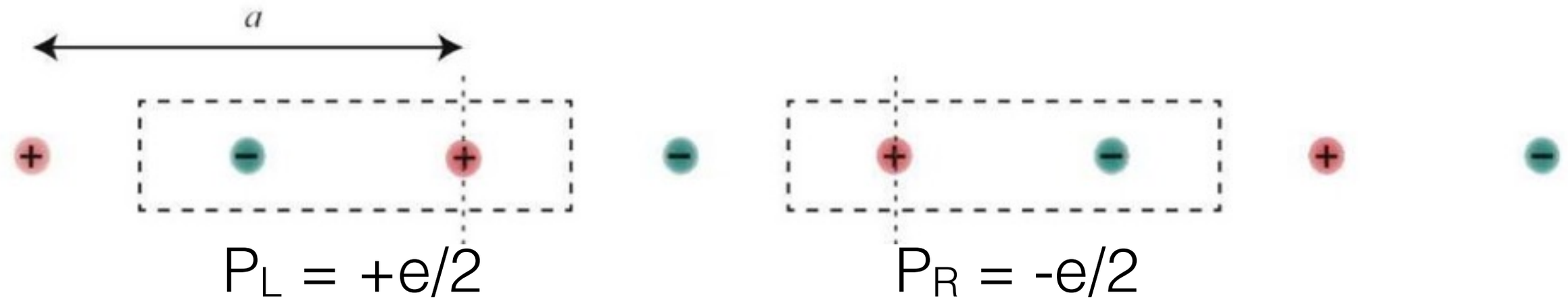
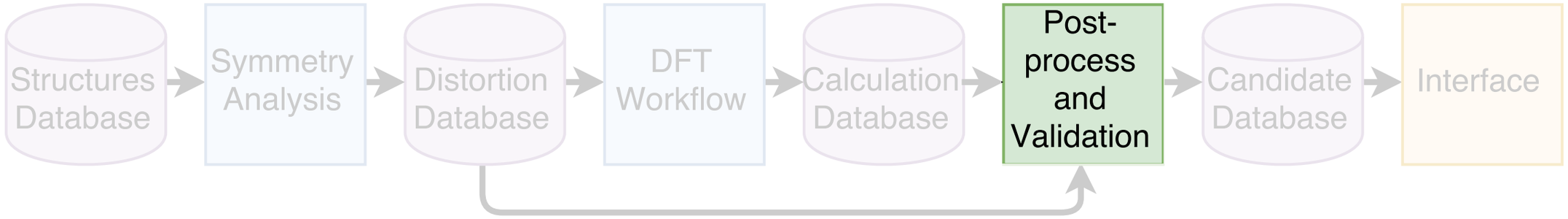


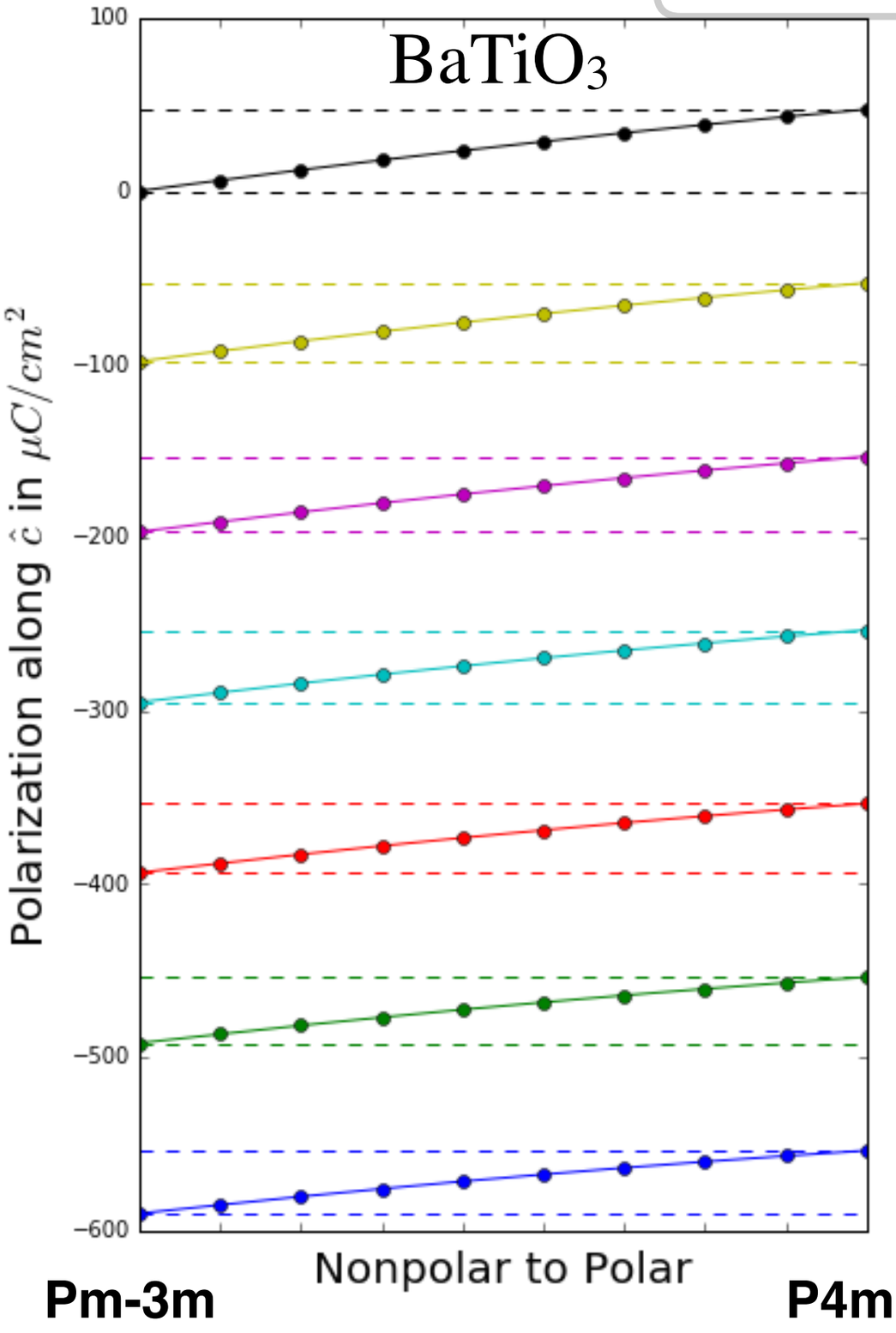
Polarization is not uniquely defined.



Polarization is defined on a lattice

$$\vec{P} = \vec{P}_0 + \sum_{i \in 1,2,3} \frac{e\vec{R}_i}{\Omega}$$

e: electron charge
R: lattice vector
Ω: unit cell volume



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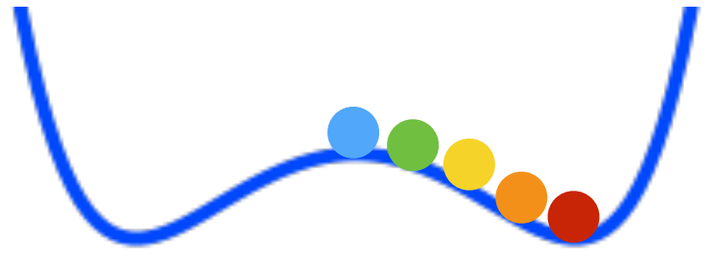
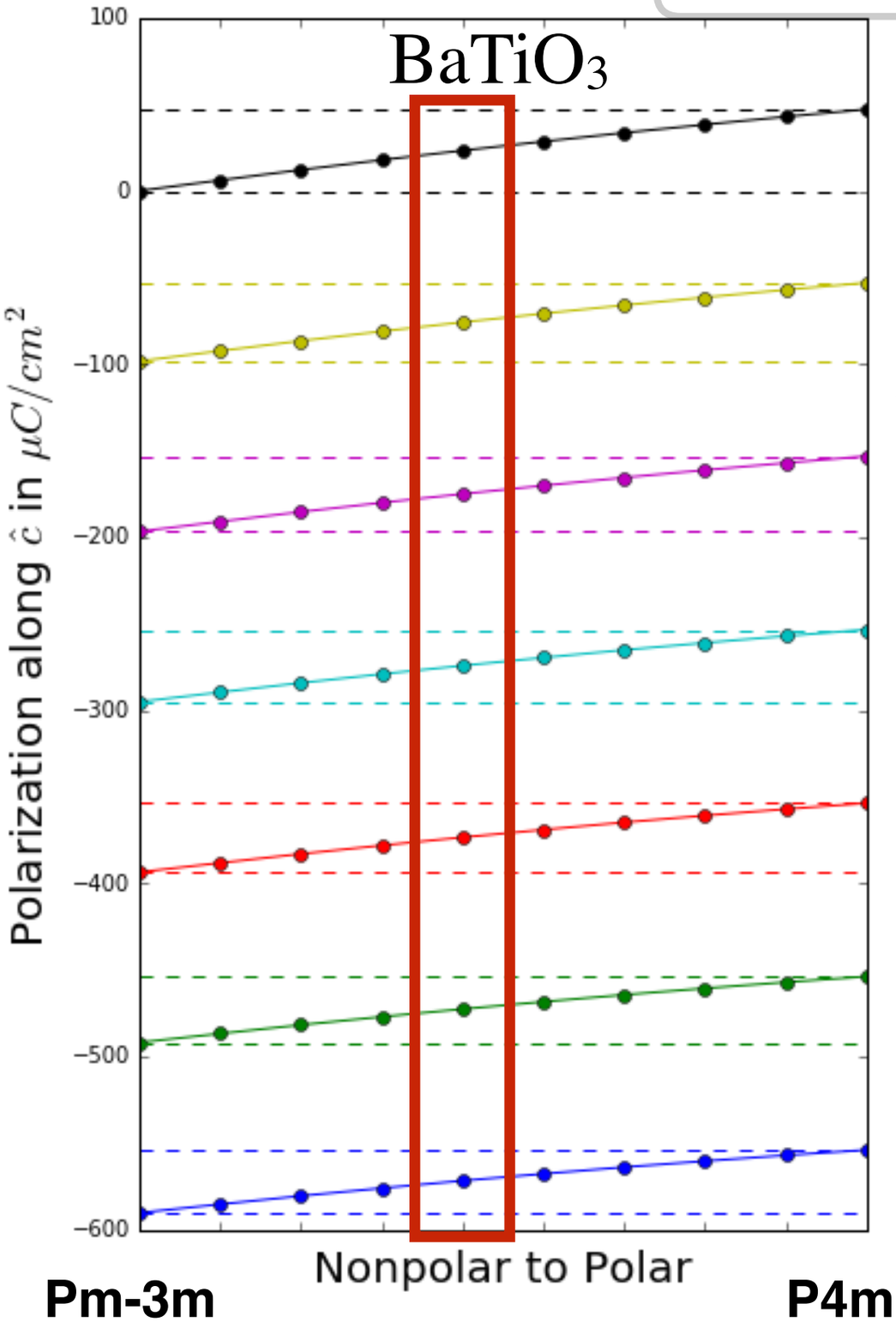
We calculate polarization for structures along the distortion path.





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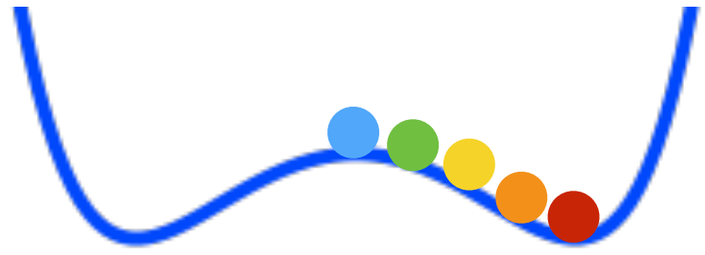
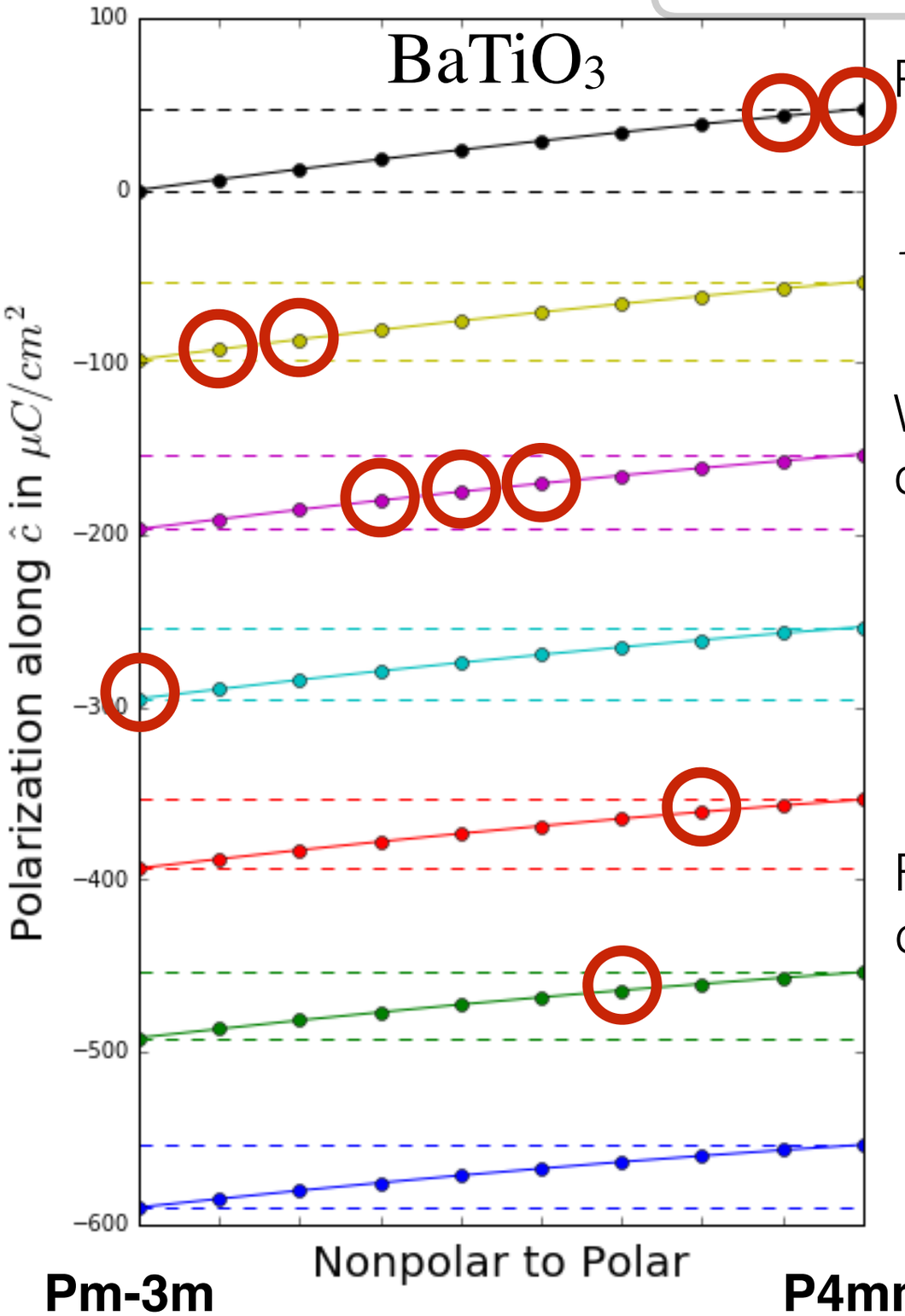


For a given structure, the calculated polarization can be any lattice image.



Polarization is defined on a lattice

$$\vec{P} = \vec{P}_0 + \sum_{i \in 1,2,3} \frac{e\vec{R}_i}{\Omega}$$

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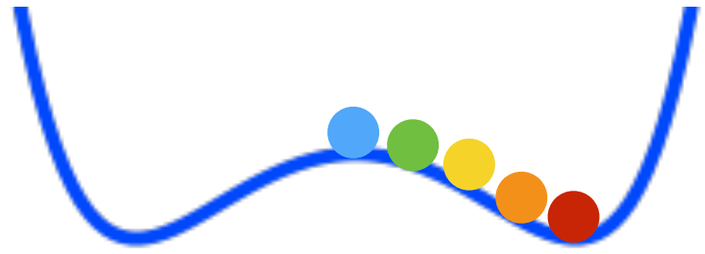
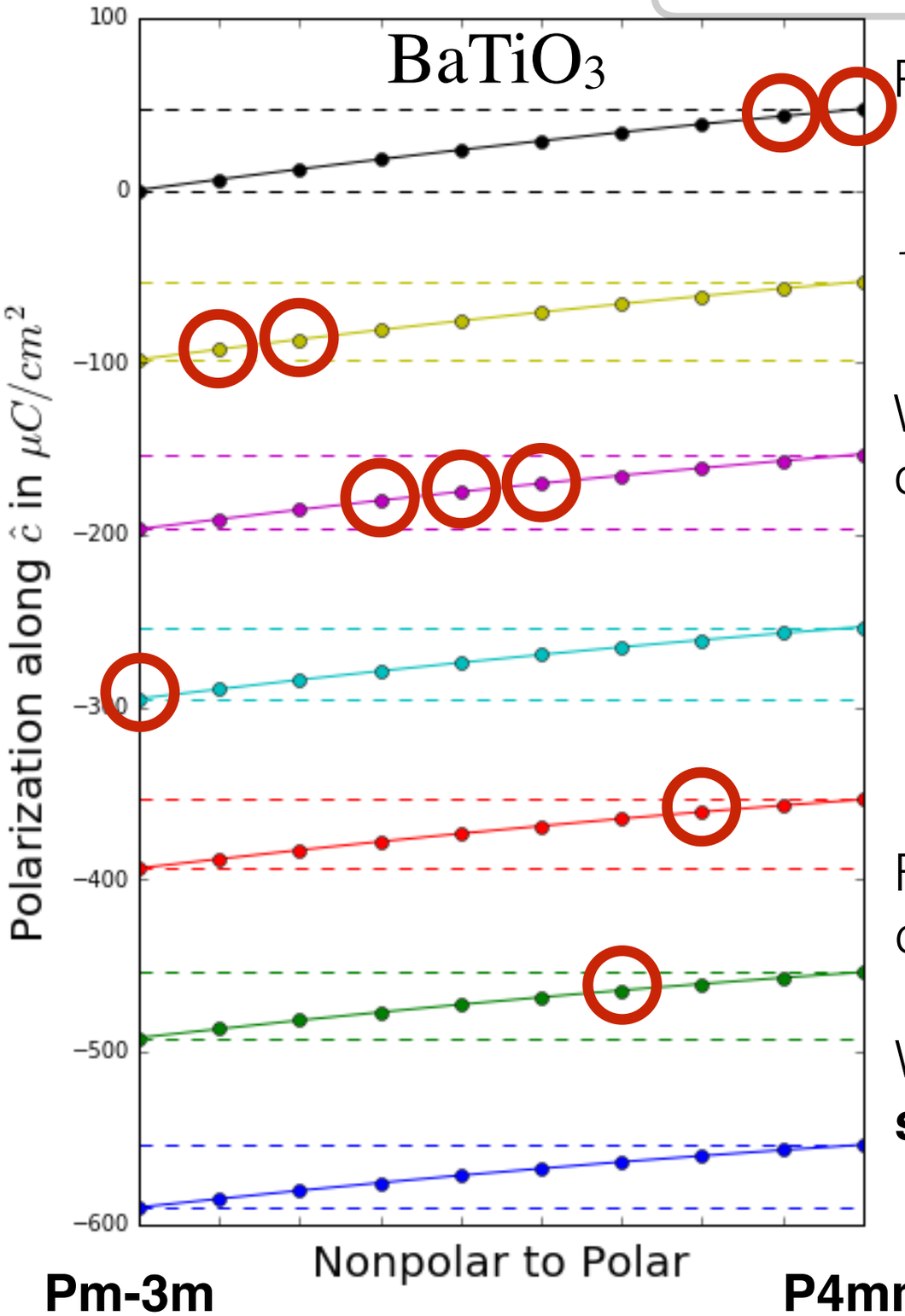
Ω: unit cell volume

We calculate polarization for structures along the distortion path.



For a given structure, the calculated polarization can be any lattice image.



Polarization is defined on a lattice

$$\vec{P} = \vec{P}_0 + \sum_{i \in 1,2,3} \frac{e\vec{R}_i}{\Omega}$$

e: electron charge
R: lattice vector
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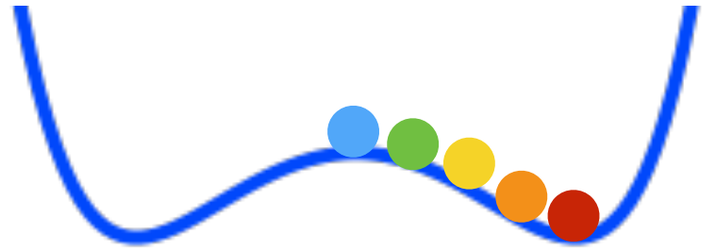
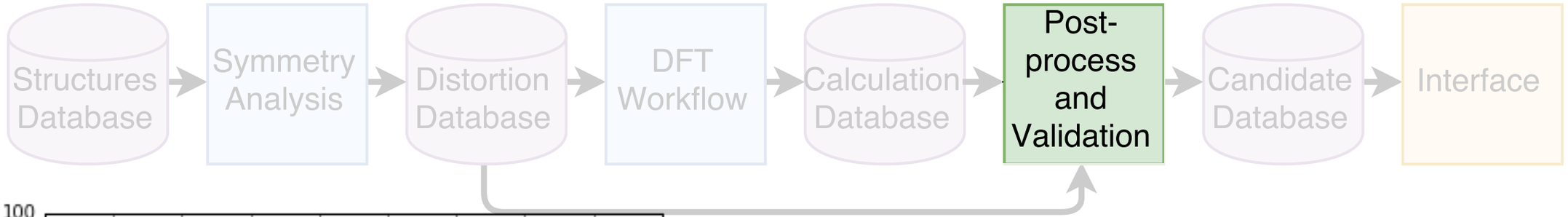
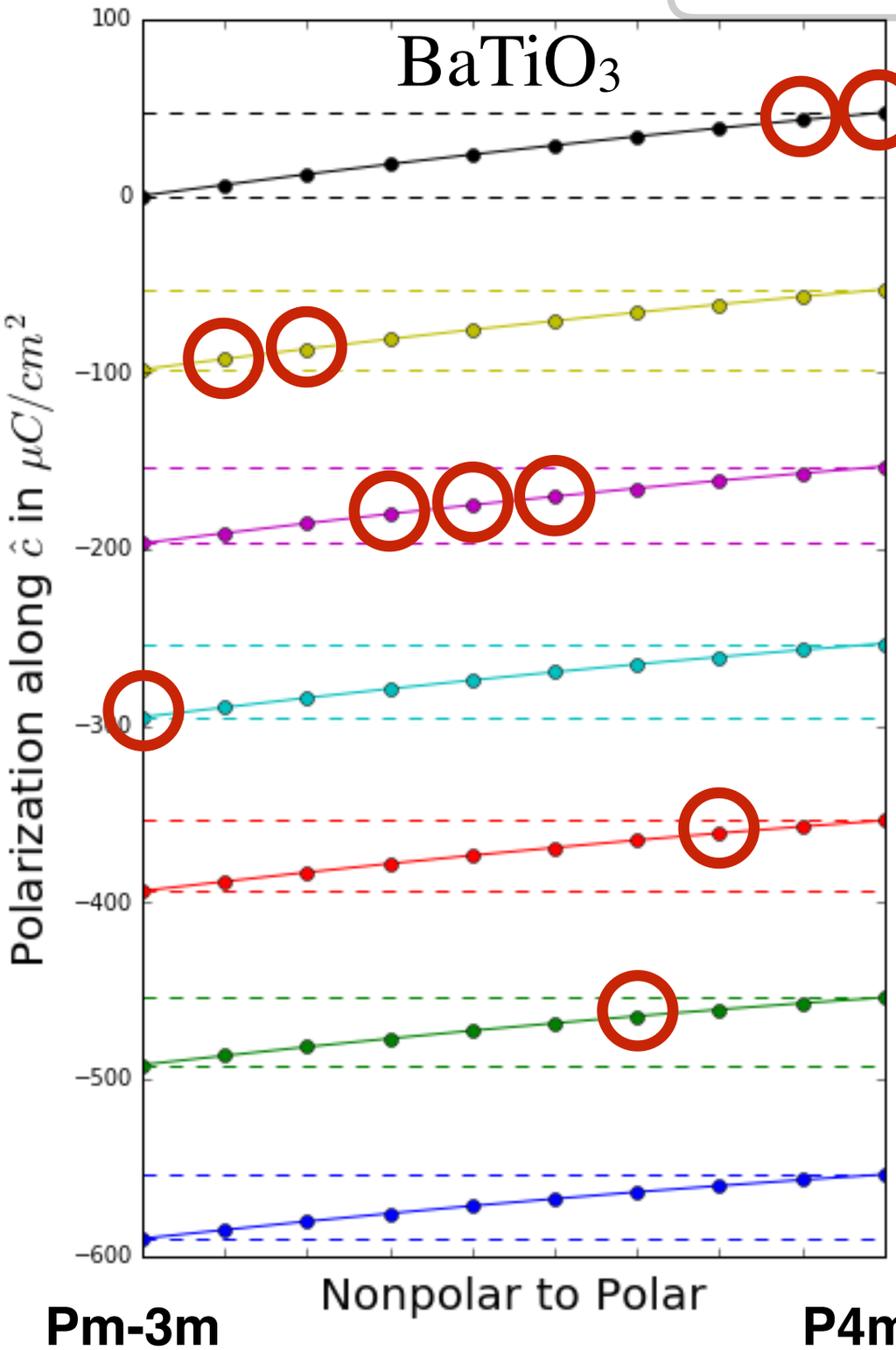
We calculate polarization for structures along the distortion path.



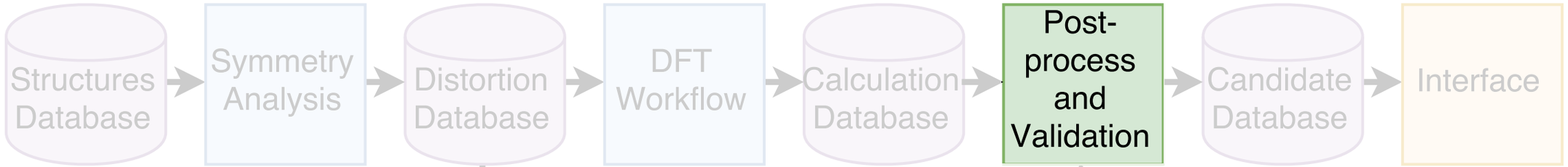
For a given structure, the calculated polarization can be any lattice image.

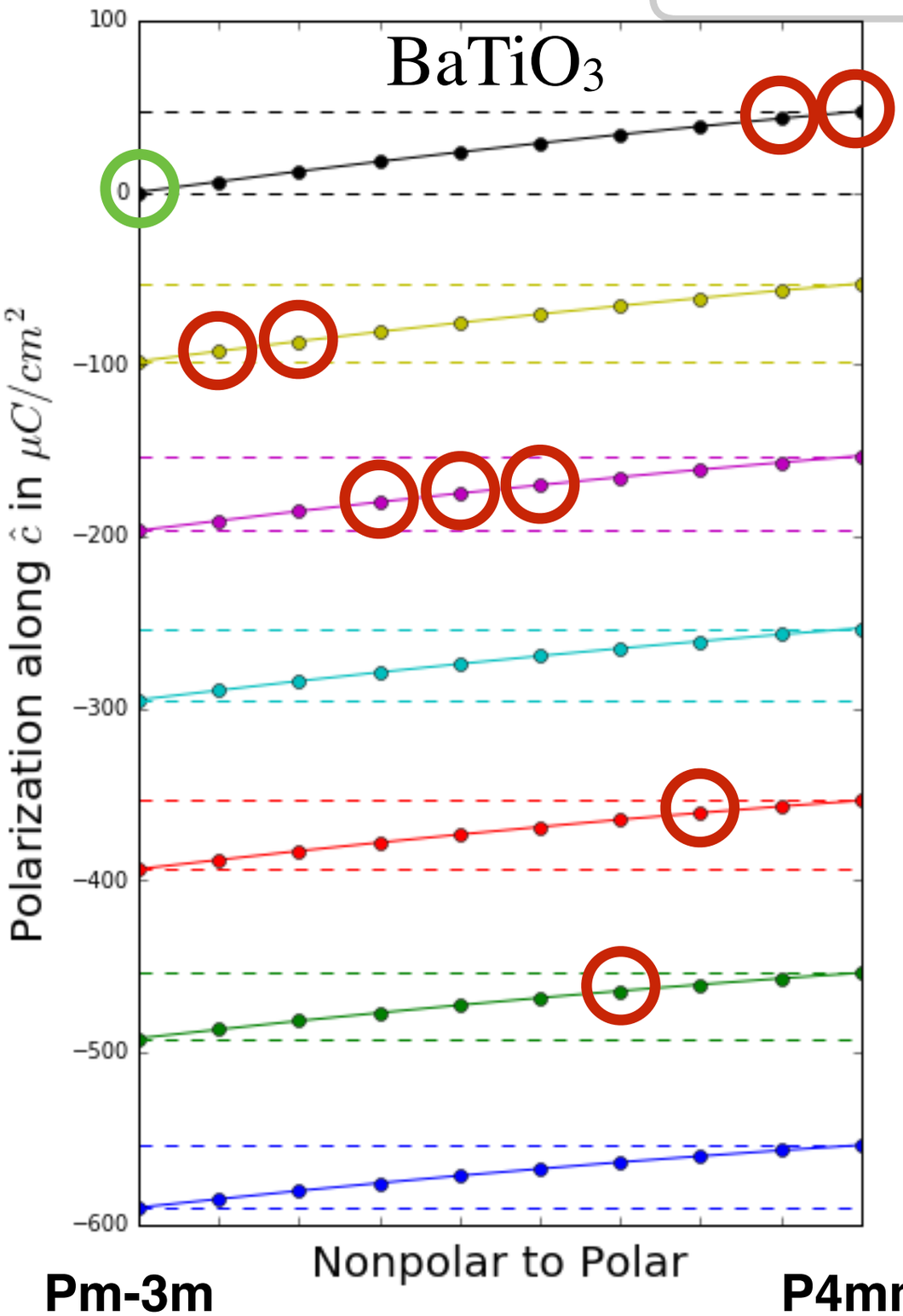
We have to adjust the polarizations to be on the **same branch.** We write an algorithm to do this.





First, we adjust the nonpolar polarization to be closest to zero.





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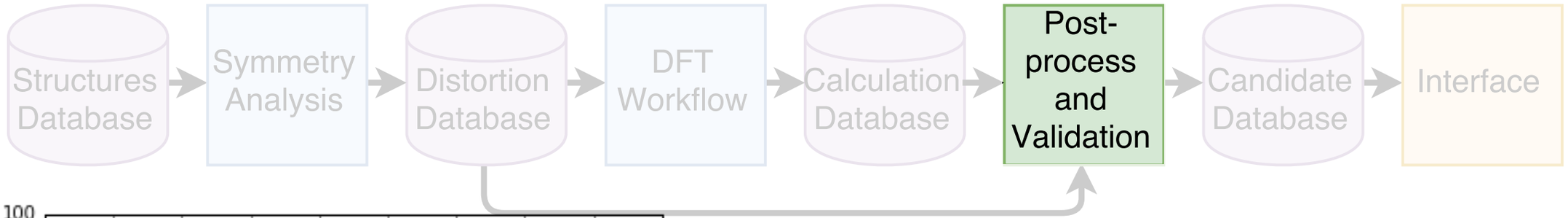
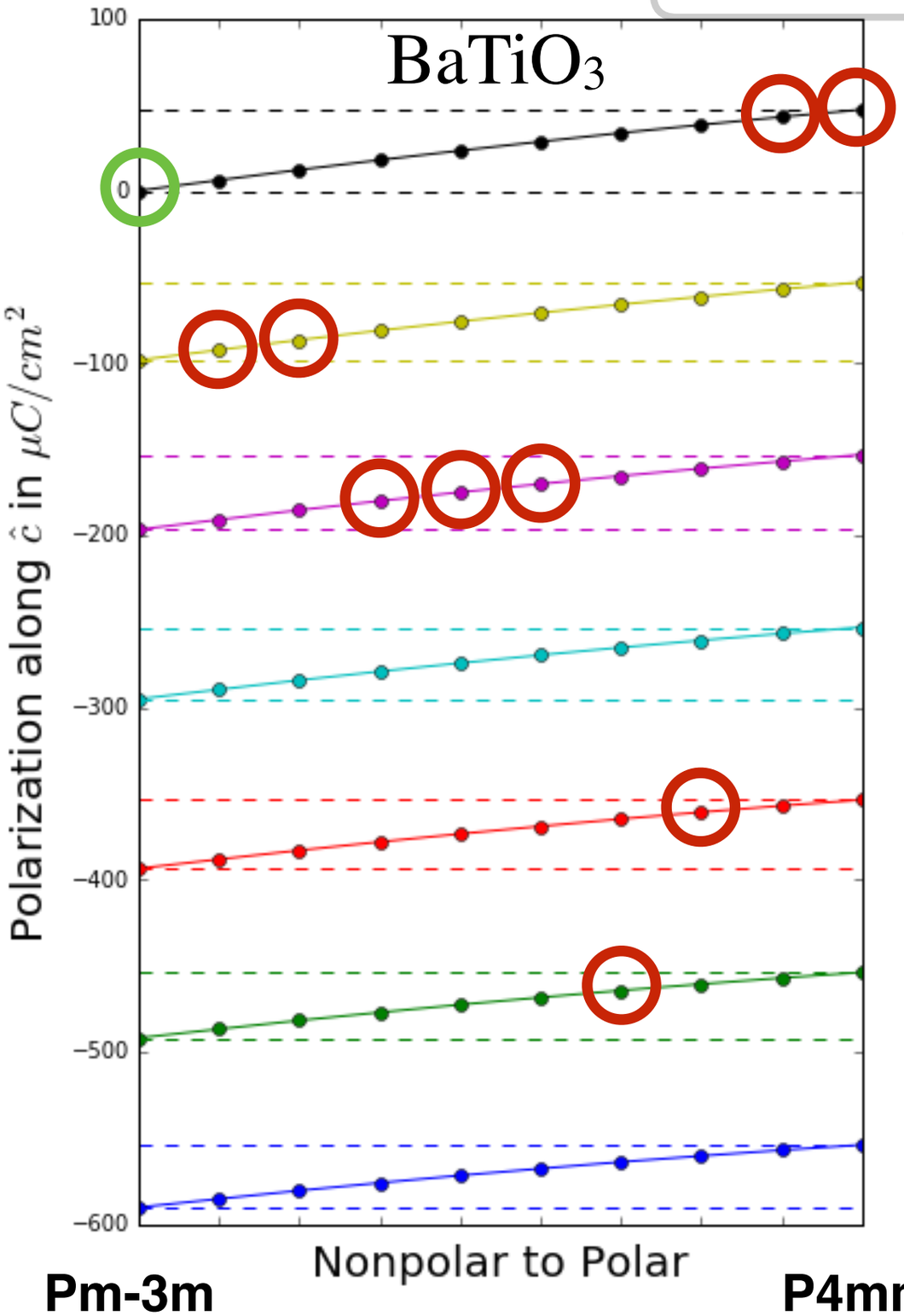
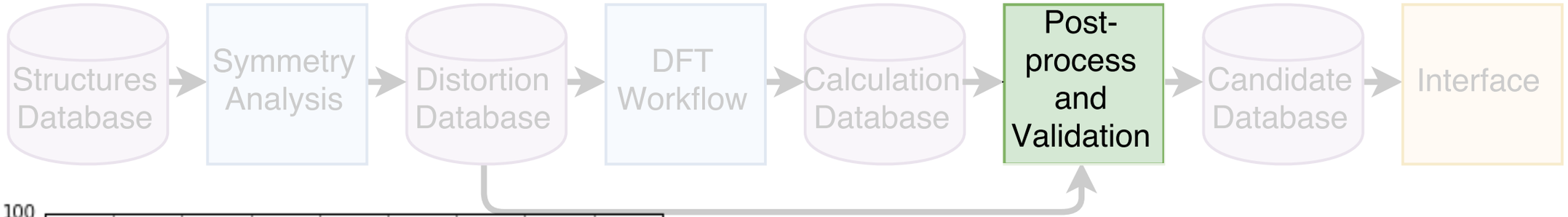
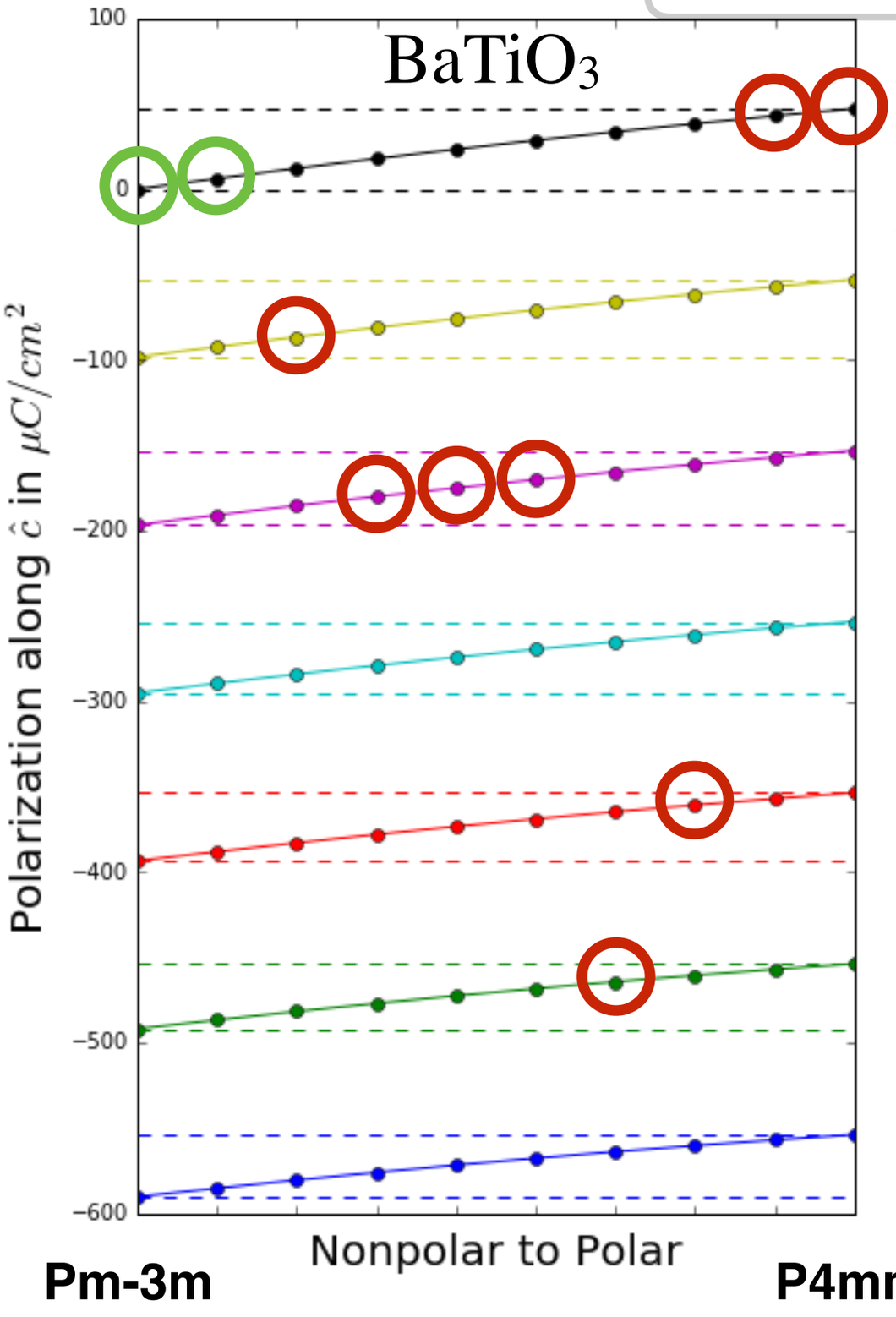




First, we adjust the nonpolar polarization to be closest to zero.

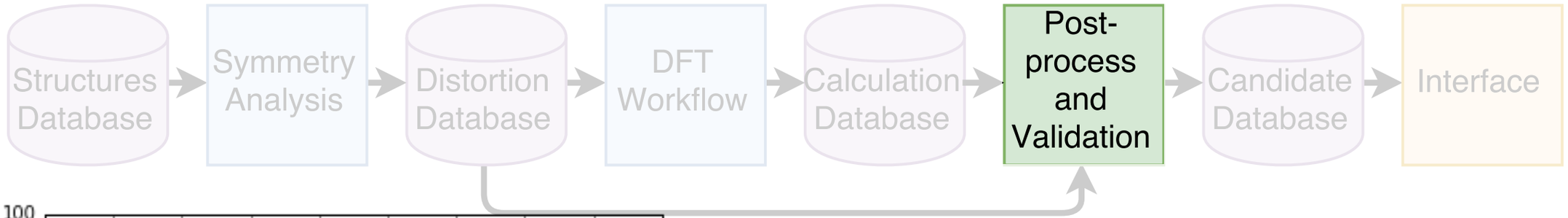
Then, we take the next structure's polarization and move it closest to the previous structure's polarization.

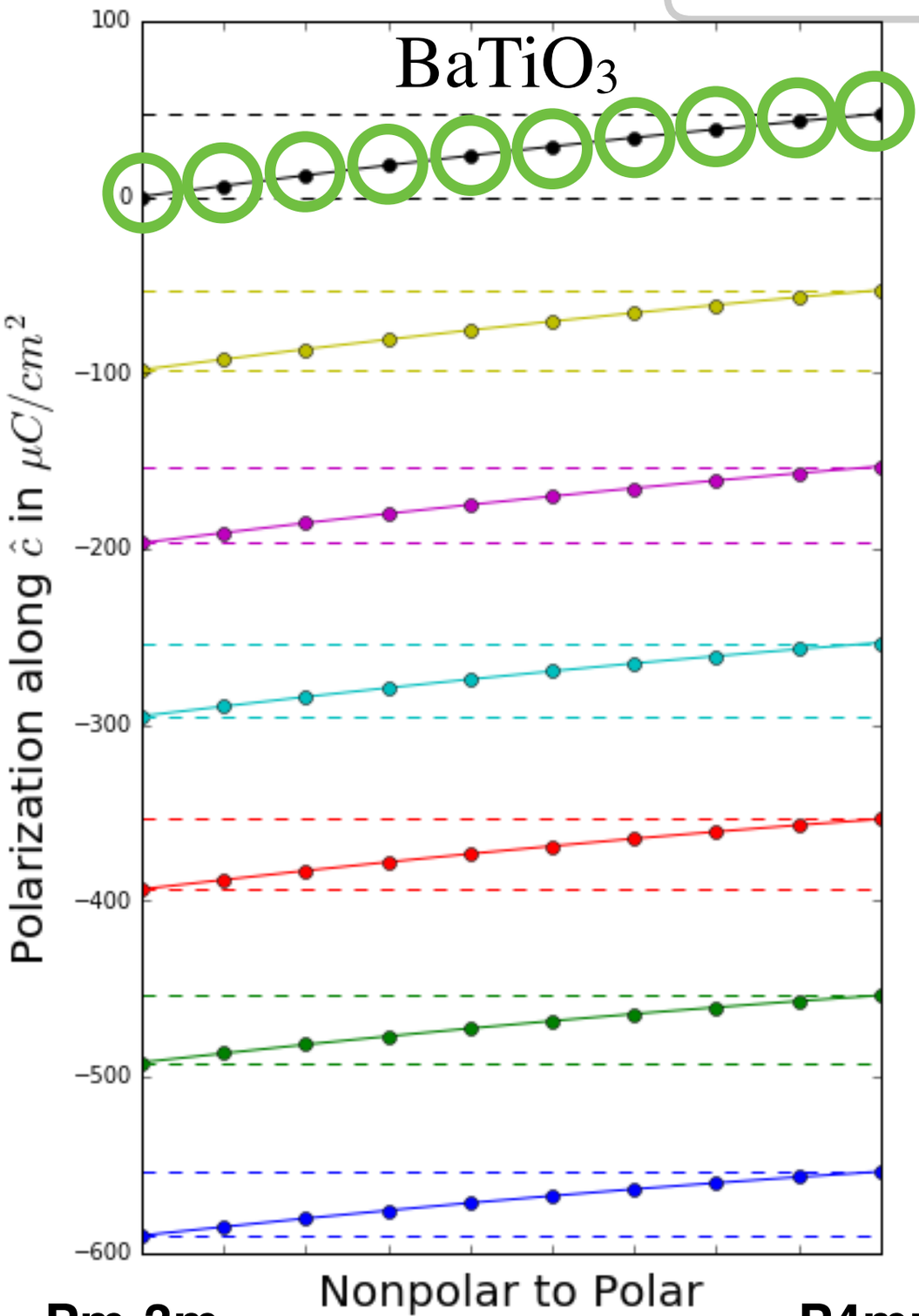




First, we adjust the nonpolar polarization to be closest to zero.

Then, we take the next structure's polarization and move it closest to the previous structure's polarization.





First, we adjust the nonpolar polarization to be closest to zero.

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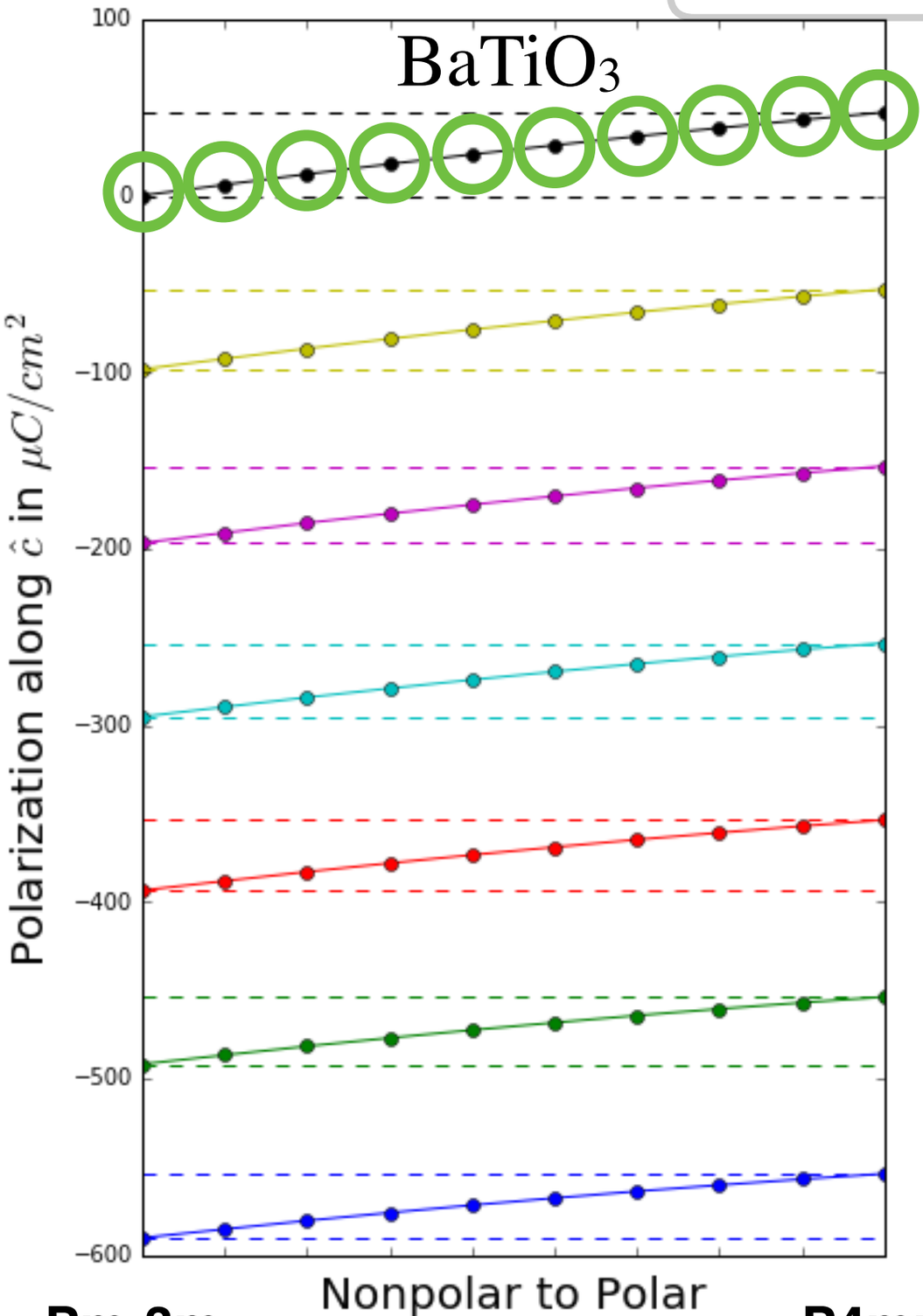
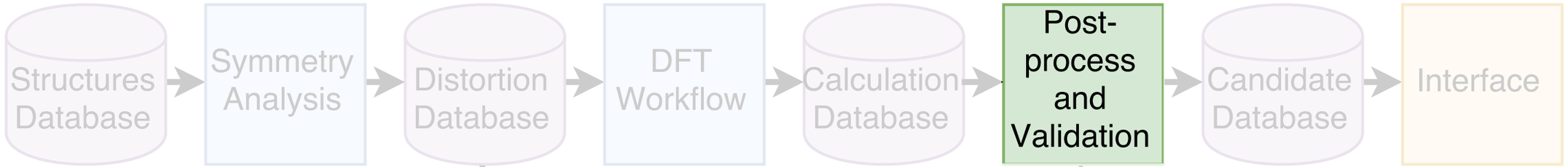
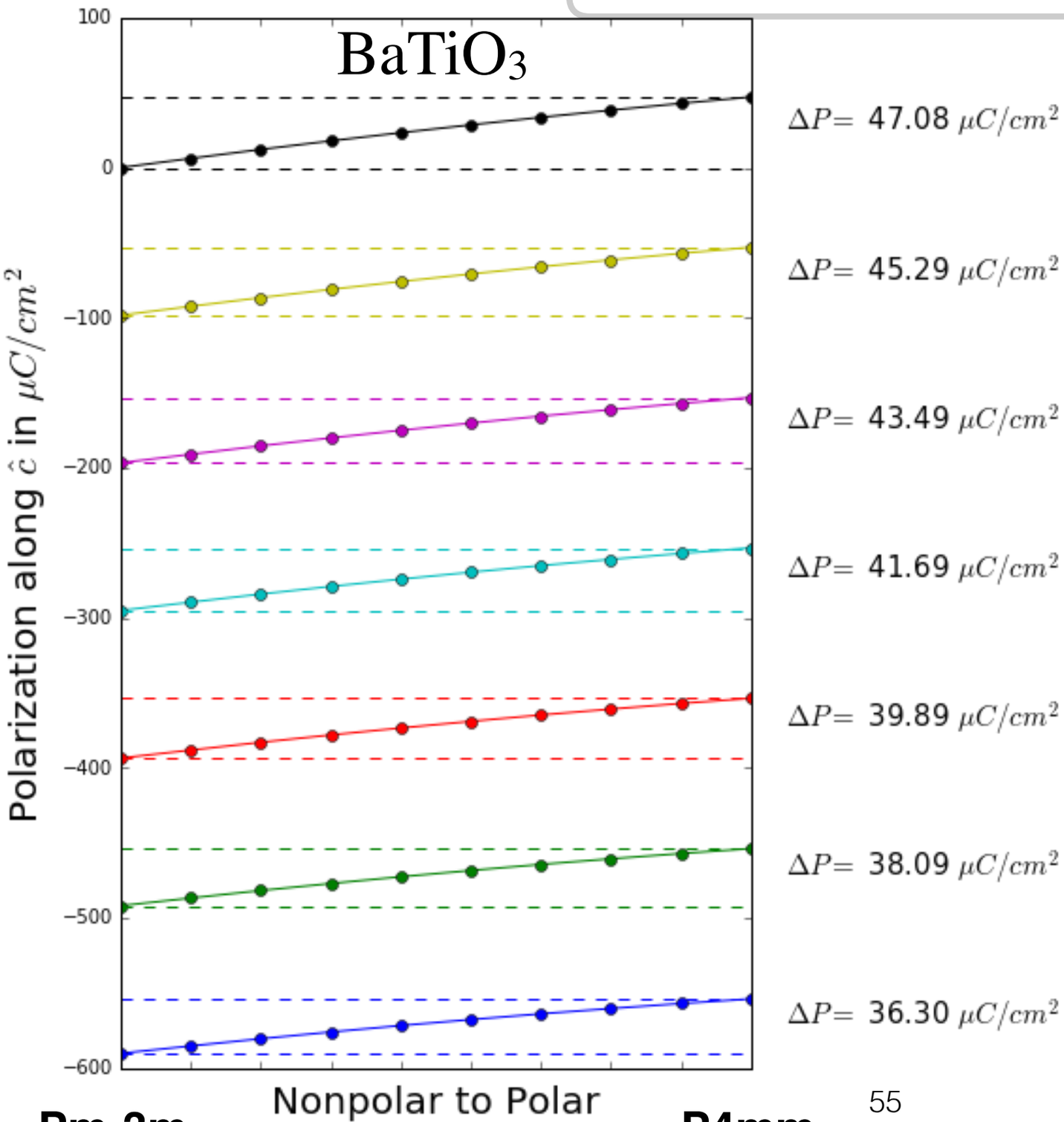


First, we adjust the nonpolar polarization to be closest to zero.

Then, we take the next structure's polarization and move it closest to the previous structure's polarization.

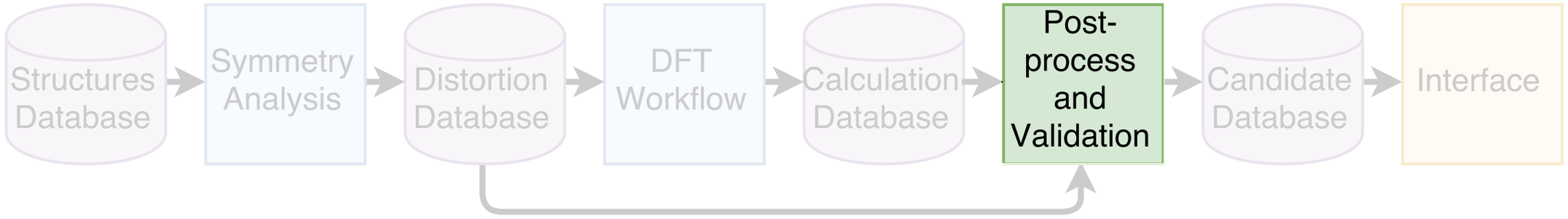
$$P_s = P_p - P_{np}$$





Changes in the structure lattice change the polarization lattice.

We use a new lattice for each interpolation.



We use the smoothness of splines fitted to the total energy and polarization to validate our calculations.

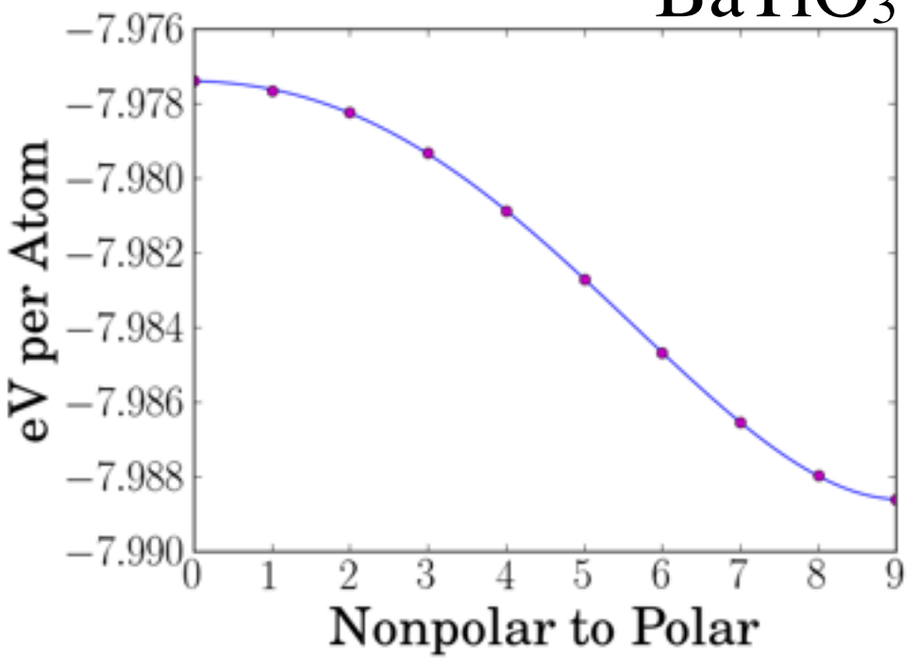
We use the following criteria for validating a given candidate:

The max difference of the polarization fitted spline must be < 1 μC/cm^2.

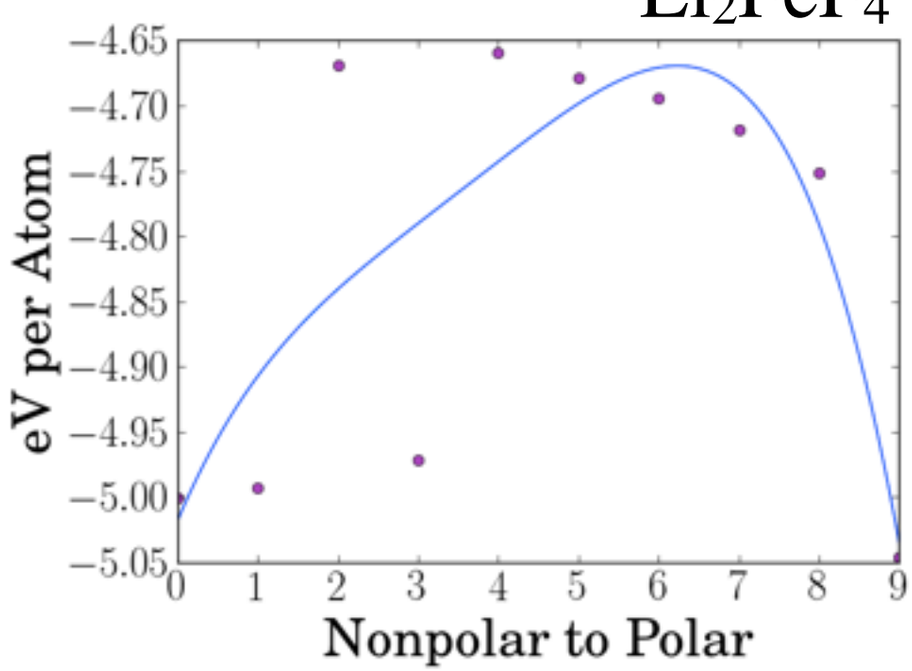
The max difference of the energy fitted spline must be < 10 meV.

These cutoffs are determined empirically.

Good



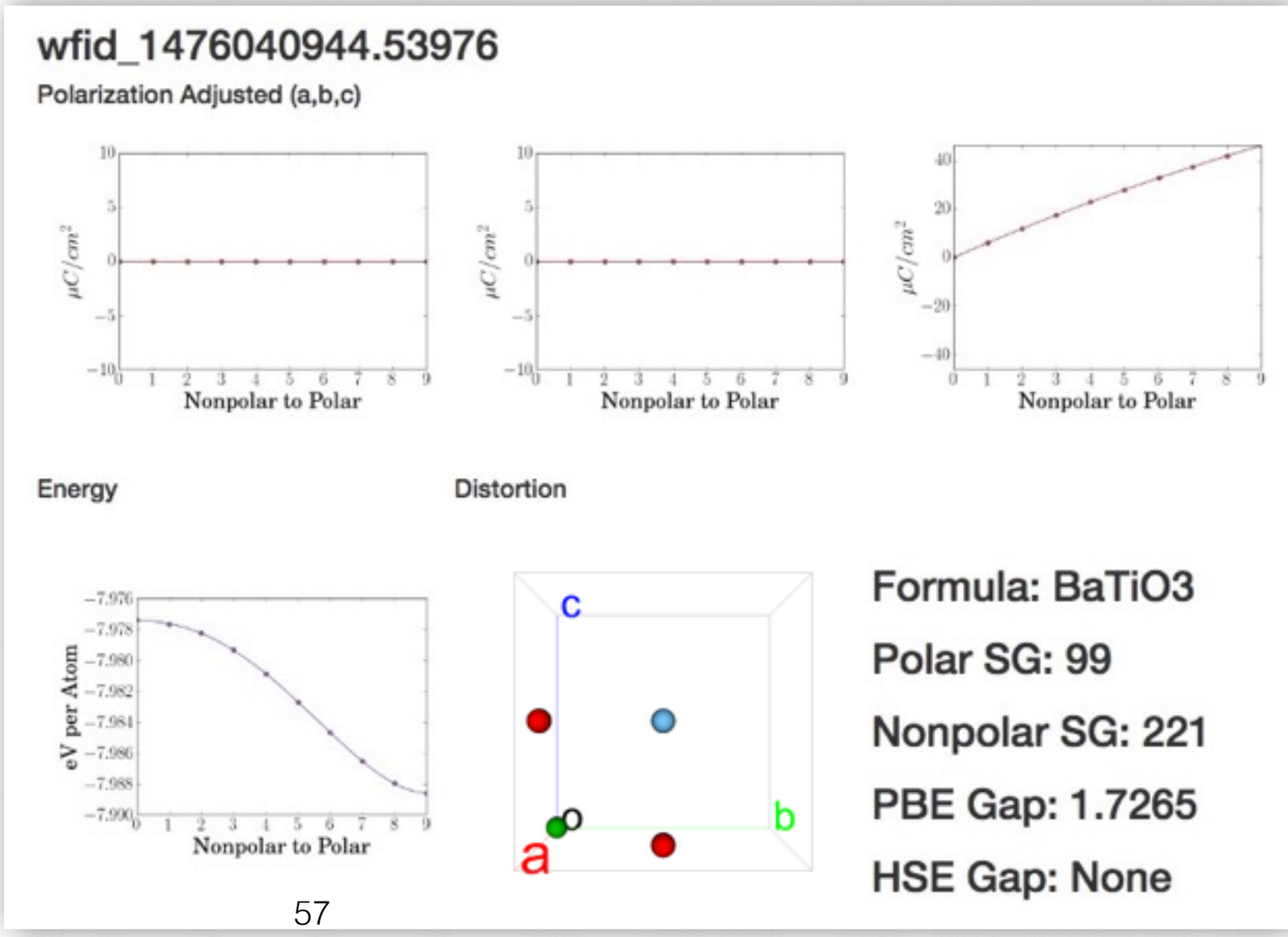
Bad



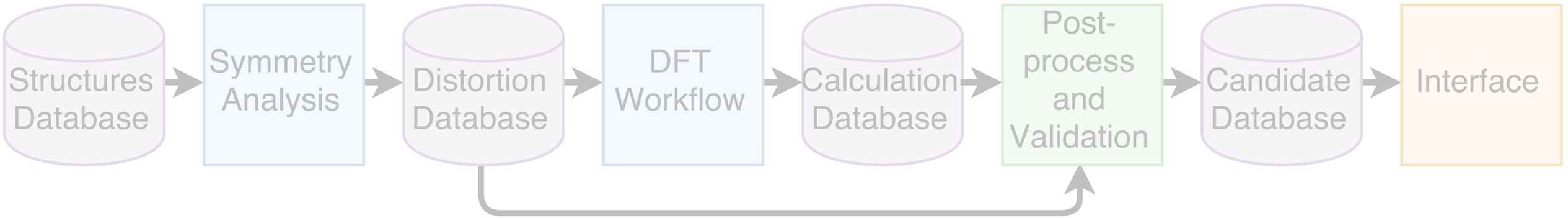
http://127.0.0.1:4800/candidate_fast?id=wfid_1476040786.20162

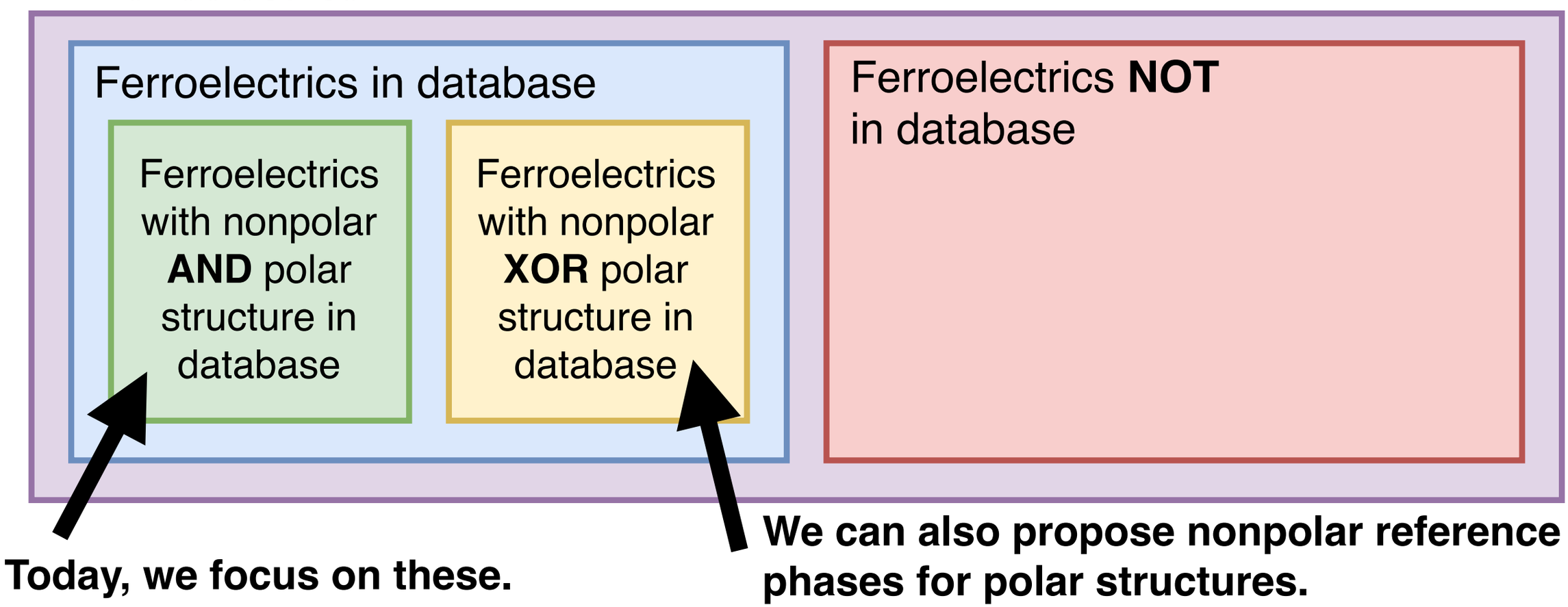
Interface: To more easily look at our data in aggregate, we created an interface generated from our calculation database.

Workflow ID	↓Formula	MP Polar ID	MP Nonpolar ID	P Smooth (a)	P Smooth (b)	P Smooth (c)	E Smooth	Polar Minimum?	Nonpolar Minimum?	Polar Spacegroup	Nonpolar Spacegroup	P Change (muC/cm^2)	E Change (meV)	Max Nonpolar Polarization	Polar Above Hull Energy (meV)	PBE Band Gap (eV)	D_max (AA)	Relaxed D_max (AA)	Max % diff. Lattice	Max % diff. Angles	Volume % diff.
wfid_1476040203.326613	Ag(CO)2	mp-600237	mp-654937	0.000	0.000	0.000	0.000	True	True	5	15	0.039	2.348	0.000	15.559	0.9804	0.0760	0.1080	-0.000	0.000	-0.016
wfid_1476040837.97019	Ag2S	mp-32669	mp-36216	0.000	0.000	0.000	0.000	True	True	36	63	0.372	-2.473	0.000	75.240	1.3419	0.1011	0.0931	0.012	0.000	0.006
wfid_1484444992.013915	Ag3SI	mp-675879	mp-558189	0.000	0.012	0.000	0.000	True	True	4	221	0.686	-40.675	0.000	79.837	0.26	0.7567	2.2343	0.014	0.008	-0.012
wfid_1476041051.123043	Ag3SI	mp-22995	mp-558189	0.000	0.000	0.007	0.000	True	True	146	221	11.755	-49.922	0.000	70.659	0.5052	0.5980	0.6009	-0.006	0.000	-0.028
wfid_1476040056.258909	Al(HO)3	mp-626435	mp-626414	0.068	0.097	0.069	0.000	True	True	1	2	1.455	-9.493	5.544	4.119	4.9631	0.4207	0.3259	0.031	-0.007	-0.019
wfid_1476040897.624205	Al11AgO17	mp-849760	mp-766293	0.000	0.000	0.007															.002
wfid_1476040966.672844	Al3Pb5F19	mp-541732	mp-557911	0.000	0.000	0.006															.001
wfid_1484445148.273011	AlBiO3	mp-551918	mp-23080	0.005	0.003	0.063															.046
wfid_1476040452.983312	AlHg2SbCl4	mp-570828	mp-568001	0.000	0.000	0.000															.007
wfid_1476040139.05518	Ba2YF7	mp-768350	mp-777744	0.000	0.003	0.000															.055
wfid_1484694771.994384	BaAl2O4	mp-4202	mp-3828	0.000	0.000	0.000															.002
wfid_1484444978.482971	BaAl2O4	mp-4202	mp-619456	0.000	0.000	0.000															.003
wfid_1476040115.133166	BaCO3	mp-762225	mp-34195	0.000	0.065	0.000															.017
wfid_1476040109.318651	BaCa(CO3)2	mp-644852	mp-6568	0.000	0.010	0.000															.061
wfid_1484445295.230944	BaLaCl5	mp-770427	mp-770125	0.000	0.011	0.000															.048
wfid_1476041035.850896	BaNiO3	mp-19241	mp-19138	0.000	0.000	0.001															.002
wfid_1476040196.242976	BaTi2O5	mp-555966	mp-3943	0.000	0.008	0.000															.002
wfid_1484444953.778541	BaTiO3	mp-5777	mp-2998	0.000	0.000	0.051															.031
wfid_1476040947.794782	BaTiO3	mp-12992	mp-2998	0.000	0.000	0.018															.028
wfid_1476040944.53976	BaTiO3	mp-5986	mp-2998	0.000	0.000	0.035															.029
wfid_1484445287.593799	BeH8(NF2)2	mp-24614	mp-720982	0.000	0.000	0.000															.020
wfid_1484445283.158561	BeH8(NF2)2	mp-24614	mp-604245	0.000	0.000	0.000															.014
wfid_1484445014.628732	Ca3Mn2O7	mvc-11576	mp-19610	0.001	0.000	0.001															.002
wfid_1476040851.179557	Ca3Mn2O7	mp-19042	mp-19610	0.001	0.000	0.001	0.000	True	True	36	63	5.856	-9.573	0.000	41.817	0.3003	0.3341	0.3334	0.009	0.000	-0.002
wfid_1476040992.366616	Ca5P3ClO12	mp-39460	mp-554236	0.000	0.000	0.002	0.000	True	True	173	176	2.131	-0.688	9.570	18.482	5.3528	0.4444	0.4460	0.005	0.000	0.004

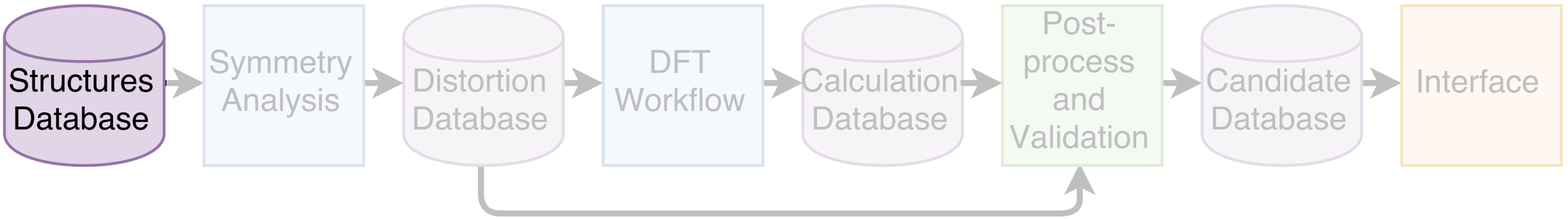


Candidates


Structures Database
Symmetry Analysis
Distortion Database
DFT Workflow
Calculation Database
Post-process and Validation
Candidate Database
Interface


All Ferroelectrics
Ferroelectrics in database
Ferroelectrics with nonpolar **AND** polar structure in database
Ferroelectrics with nonpolar **XOR** polar structure in database
Ferroelectrics **NOT** in database
Today, we focus on these.
We can also propose nonpolar reference phases for polar structures.

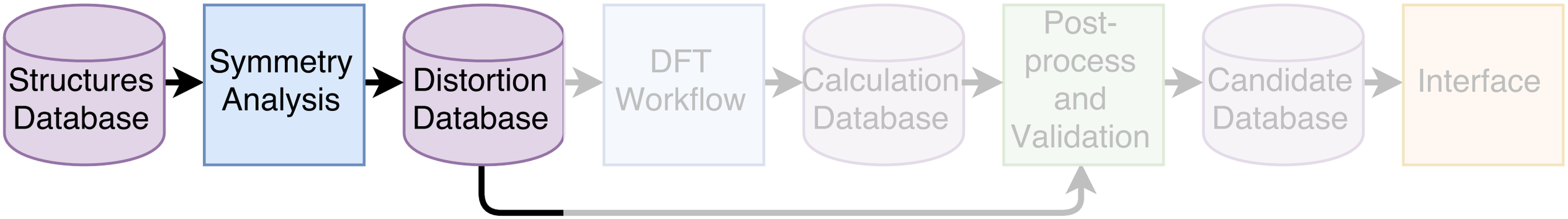
Candidates



MATERIALS PROJECT

Materials Project db contains **67,487** structures. **15,310** are polar.
(**10,242** distinct polar compositions).

Candidates

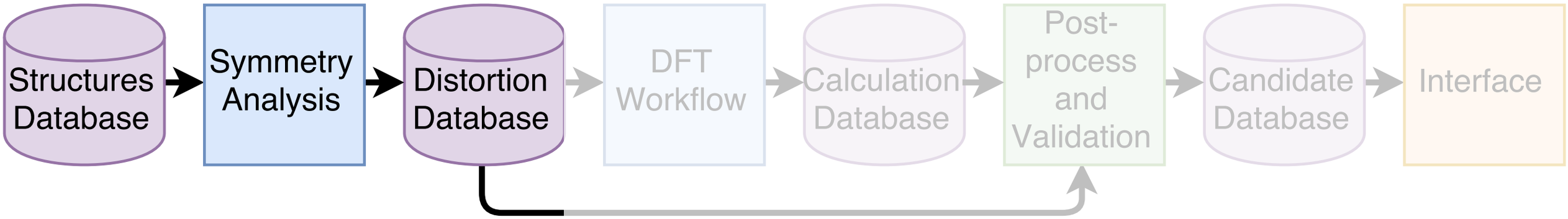


Materials Project db contains **67,487** structures. **15,310** are polar. (**10,242** distinct polar compositions).

pymatgen

17,386 pairs satisfy basic group-subgroup relations (**1,615** distinct polar compositions).

Candidates



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pymatgen

bilbao crystallographic server

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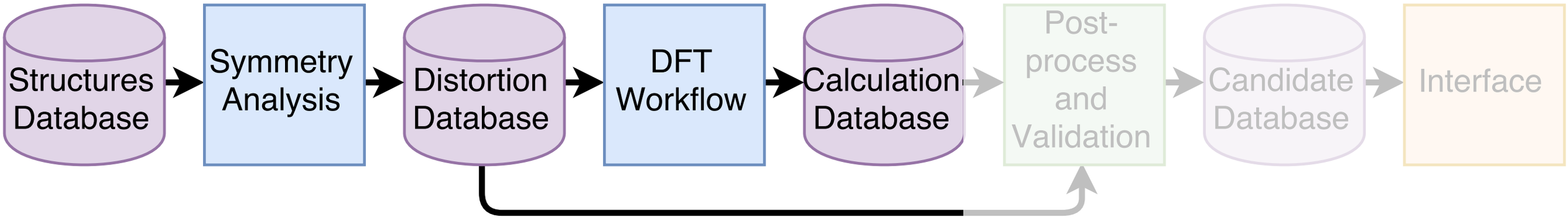
432 have valid transformation matrices for < 1.5 Å distortion.

Candidates



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pymatgen

bilbao crystallographic server

b-initio VASP Vienna ackage imulation

FireWorks

atomate

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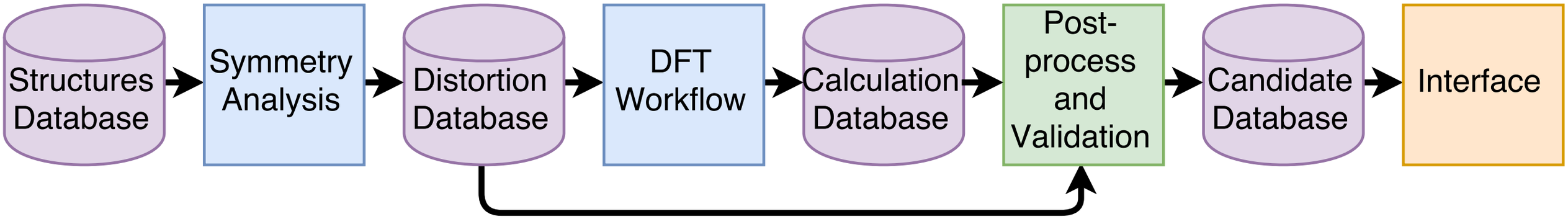
240 candidates are insulating.

Candidates



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pymatgen

bilbao crystallographic server

b-initio VASP ackage imulation ienna

FireWorks

atomate

17,386 pairs satisfy basic group-subgroup relations (**1,615** distinct polar compositions).

432 have valid transformation matrices for < 1.5 Å distortion.

240 candidates are insulating.

184 candidates are validated as high quality.

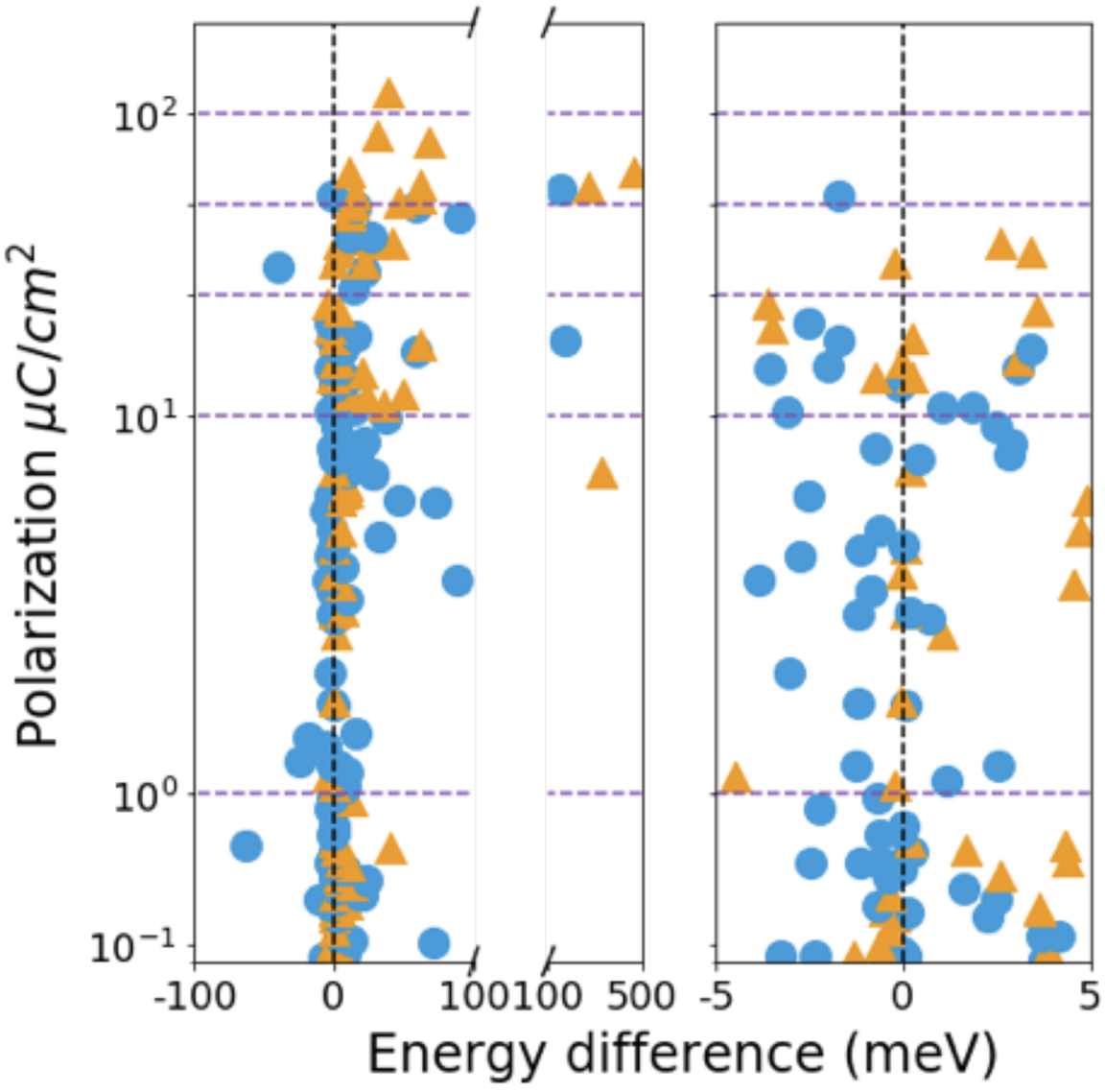
Are there any markers that distinguish known from new ferroelectrics in our high-quality candidates?

Known or Proposed (**77**)

New (**107**)

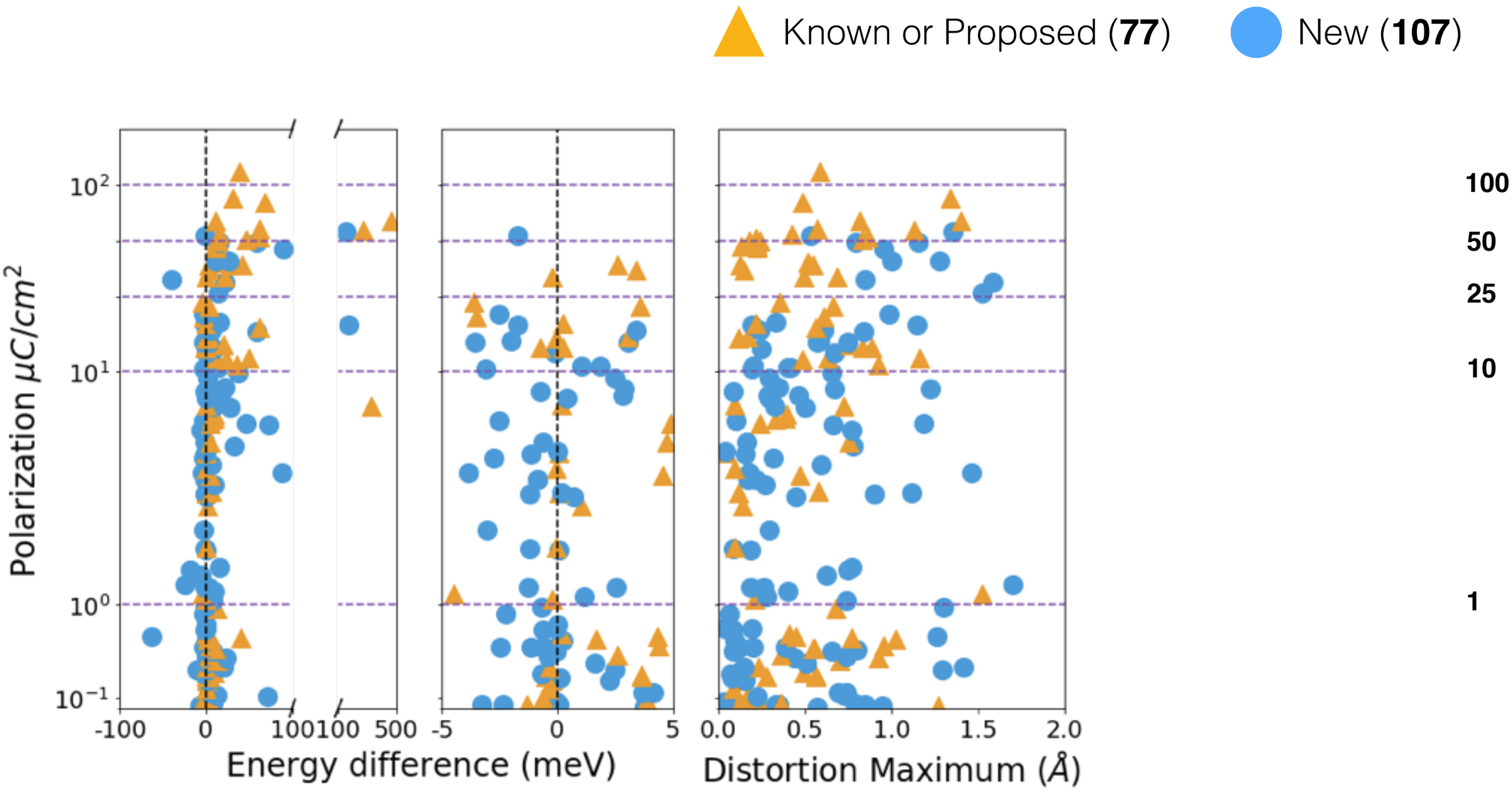
Are there any markers that distinguish known from new ferroelectrics in our high-quality candidates?

Known or Proposed (**77**) New (**107**)



100
50
25
10
1

Are there any markers that distinguish known from new ferroelectrics in our high-quality candidates?



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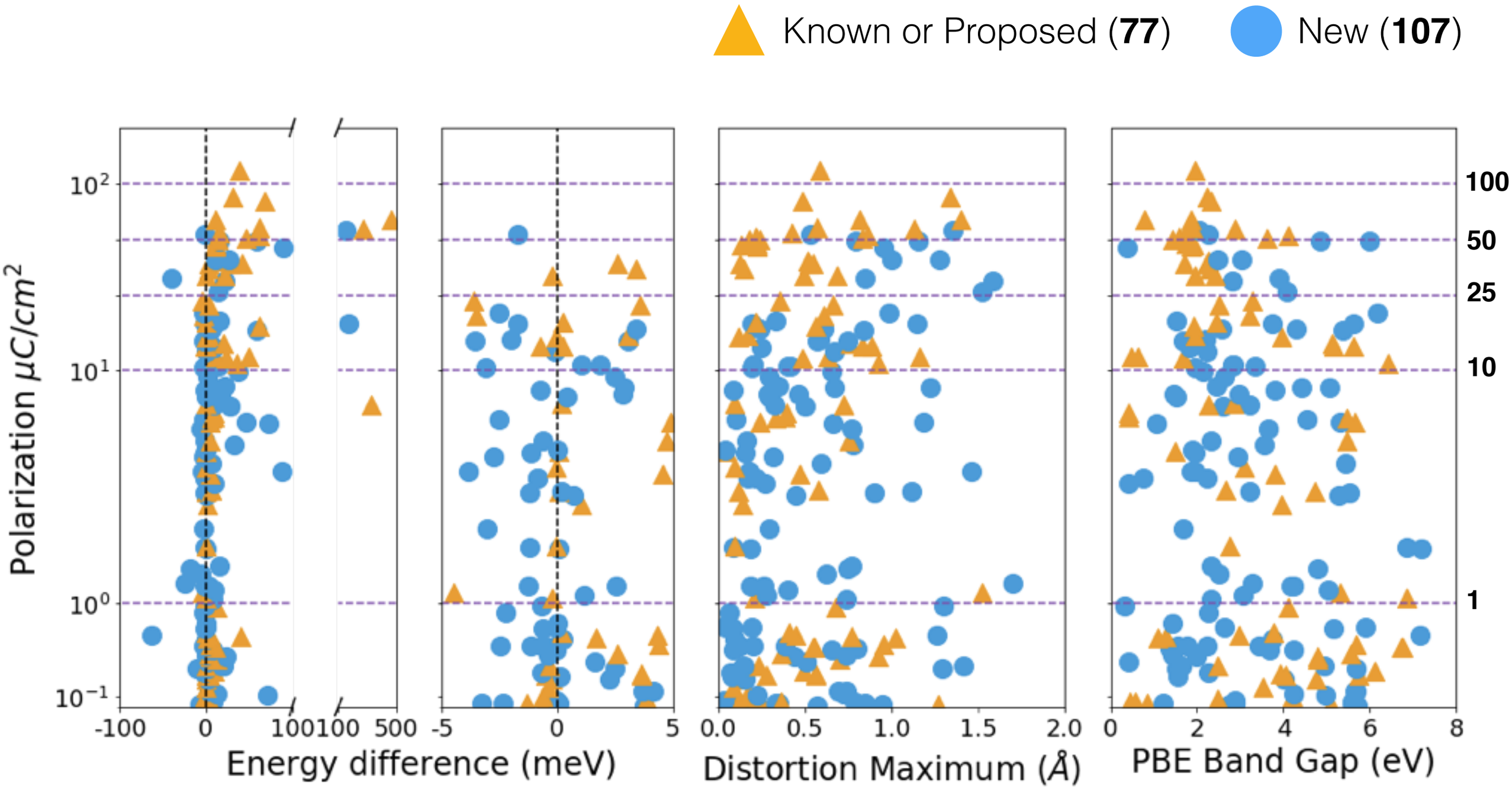
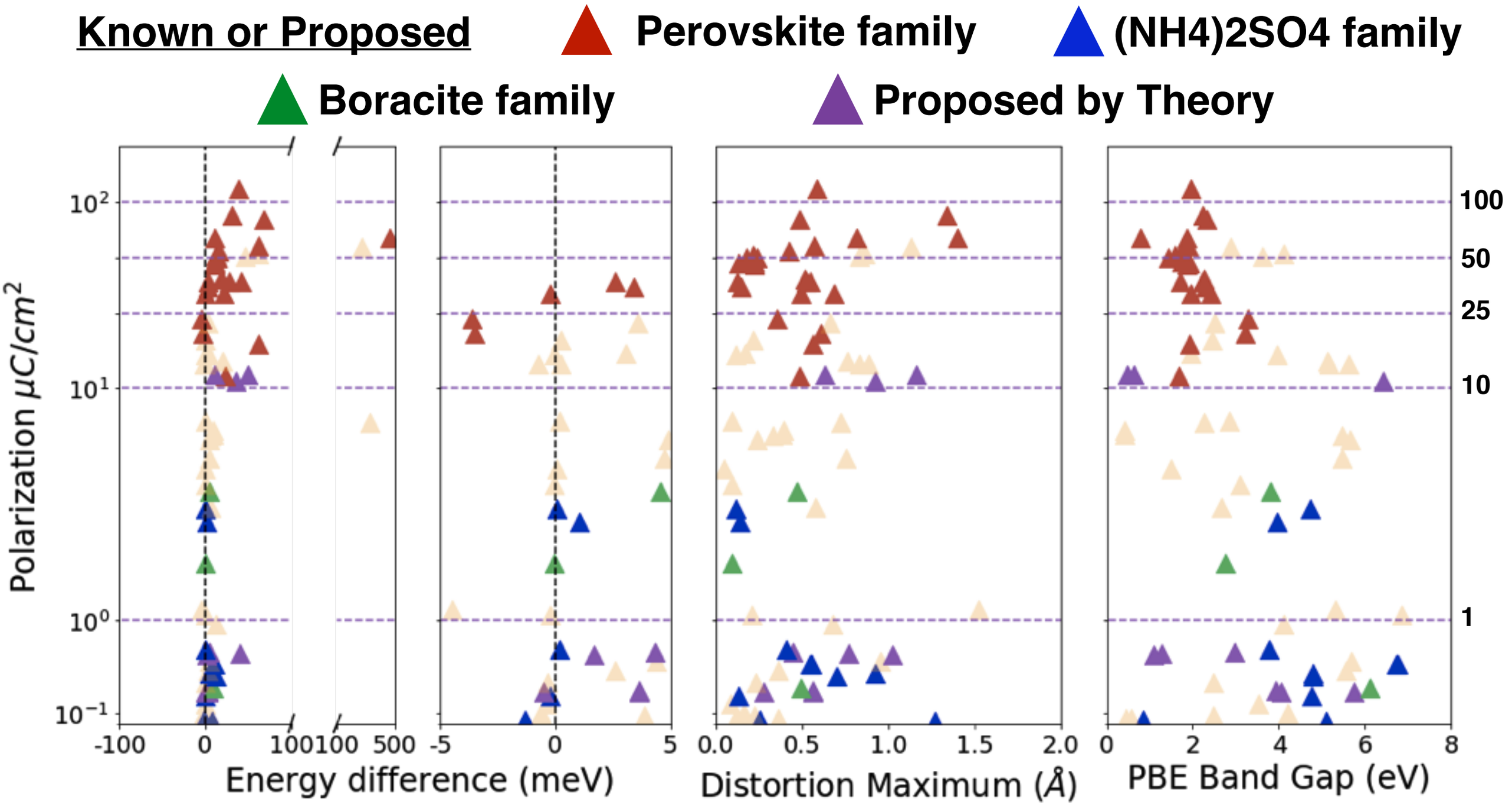
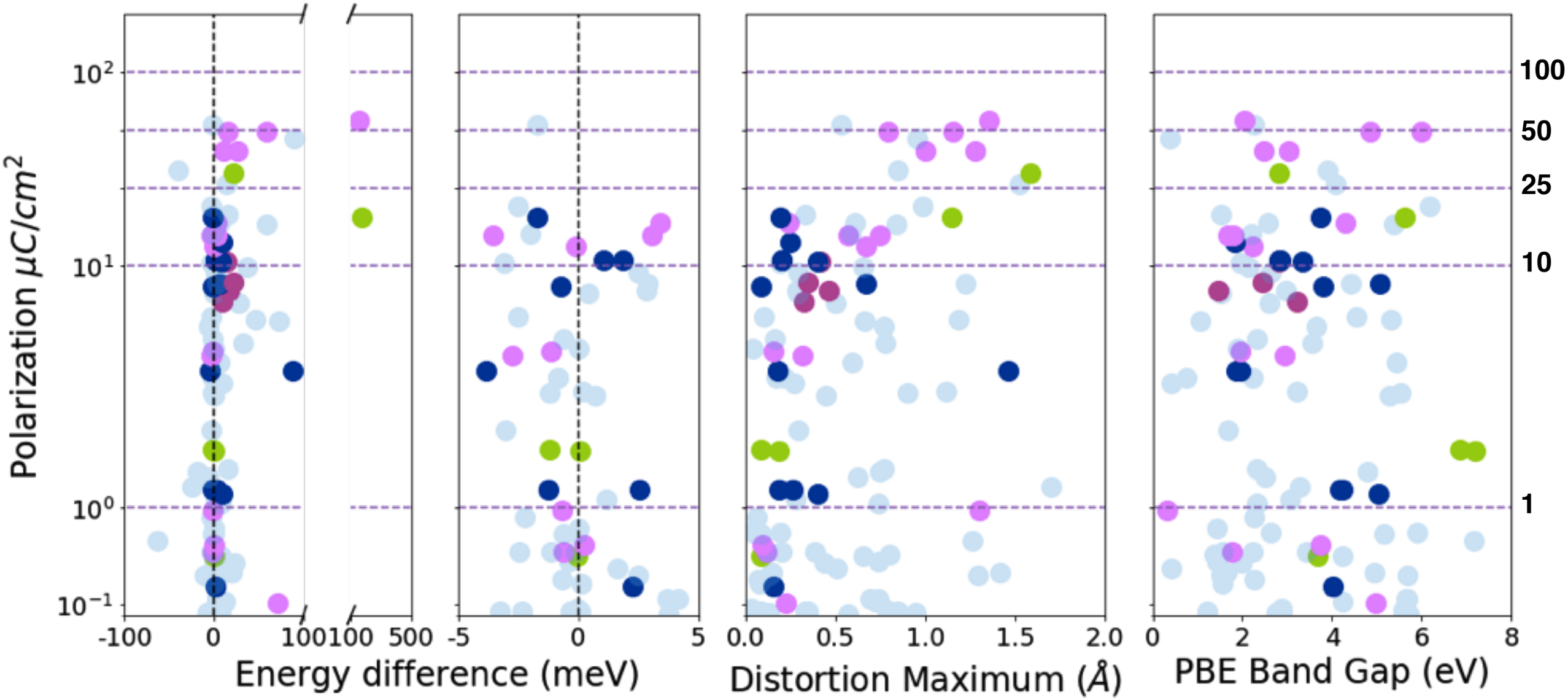



Known or Proposed
Perovskite family
(NH4)2SO4 family
Boracite family
Proposed by Theory
Polarization μC/cm²
10²
10¹
10⁰
10⁻¹
-100
0
100
100
500
-5
0
5
Energy difference (meV)
0.0
0.5
1.0
1.5
2.0
Distortion Maximum (Å)
0
2
4
6
8
PBE Band Gap (eV)
100
50
25
10
1

New ferroelectrics!

Carbonates **Fluorides**

Hexagonal Manganite-like **Hydroxides**



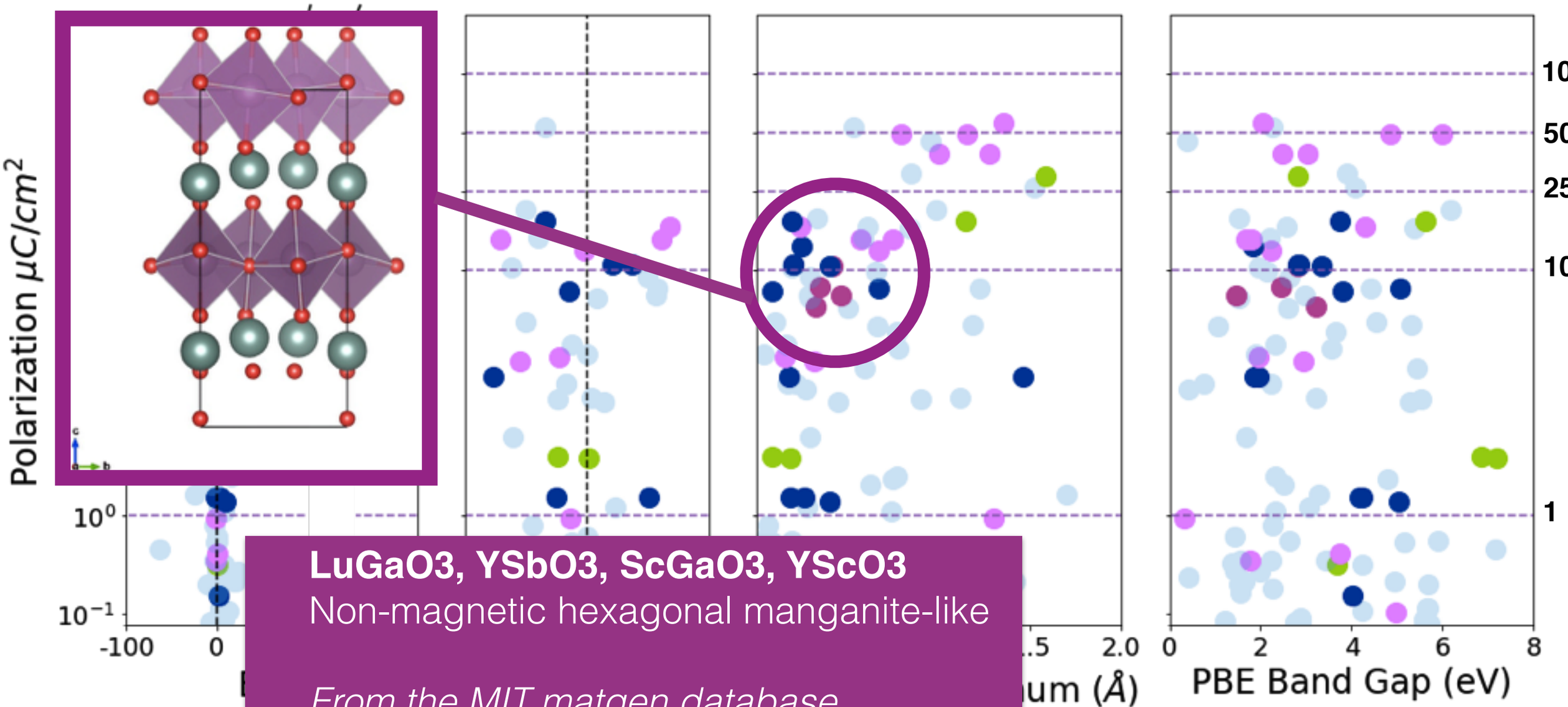
New ferroelectrics!

Carbonates

Fluorides

Hexagonal Manganite-like

Hydroxides



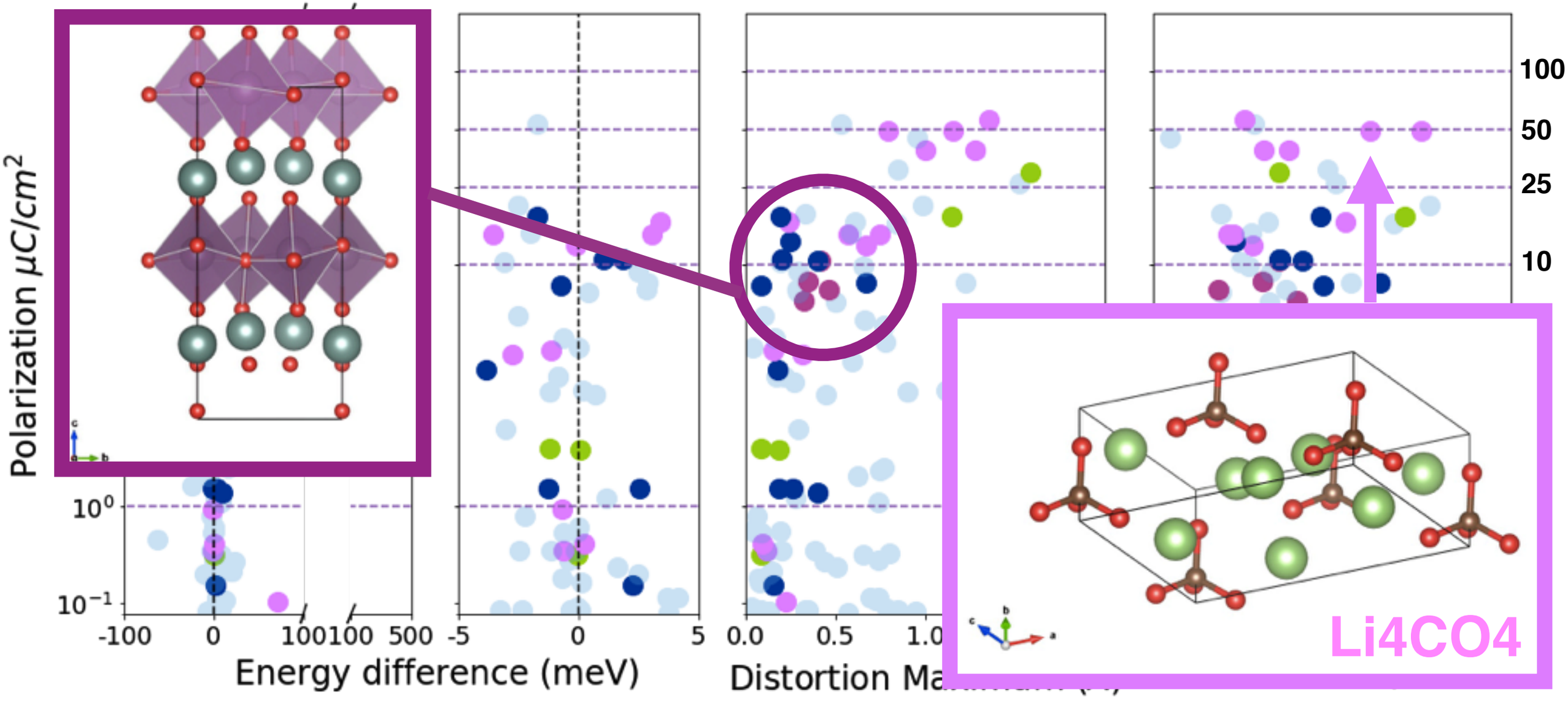
LuGaO3, YSbO3, ScGaO3, YScO3
Non-magnetic hexagonal manganite-like

From the MIT matgen database.
First three are hypothetical structures.

New ferroelectrics!

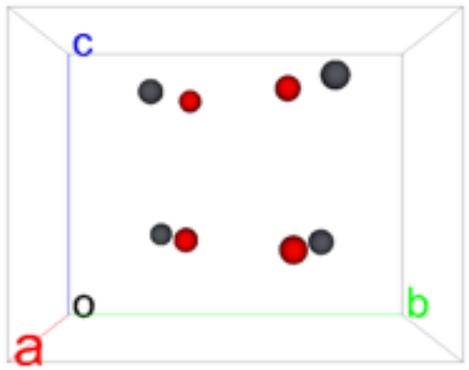
Carbonates **Fluorides**

Hexagonal Manganite-like **Hydroxides**

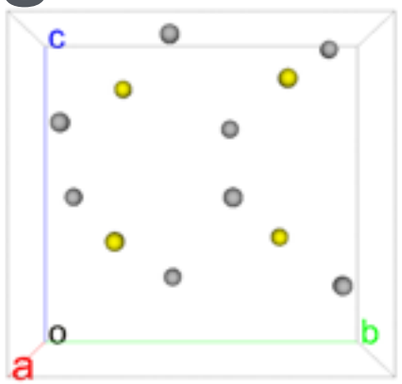


New ferroelectrics!

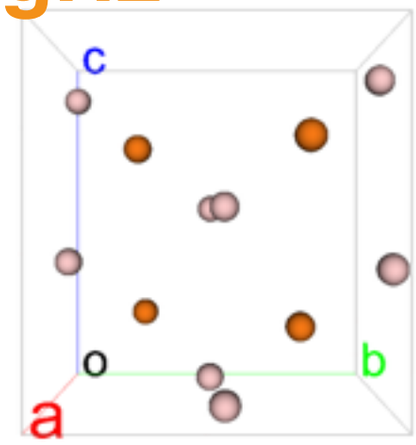
PbO



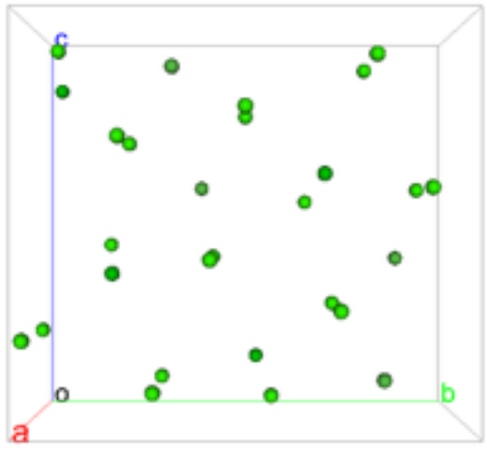
Ag2S



MgH2



BaLaCl5



Fluorides

Hydroxides

Polarization $\mu C/cm^2$

10^0

10^{-1}

-100

100

50

25

10

1

0 2 4 6 8

PBE Band Gap (eV)

Future Work

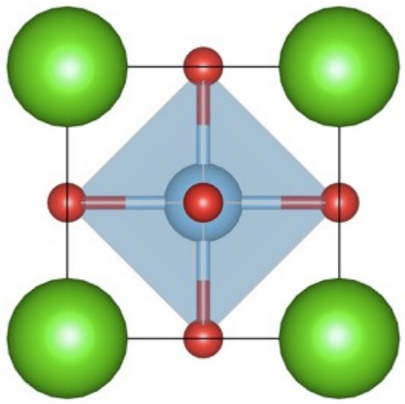
Many searches to do!

- More databases!
- Nonpolar structures through pseudosymmetry.
- **Structure types**
- Substitutions
- Strain
- Multiferroics

We must create new criteria to compare these candidates.

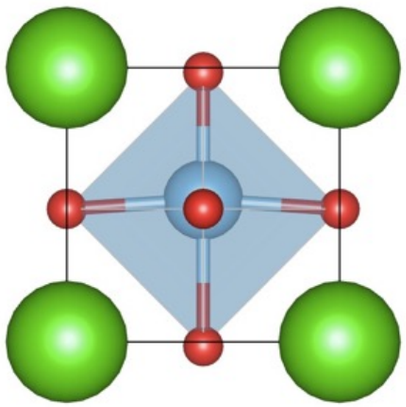
Finding structure type pairs:
Anonymize the atoms and search for nonpolar-polar structure pairs.

Nonpolar Structure Type
“Perovskite—CaTiO3”
Spacegroup 221



ABC3

Polar Structure Type
“Perovskite—PbTiO3”
Spacegroup 99



ABC3

Future Work

Shift-current photovoltaics

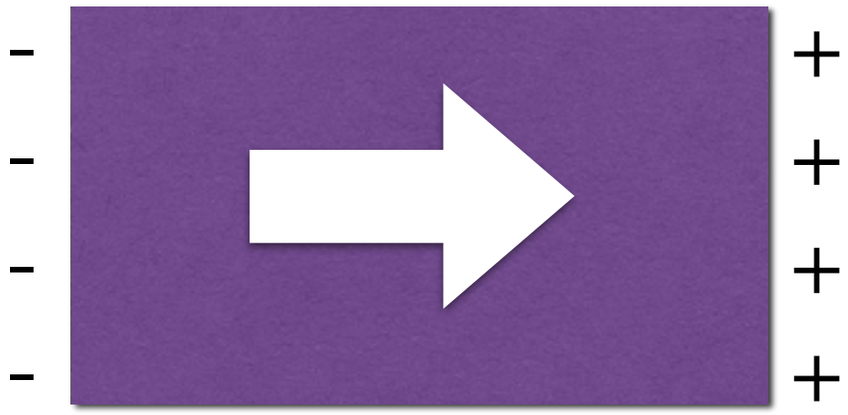
Dr. Tonatiuh Rangel Gordillo
Postdoc
Neaton Group

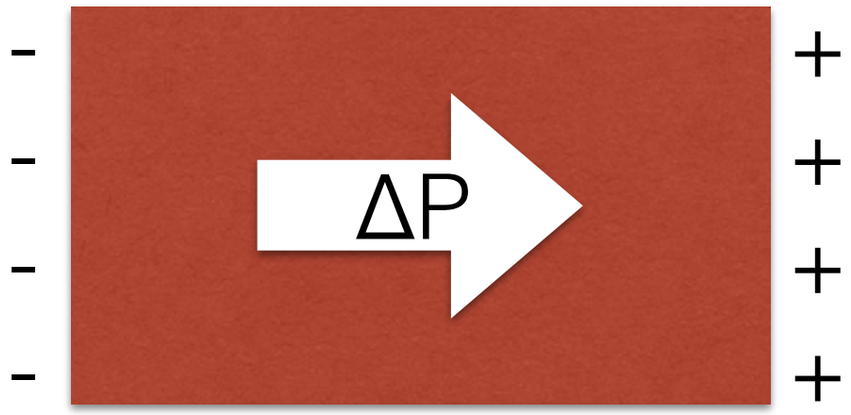
Topological ferroelectrics

Dr. Sinead Griffin
Postdoc
Neaton Group

Ferroelectric ferroaxials

Prof. Jiri Hlinka
Institute of Physics
Czech Academy of Sciences





$$\frac{dP}{dT} = J(\omega)$$

Density change induced by excitation: ρ → ρ+Δ

Future Work

Shift-current photovoltaics

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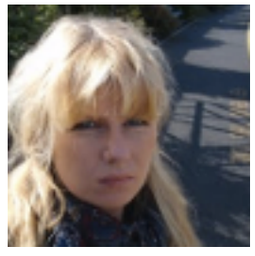
Neaton Group

Topological ferroelectrics

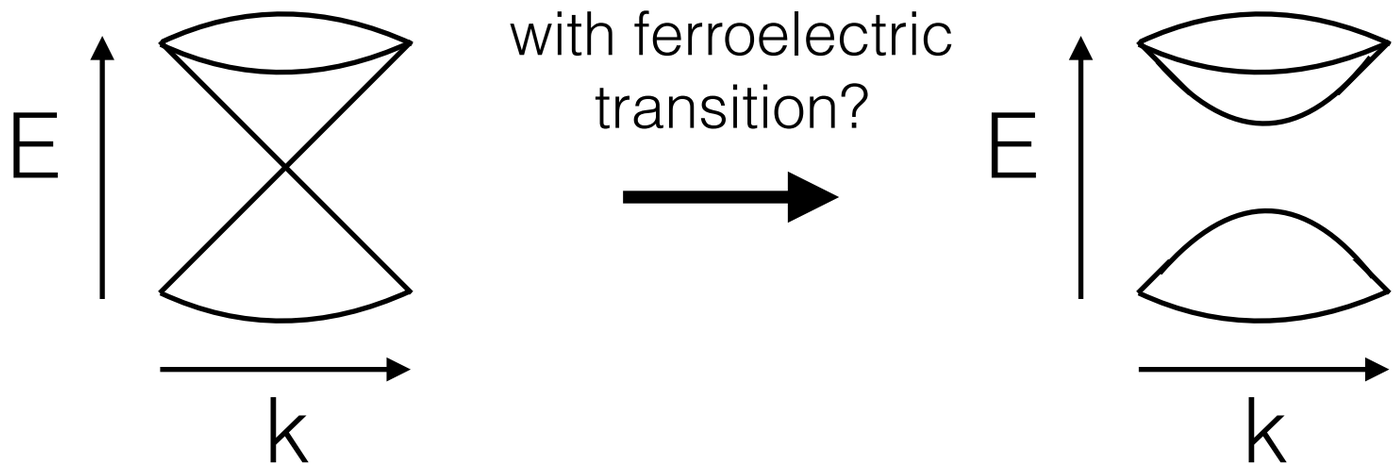


Dr. Sinead Griffin
Postdoc
Neaton Group

Ferroelectric ferroaxials

Prof. Jiri Hlinka
Institute of Physics
Czech Academy of Sciences

Break symmetry protecting topological state with ferroelectric transition?



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Dipole moment	P	T
axial toroidal dipole moment	+1	+1
electric dipole moment	−1	+1
magnetic dipole moment	+1	−1
polar toroidal dipole moment	−1	−1

PRL **116,** 177602 (2016) PHYSICAL REVIEW LETTERS week ending 29 APRIL 2016

Symmetry Guide to Ferroaxial Transitions

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Institute of Physics, The Czech Academy of Sciences, Na Slovance 2, 182 21 Prague 8, Czech Republic
(Received 17 February 2016; published 28 April 2016)

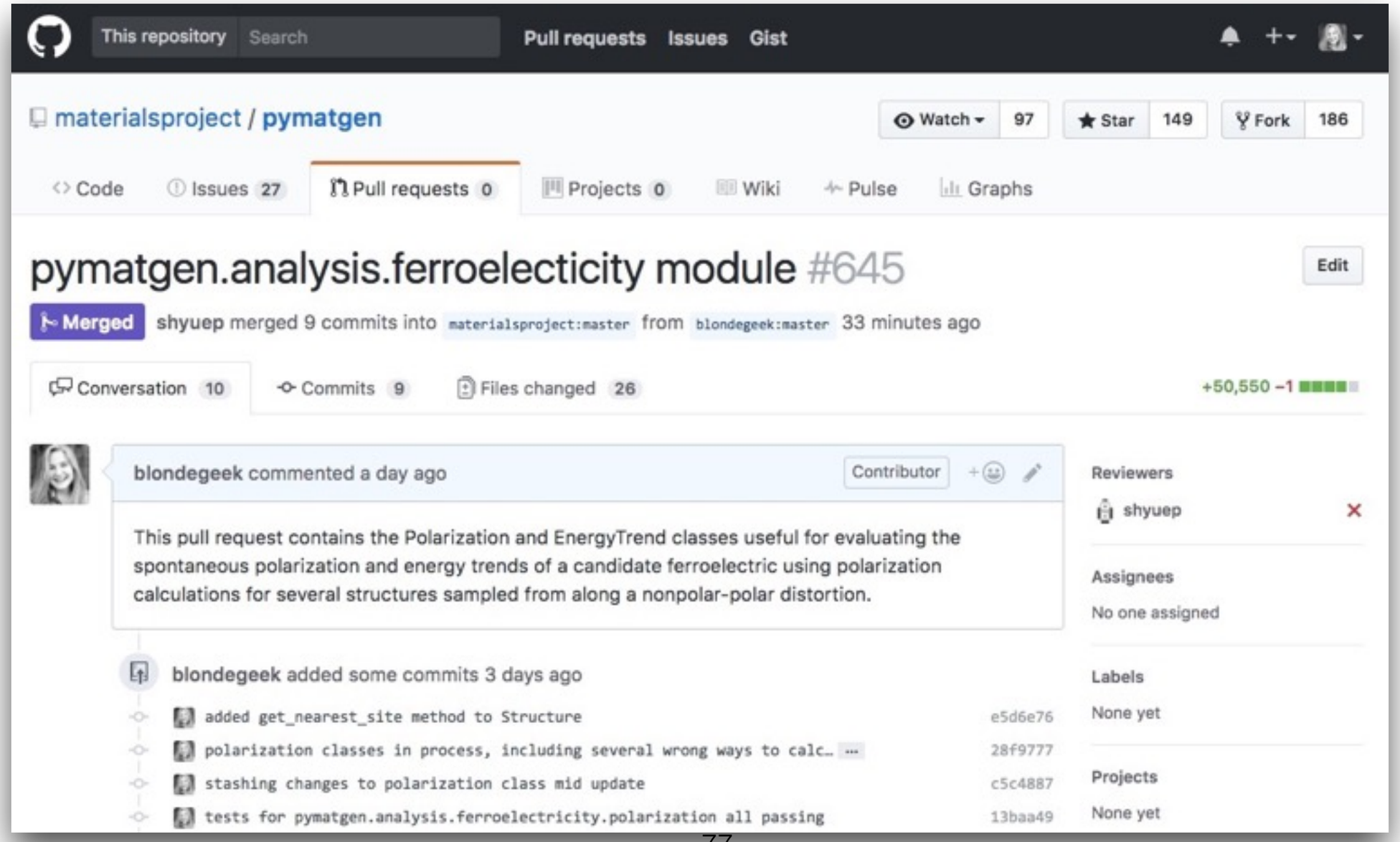
The 212 species of the structural phase transitions with a macroscopic symmetry breaking are inspected with respect to the occurrence of the ferroaxial order parameter, the electric toroidal moment. In total, 124 ferroaxial species are found, some of them being also fully ferroelectric (62) or fully ferroelastic ones (61). This ensures a possibility of electrical or mechanical switching of ferroaxial domains. Moreover, there are 12 ferroaxial species that are neither ferroelectric nor ferroelastic. For each species, we have also explicitly worked out a canonical form for a set of representative equilibrium property tensors of polar and axial nature in both high-symmetry and low-symmetry phases. This information was gathered into the set of 212 mutually different symbolic matrices, expressing graphically the presence of nonzero independent tensorial components and the symmetry-imposed links between them, for both phases simultaneously. Symmetry analysis reveals the ferroaxiality in several currently debated materials, such as VO_2, $LuFe_2O_4$, and URu_2Si_2.

DOI: 10.1103/PhysRevLett.116.177602

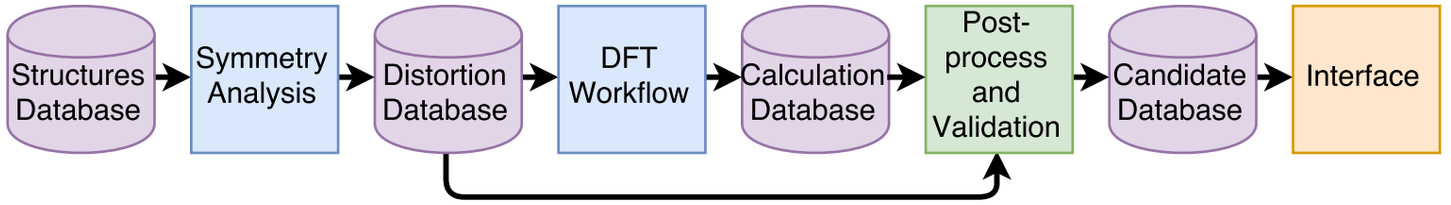
Contributed to atomate (built on FireWorks) and pymatgen

- Created atomate workflow for performing polarization calculations
- Created pymatgen.analysis.ferroelectricity module

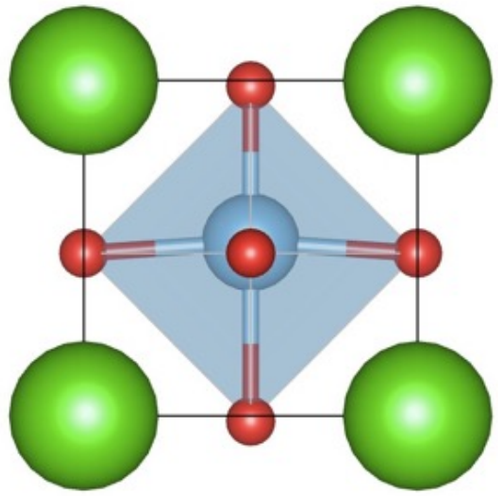
FireWorks atomate pymatgen



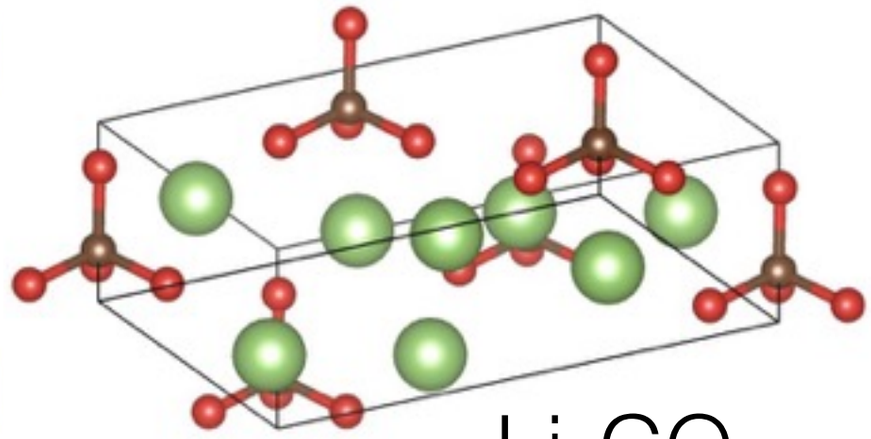
This is the first time the entire ferroelectric search workflow has been automated.



Our workflow is able to recover diverse ferroelectric candidates, known and new.



$BaTiO_3$



Li_4CO_4

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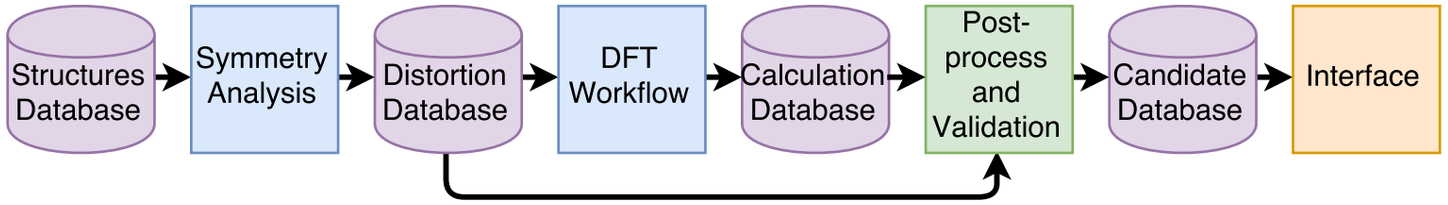

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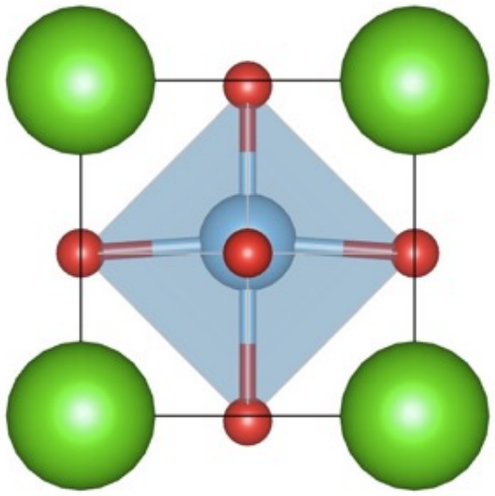

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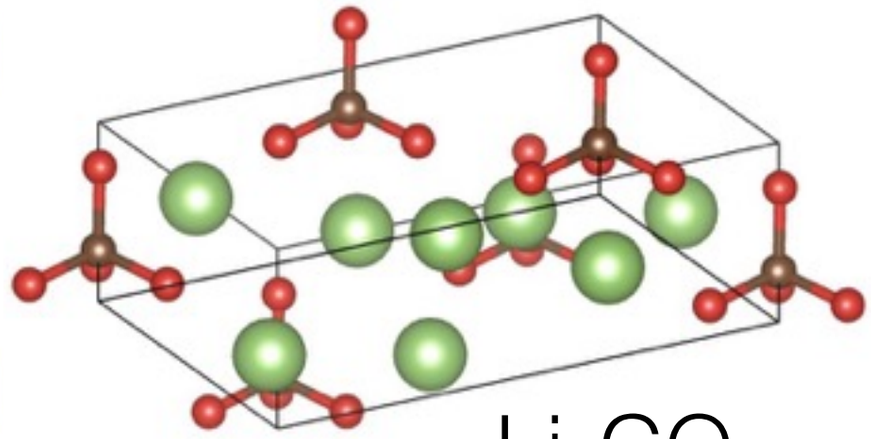
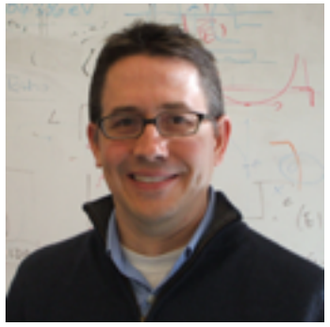


Li_4CO_4

Collaborators

Dr. Sebastian E. Reyes-Lillio
Postdoc
Neaton Group

Dr. Anubhav Jain
Research Scientist
LBL MSD



Prof. Jeff Neaton

But wait! There’s more!

My Research:

Understanding and designing complex materials from structural motifs

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An Automated Ab Initio Search for Ferroelectrics

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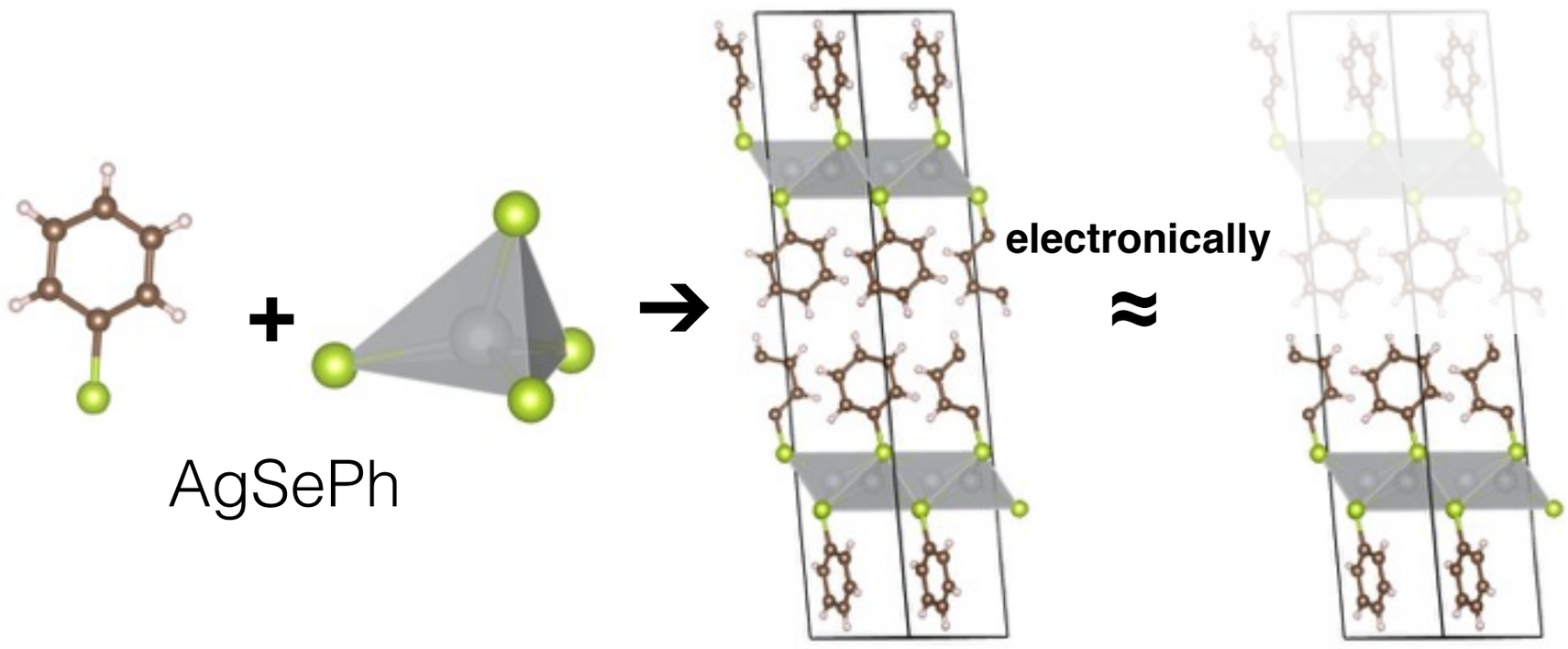

2D optoelectronic properties of bulk hybrid organic-dichalgogenides

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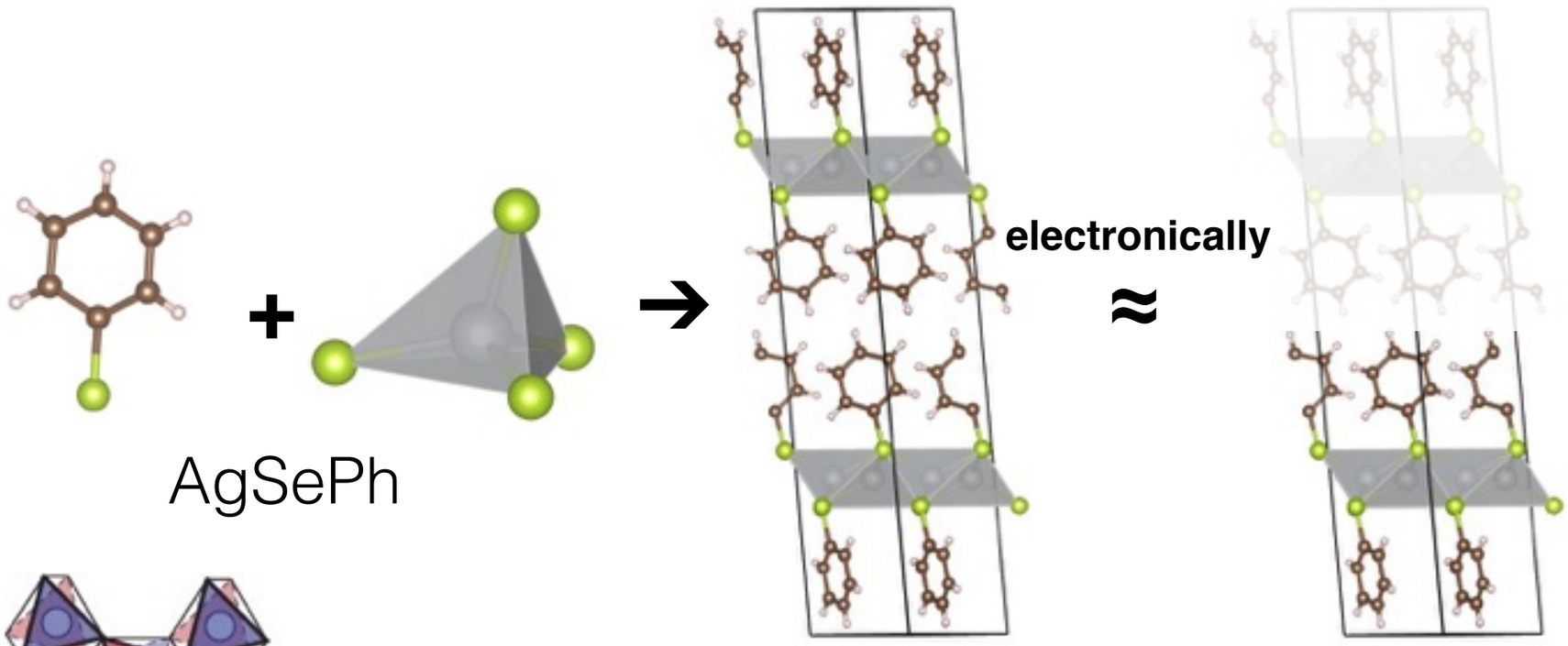

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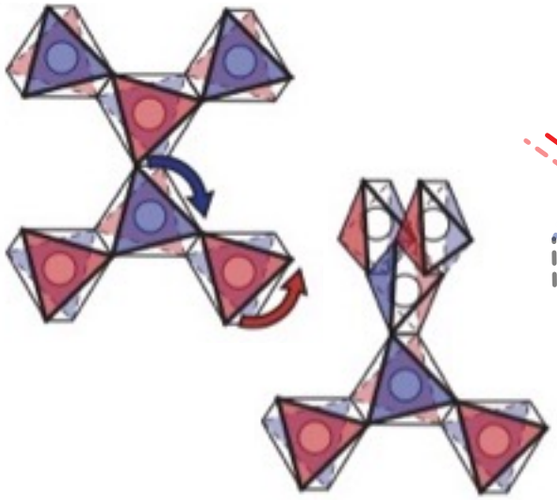

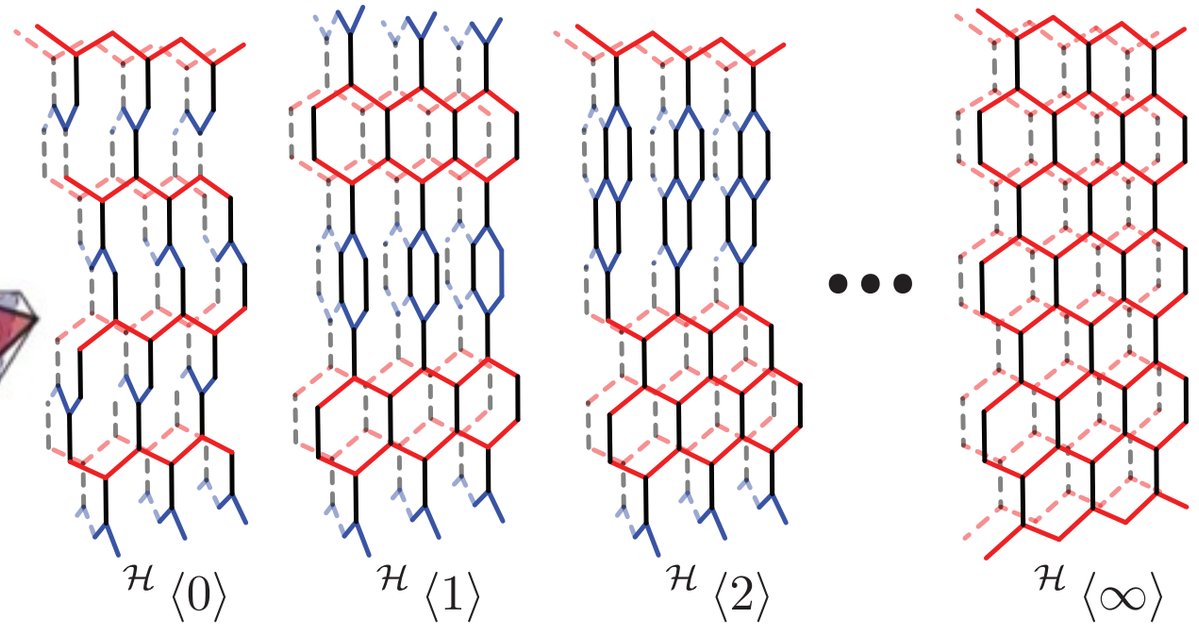

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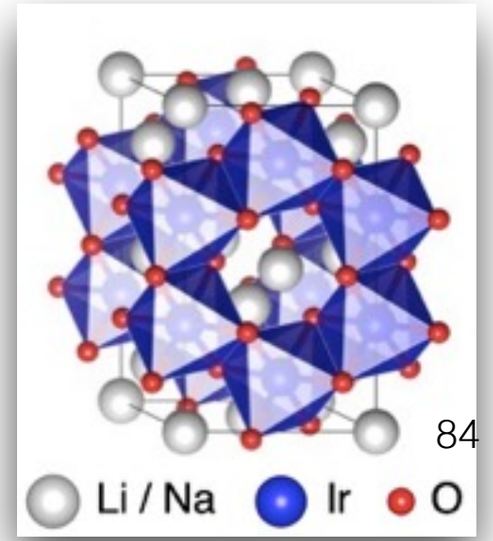

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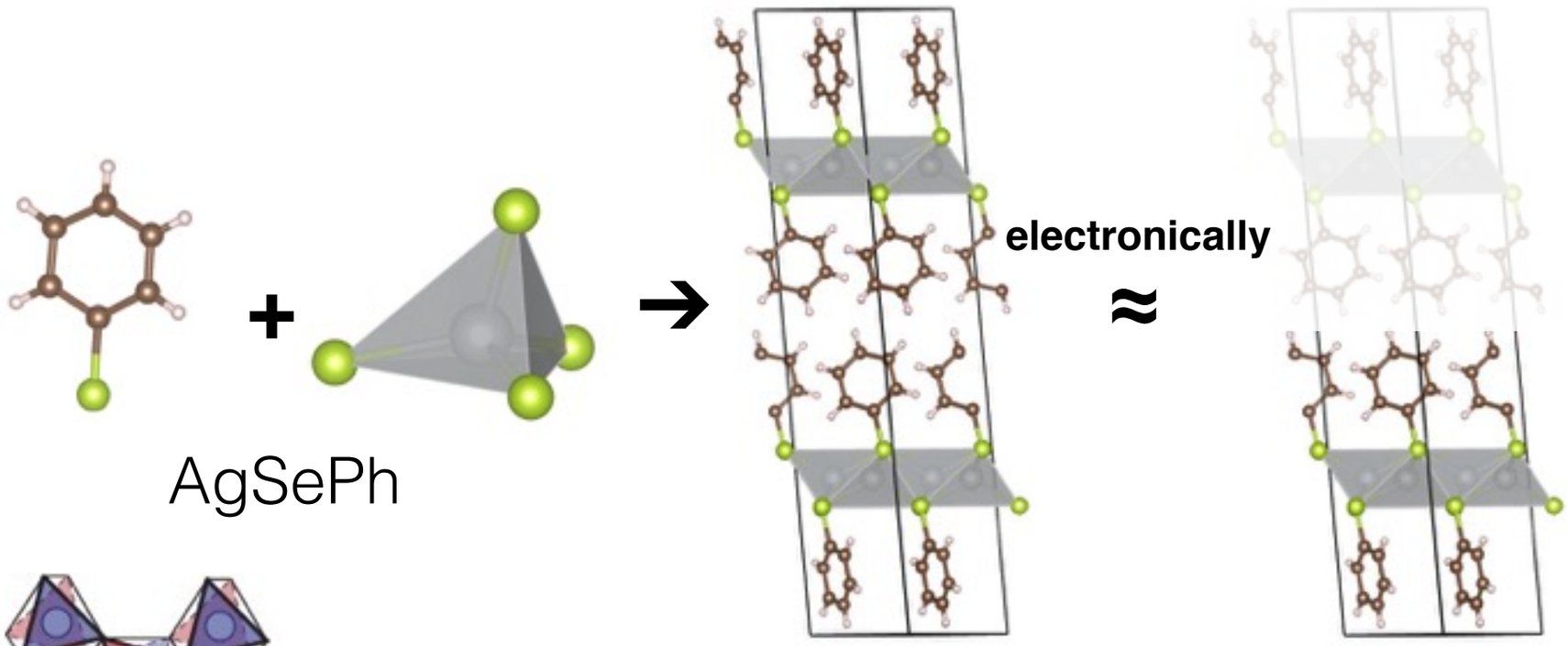

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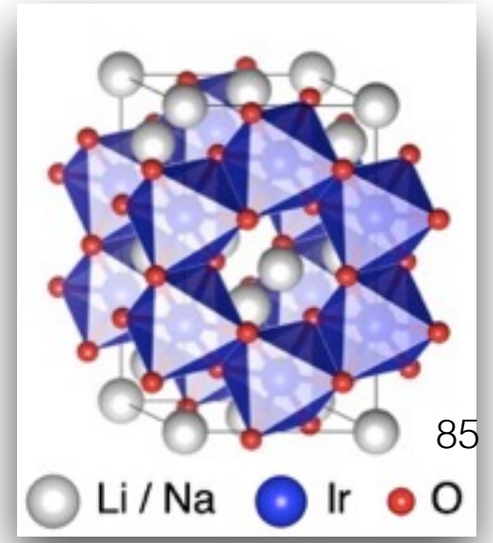

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Deep Generative Models for Materials Design

Calling for backup… slides

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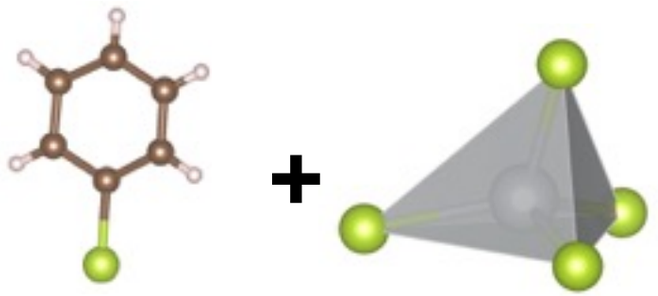
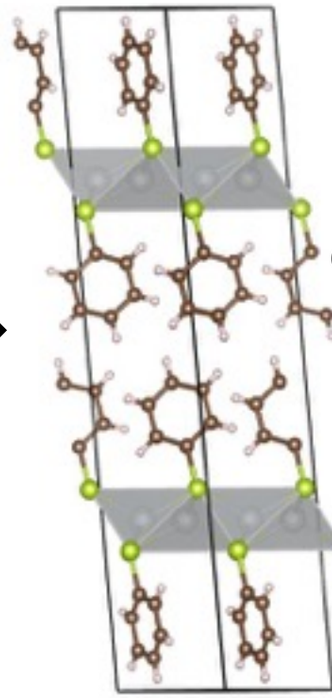
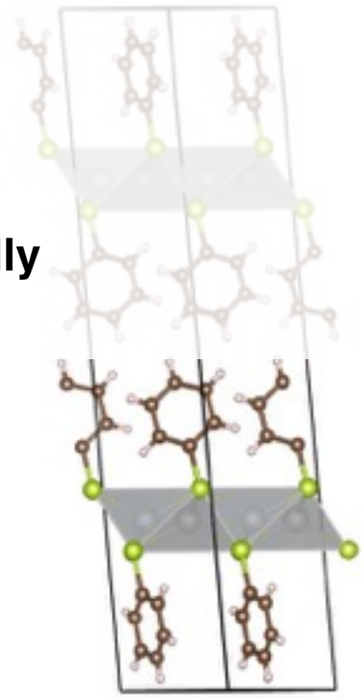


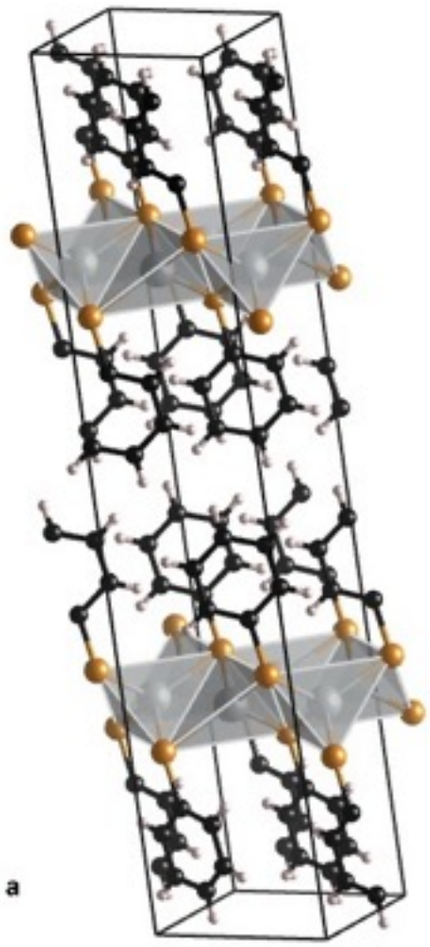
AgSePh

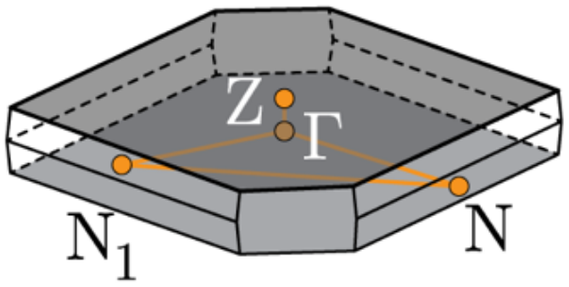


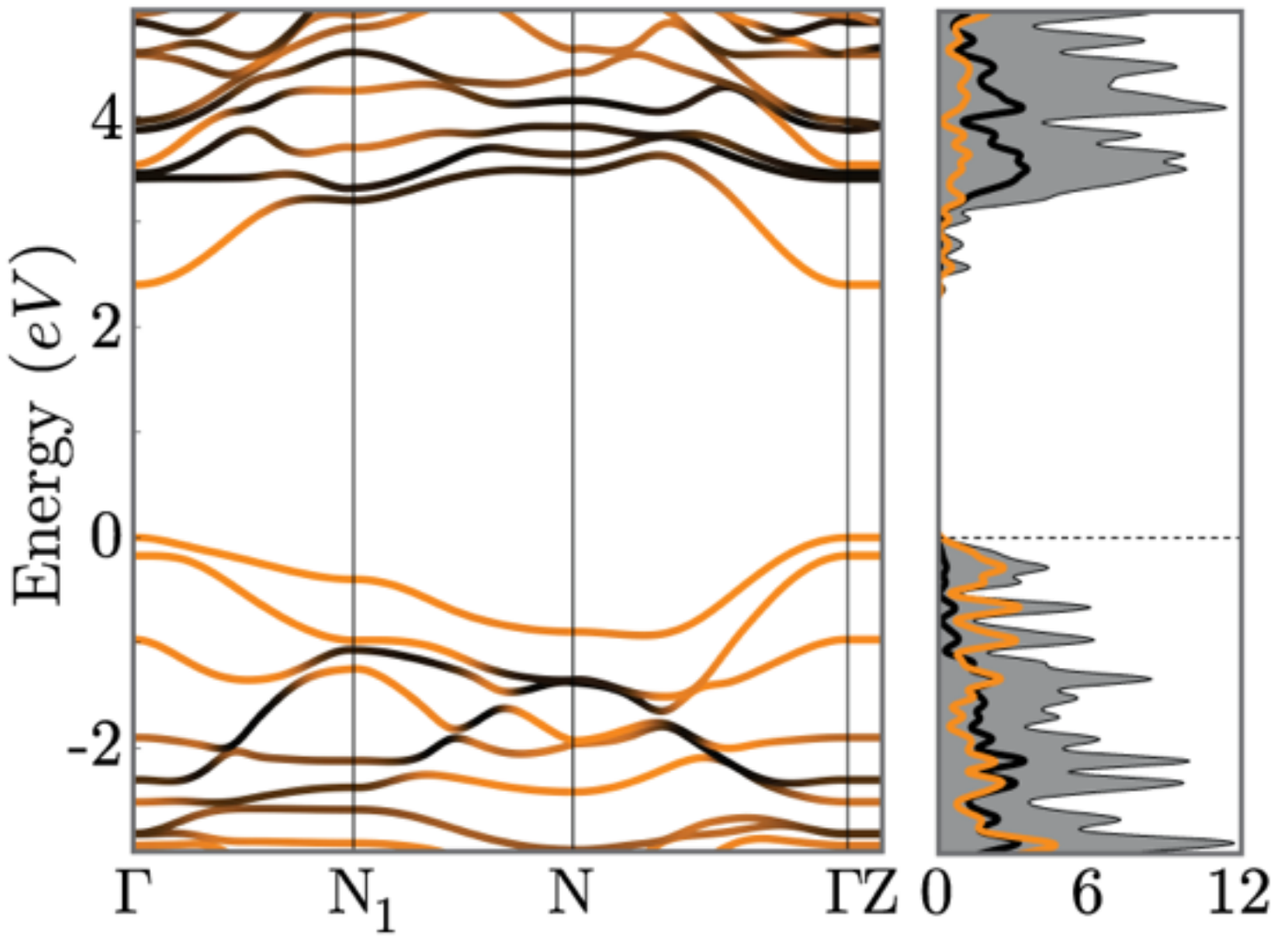
electronically

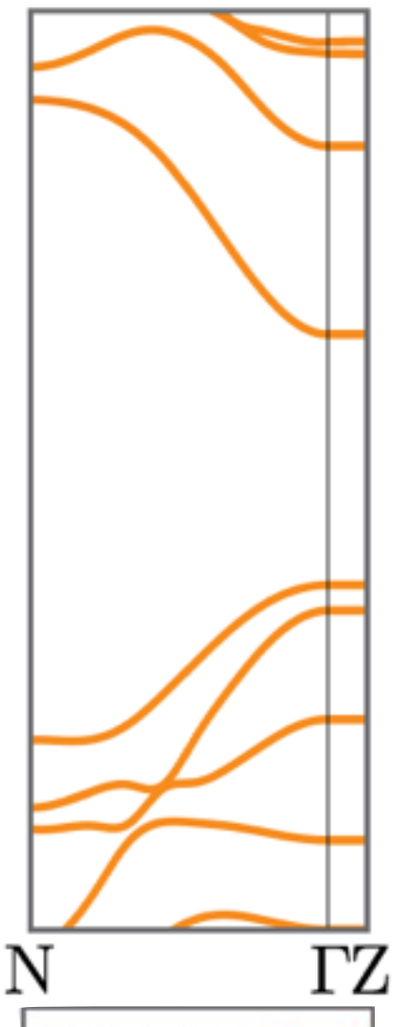
≈











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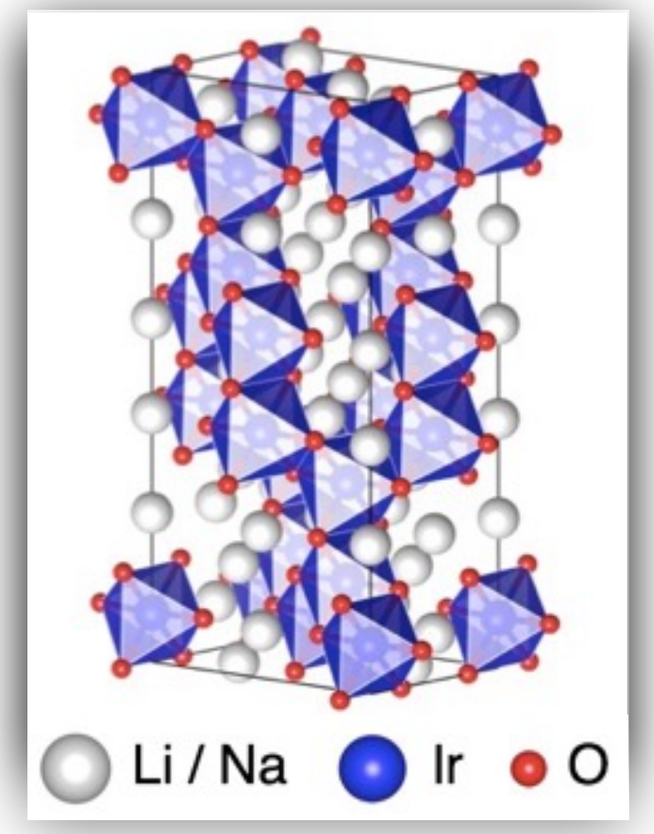
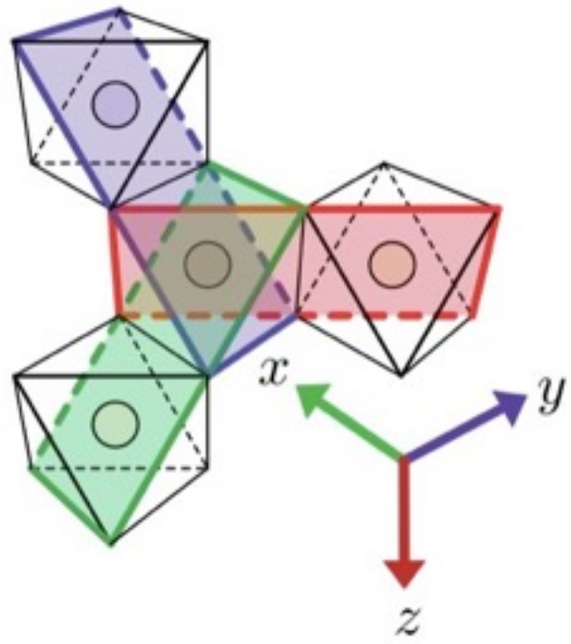
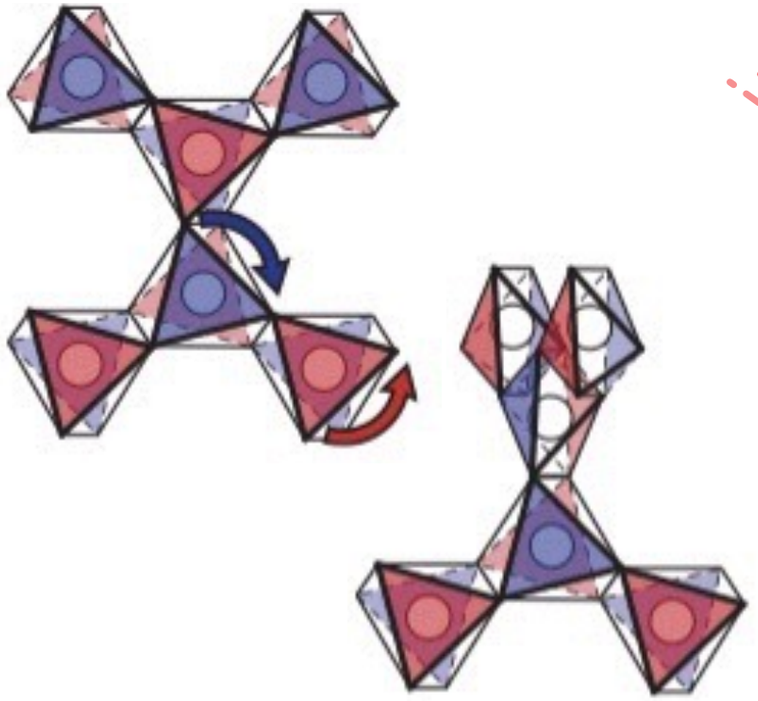
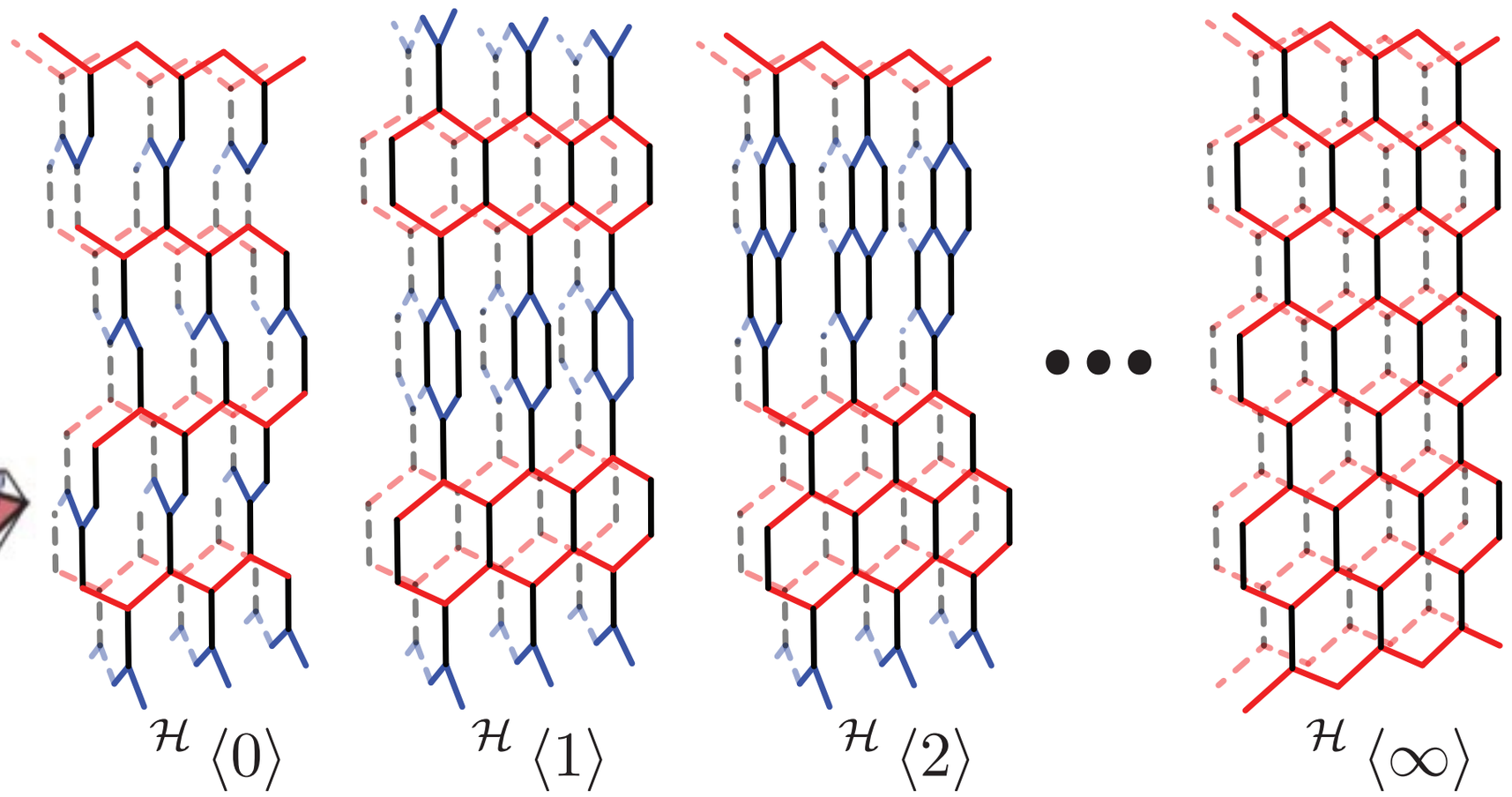






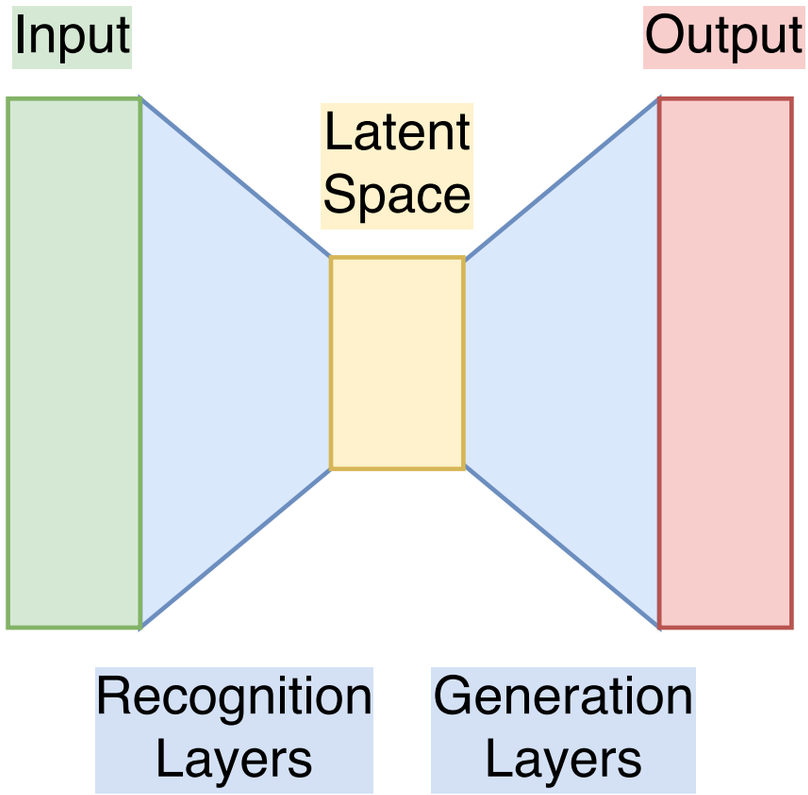


Deep Generative Models for Materials Design

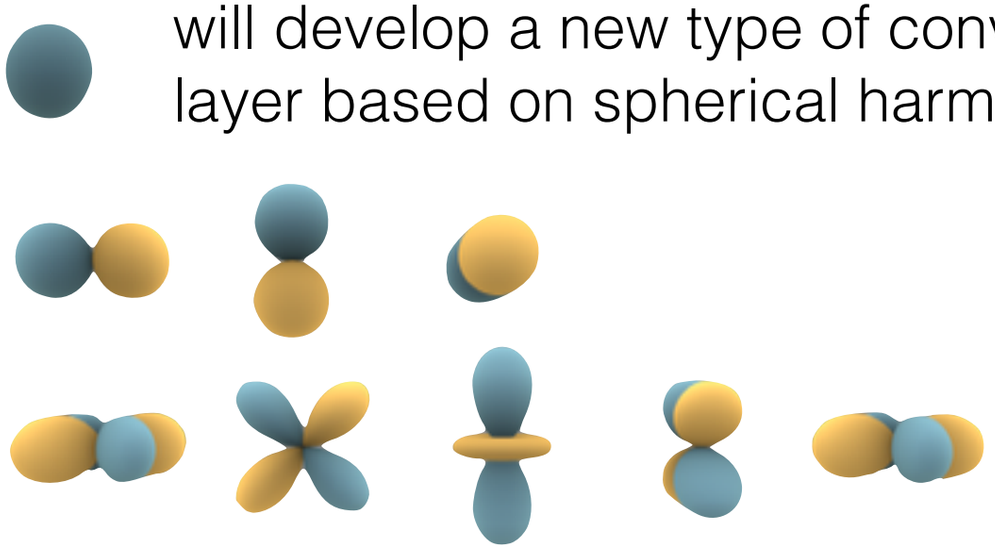
Can we train an autoencoder to learn chemical motifs and generate new material structures?

Want

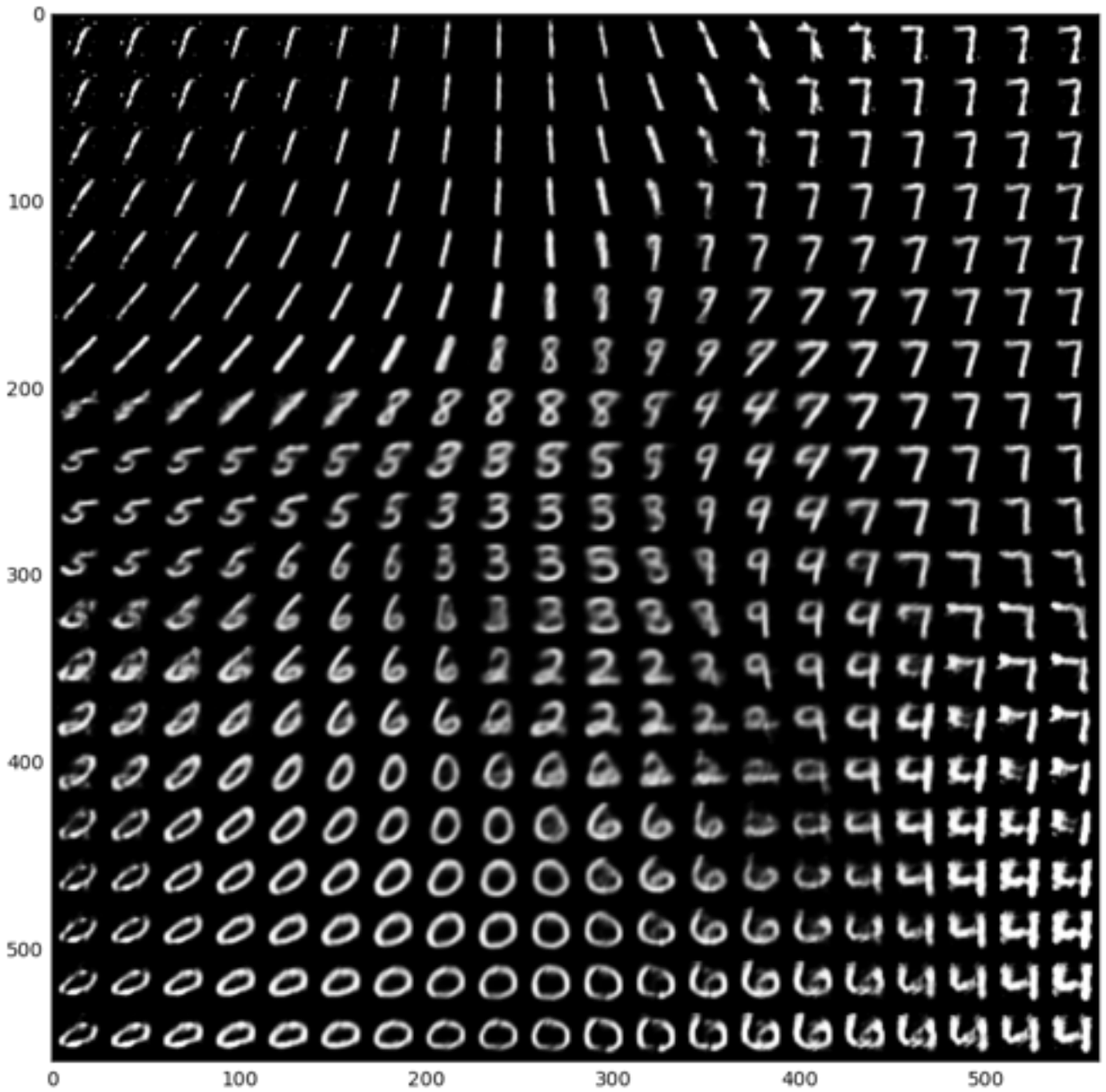
Input = Output



To encoder local rotation invariance, we will develop a new type of convolutional layer based on spherical harmonic filters.



2 dimensional latent space for autoencoder trained on MNIST handwritten digit images

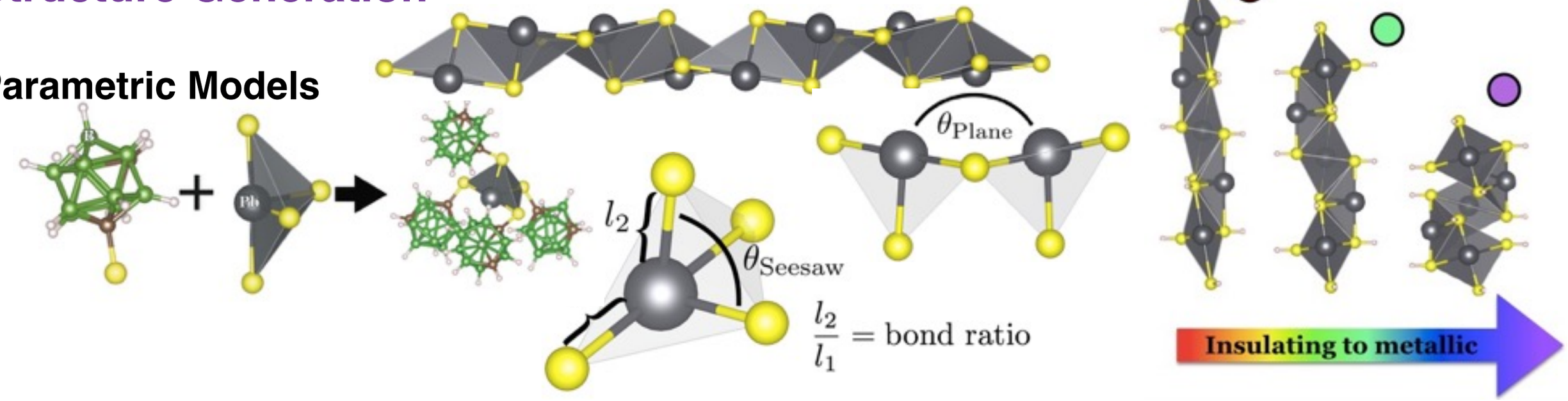


VAE Tutorial: https://jmetzen.github.io/2015-11-27/vae.html

We want to learn a smooth latent space where similar atomic structures are close together and interpolations are meaningful.

Structure Generation

Parametric Models



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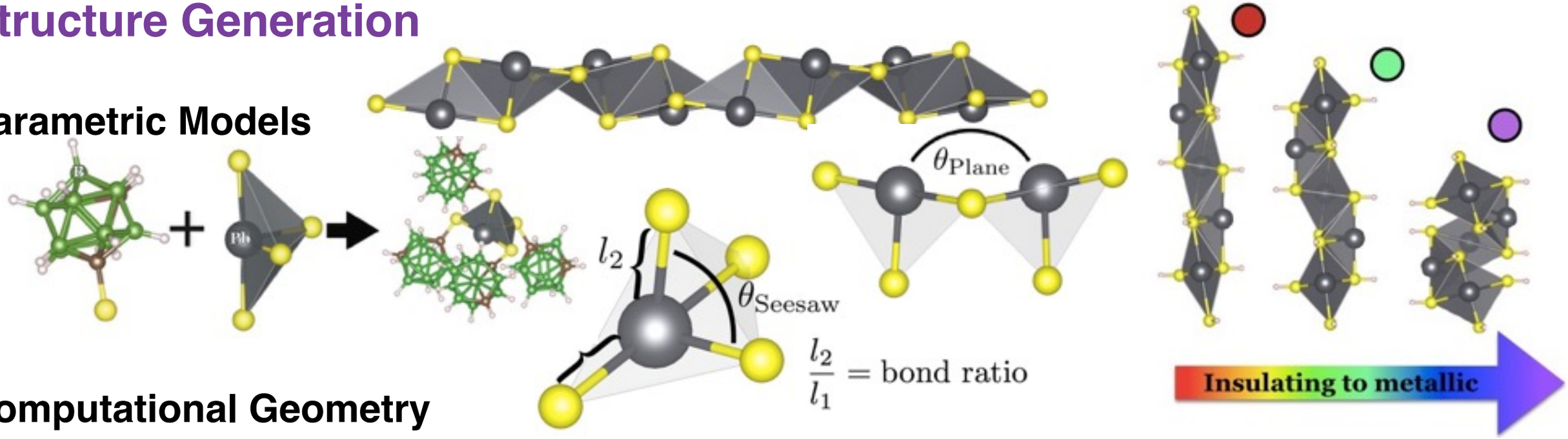
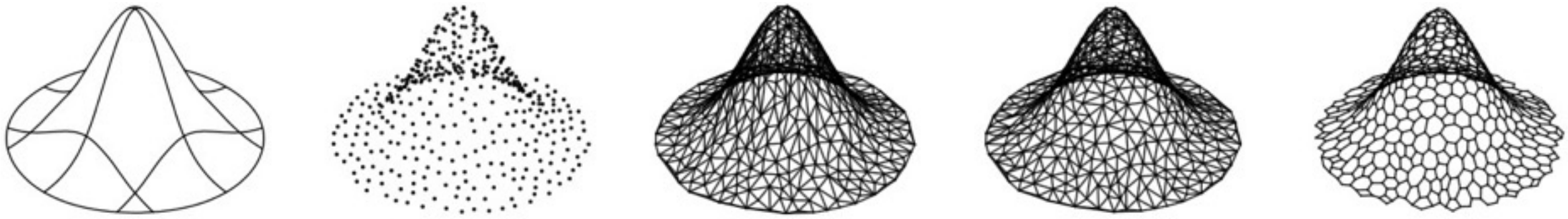


Computational Geometry



Surface

Randomly Populated Points

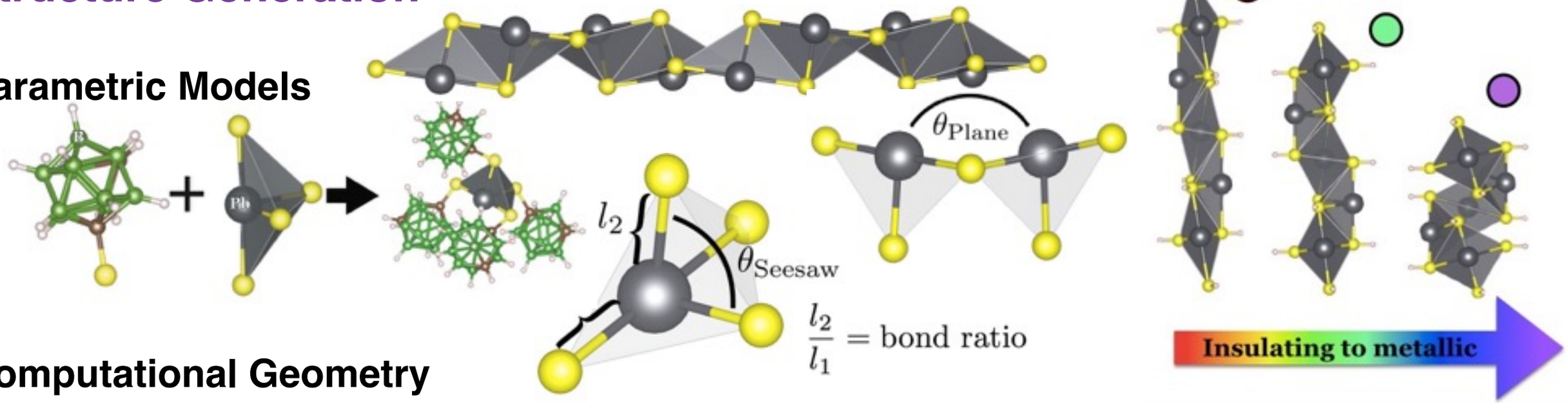
Isotropic Delaunay Triangulation

Anisotropic Delaunay Triangulation

Dual

Structure Generation

Parametric Models



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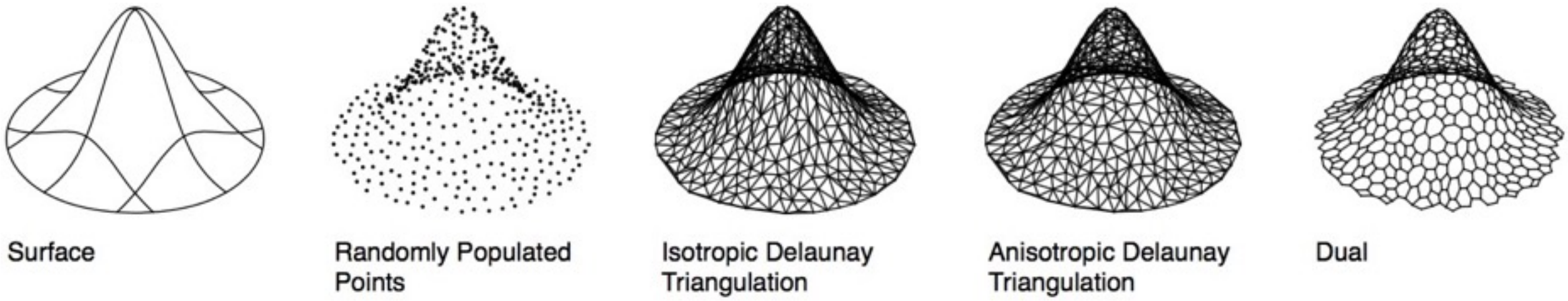

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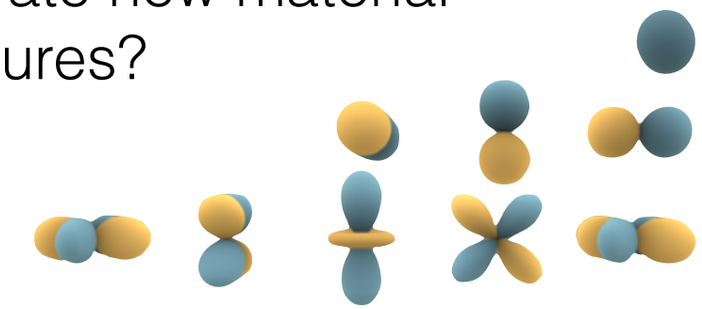
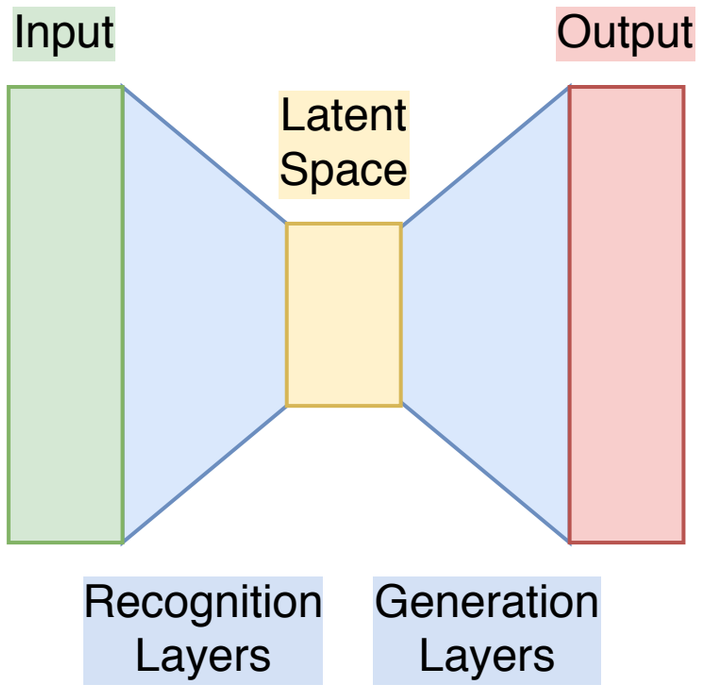
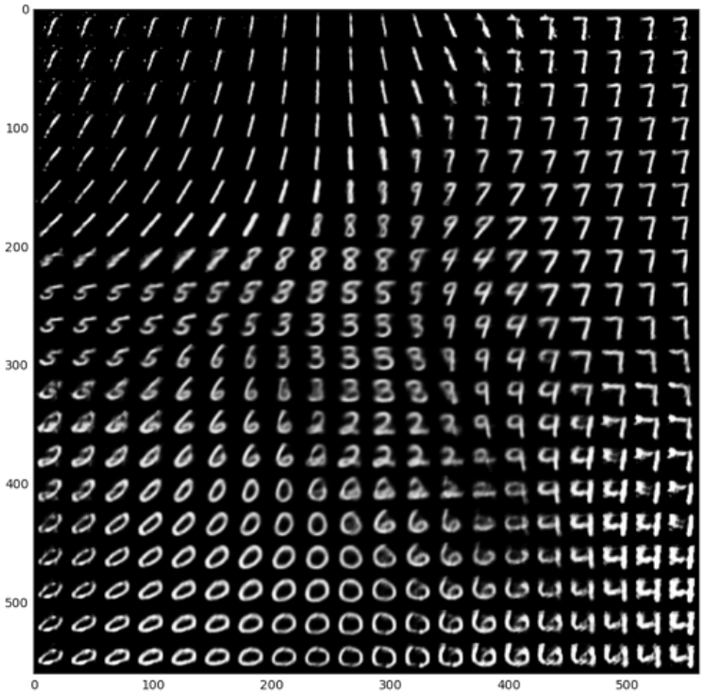
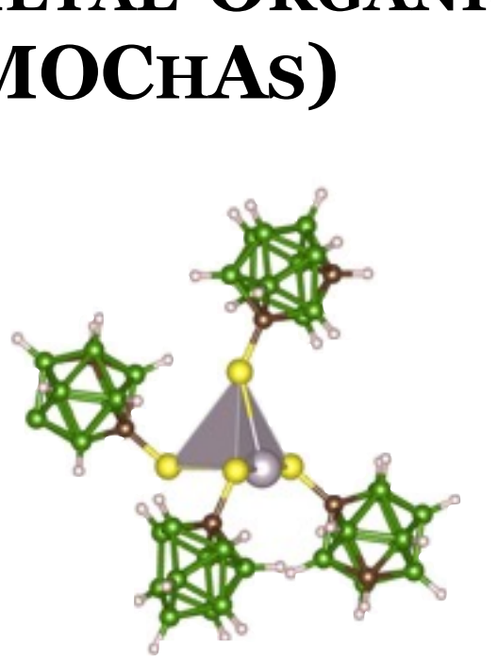
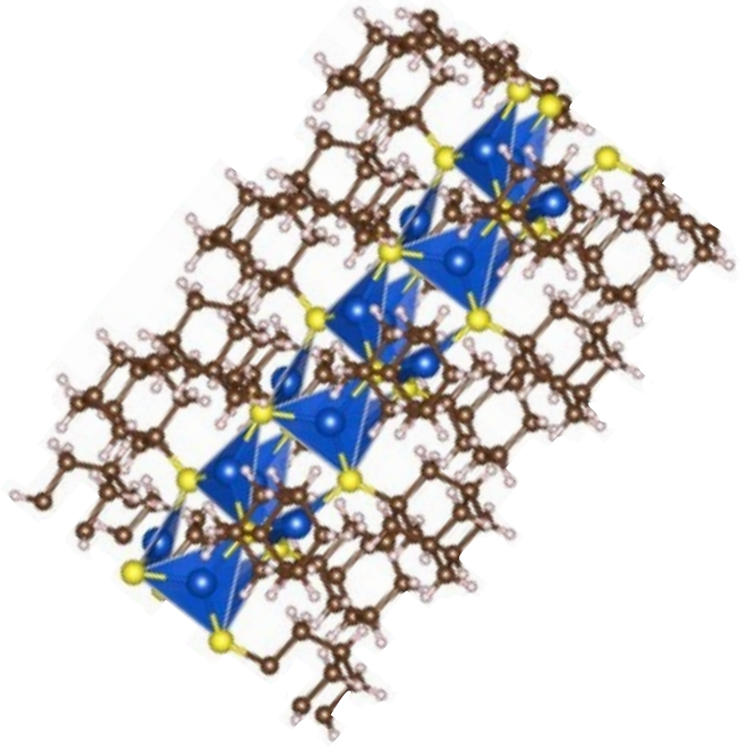


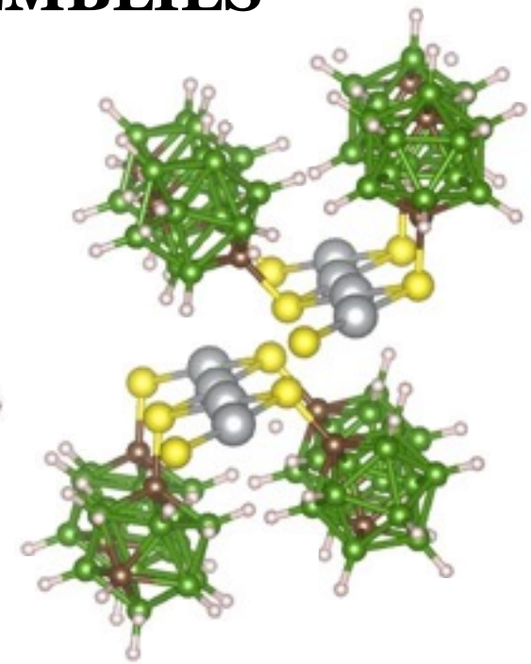


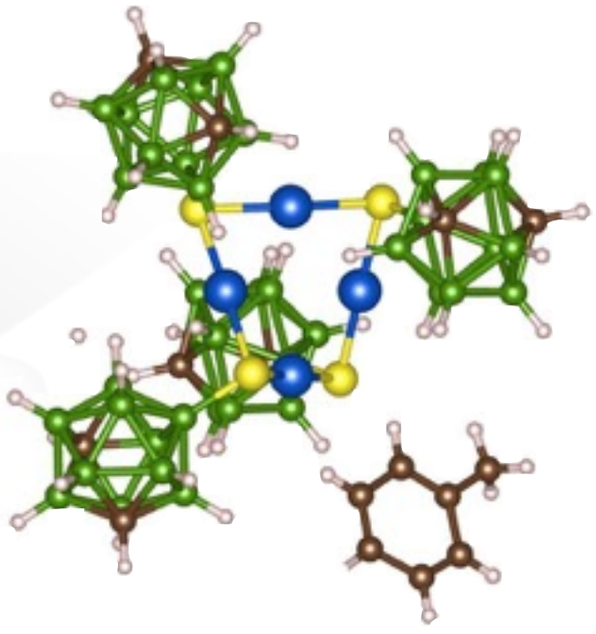


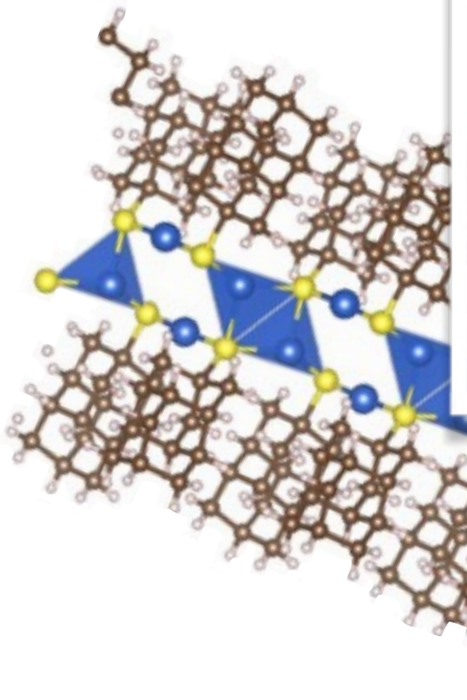
Geometry and Electronic Structure of Metal-Organic Chalcogenide Assemblies (MOChAs)

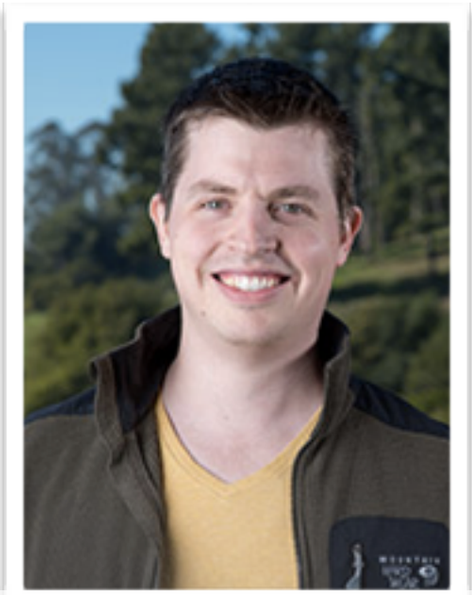




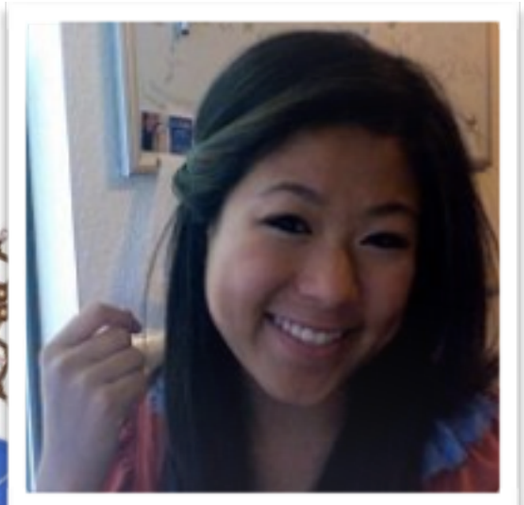








Nate Hohman

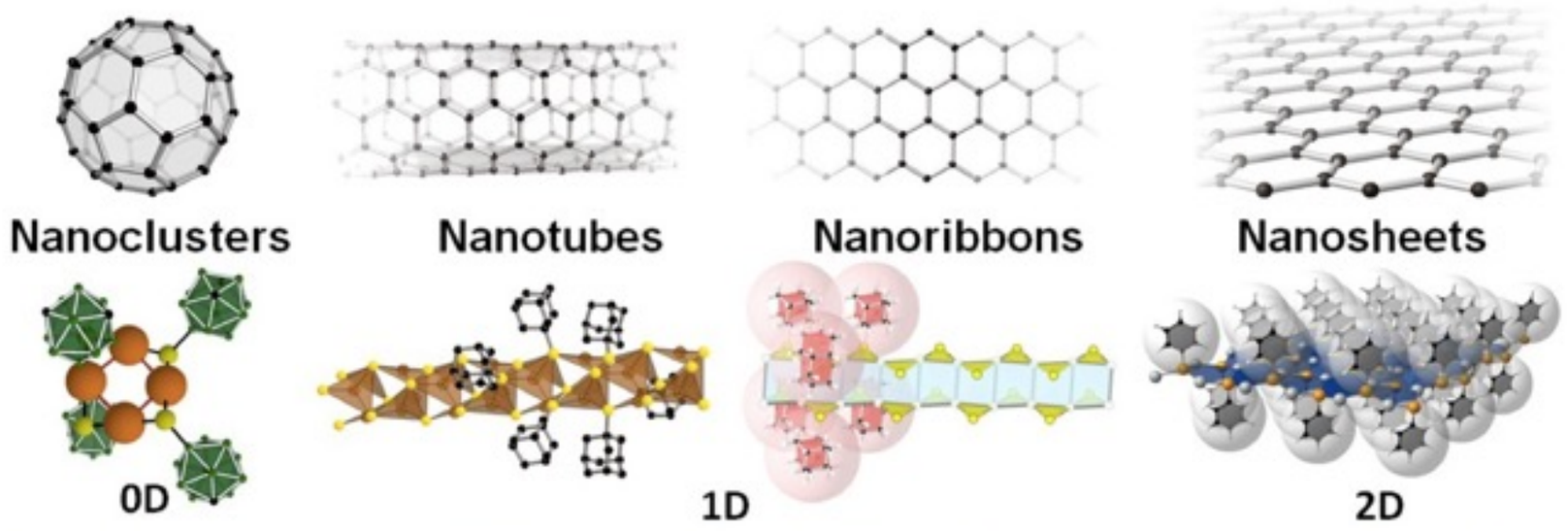


Mary Collins

MOLECULAR FOUNDRY

WHY MOCHAS?

The inorganic structure is continuous, low-dimensional, and <u>dominates electronic structure.</u>



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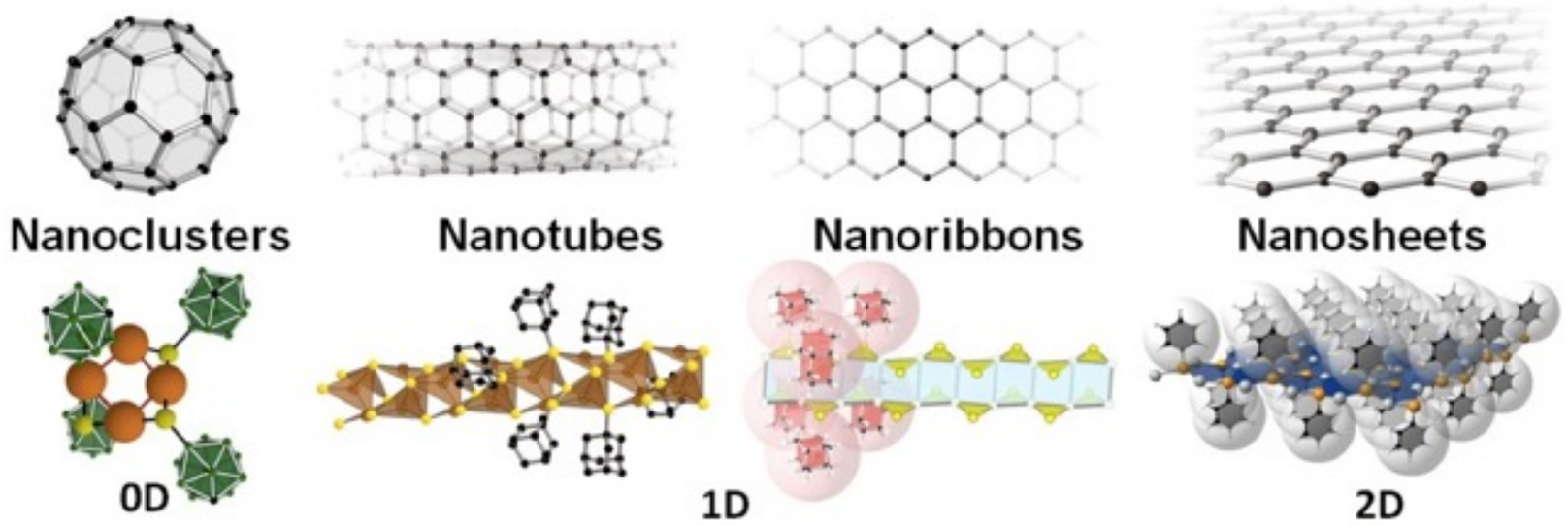
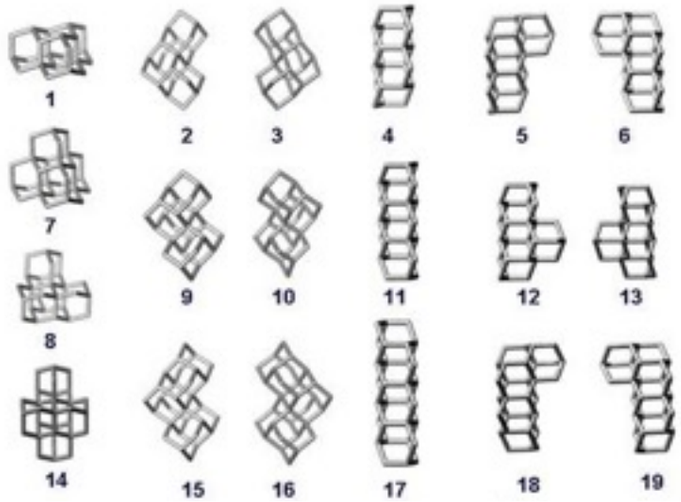
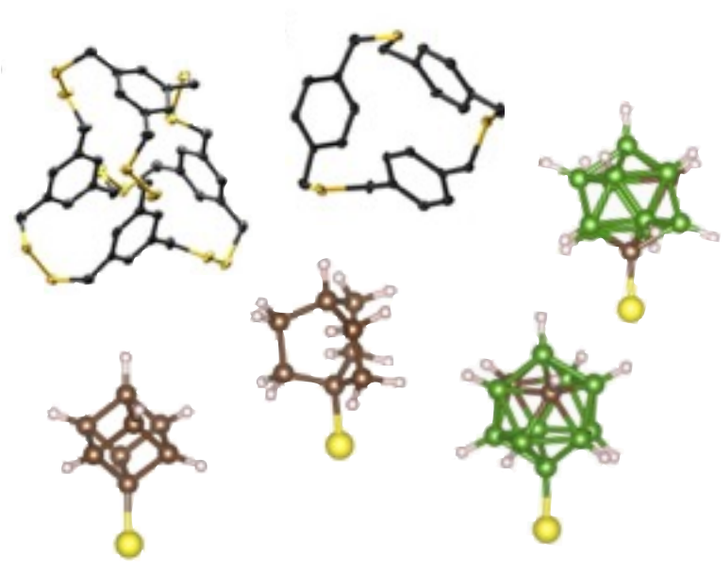


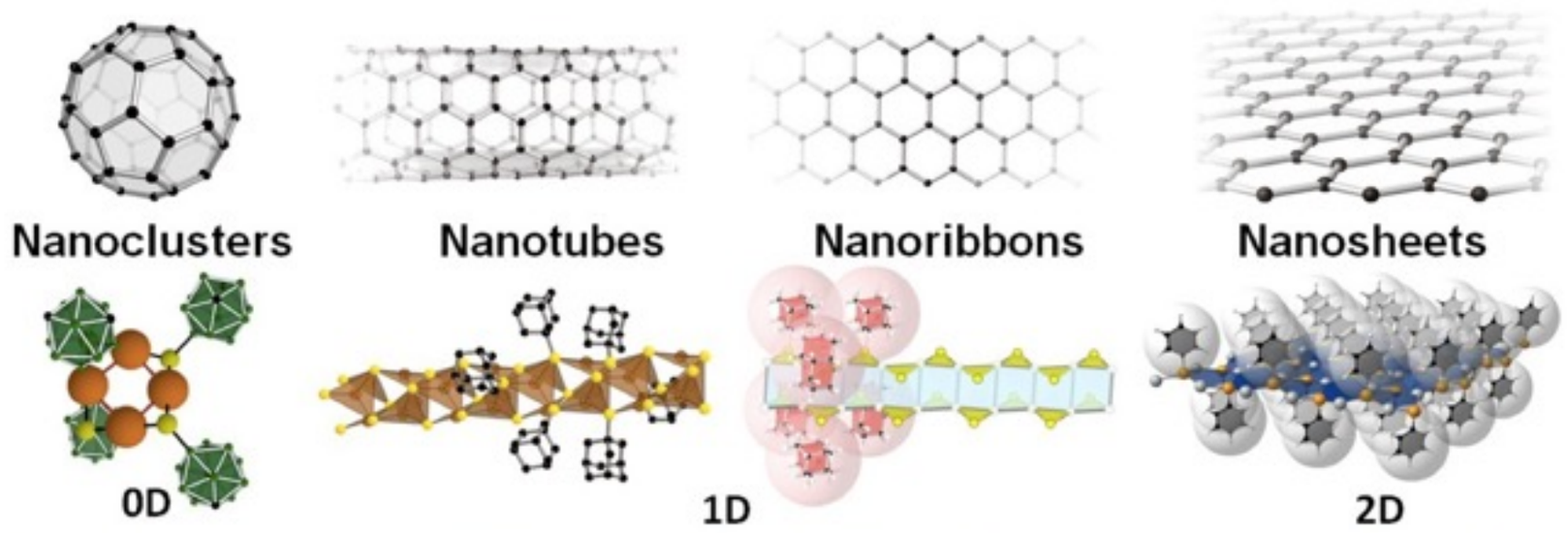
Organic ligands provide scaffolding for inorganic structure. Provides immense tunability.



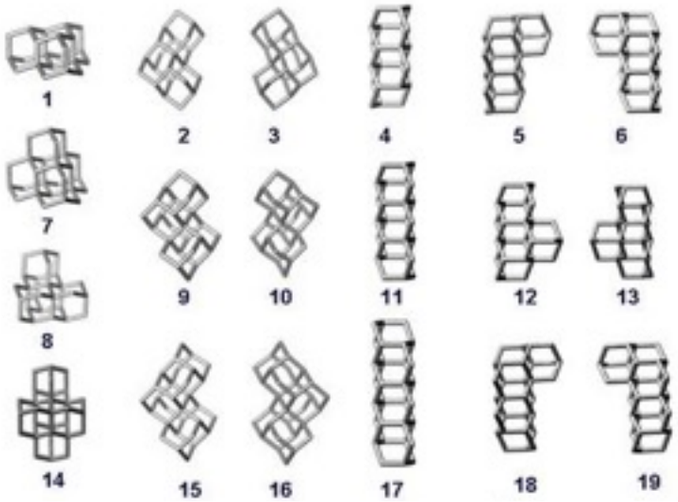


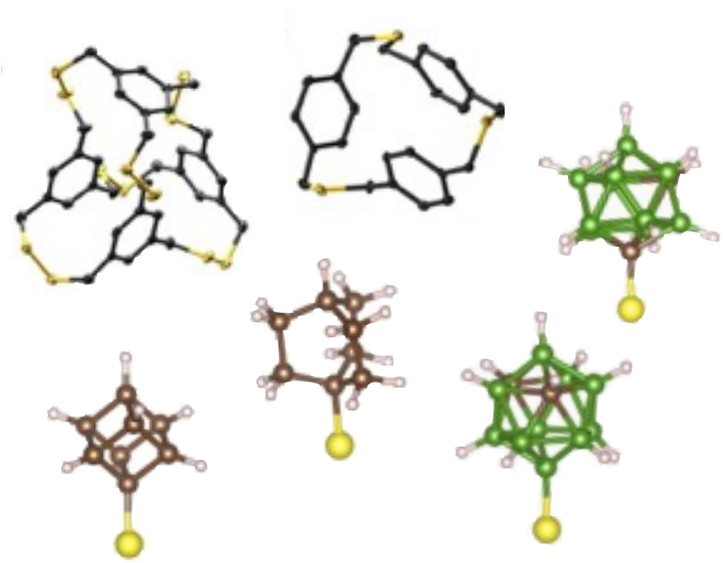
WHY MOCHAS?

The inorganic structure is continuous, low-dimensional, and <u>dominates electronic structure.</u>



Organic ligands provide scaffolding for inorganic structure. Provides immense tunability.

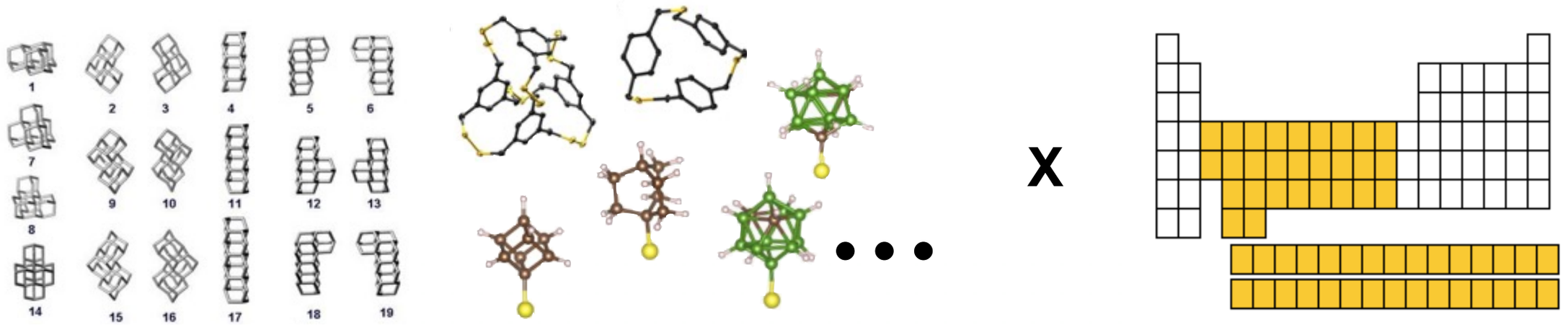




MOChAs self-assemble and can be synthesized at gram scale or as thin films.

How to design MOChAs?

Given ligand X and transition metal Y? ➜ Combinatorial explosion!

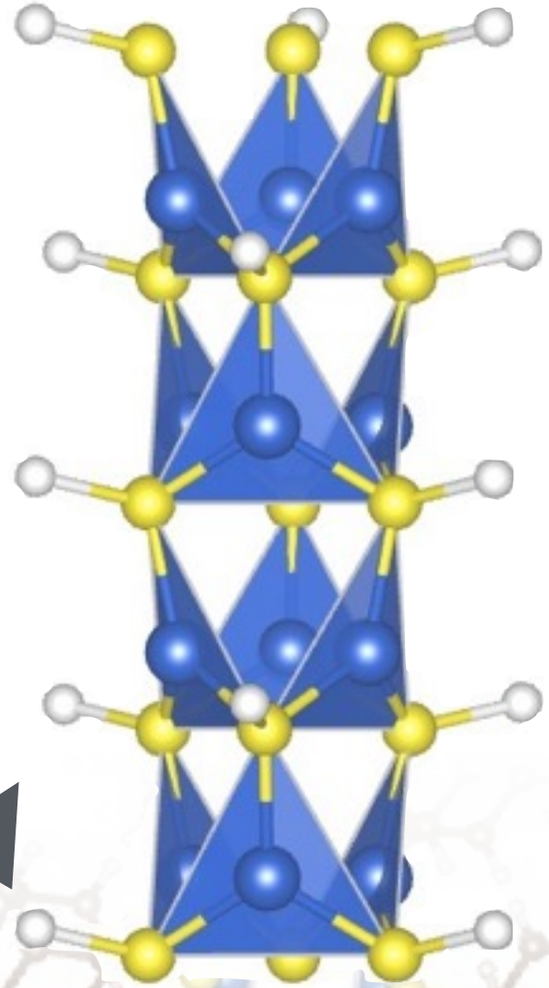


How to design MOChAs?

Simplify problem by first focusing on design of inorganic structure.

Can we explore the low-dimensional inorganic structure independent of bulk?

- How much do VdW bonded subunits interact?
- How much does the ligand impact bands near the Fermi level?



How to design MOChAs?

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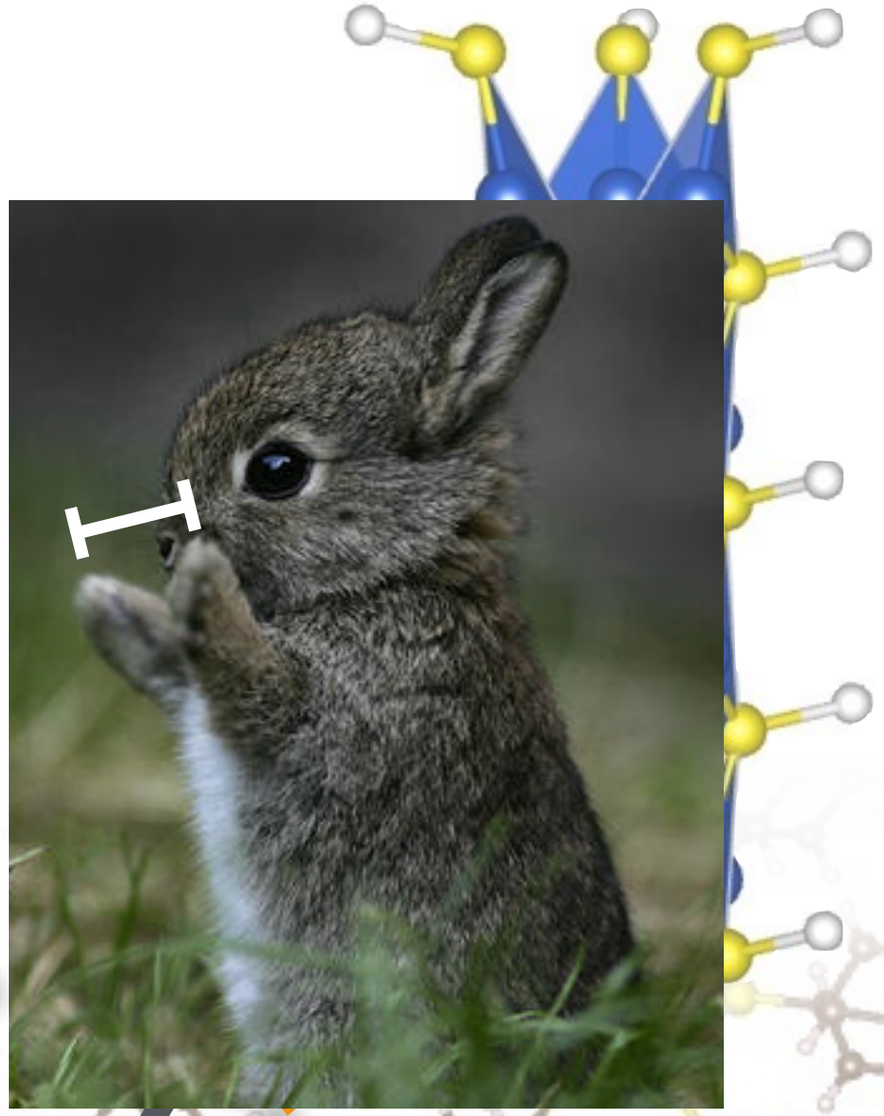
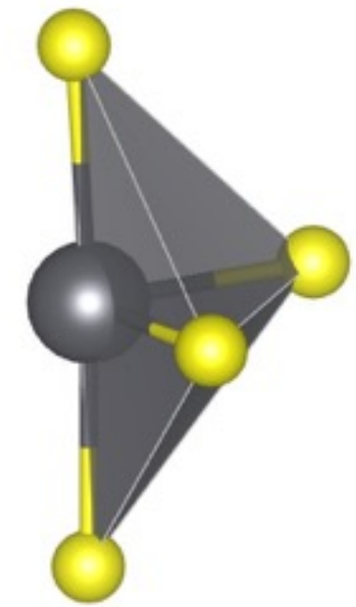
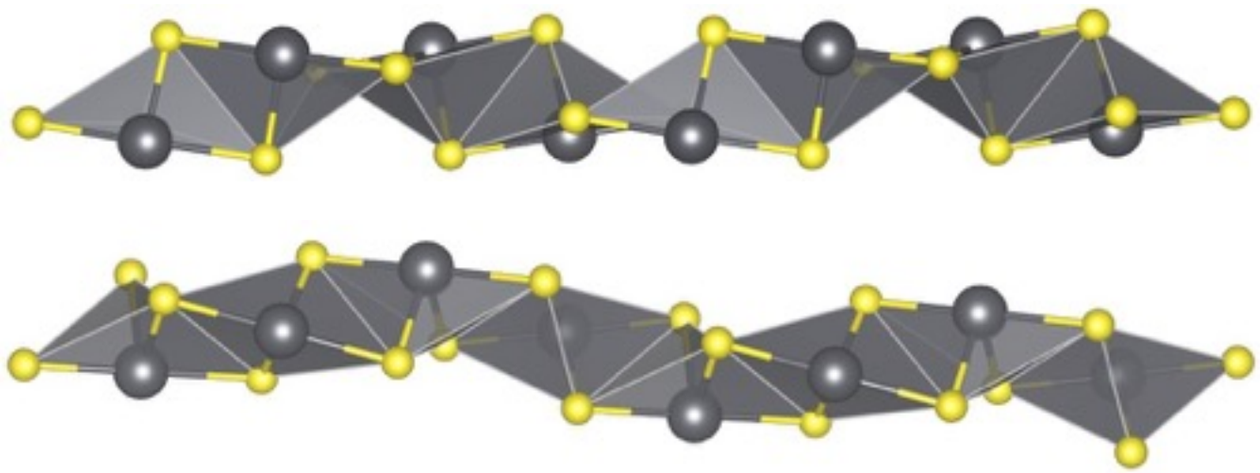


GEOMETRY CASE STUDY:
Pb Seesaw chalcogenide chains

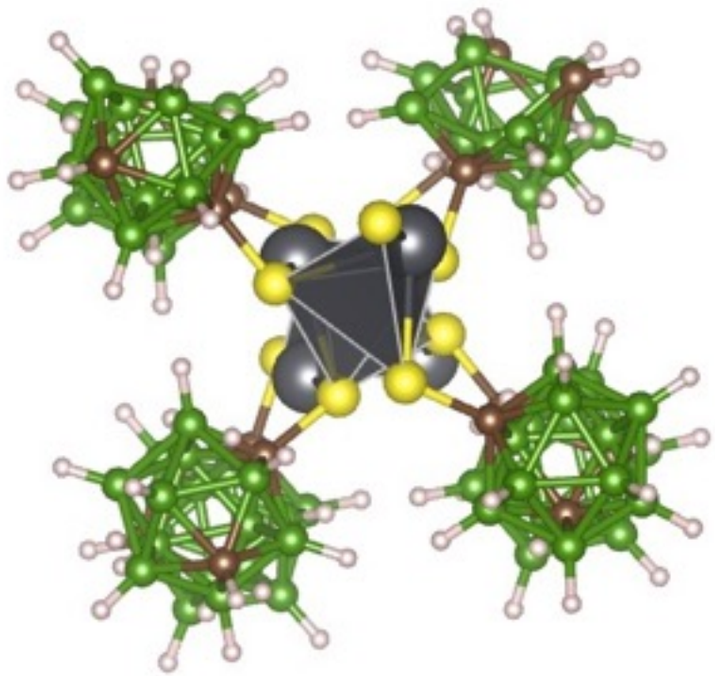
Seesaw units. Pb and S.



Chiral



C-S bonds. Carboranes coordinating chalcogenide chain.



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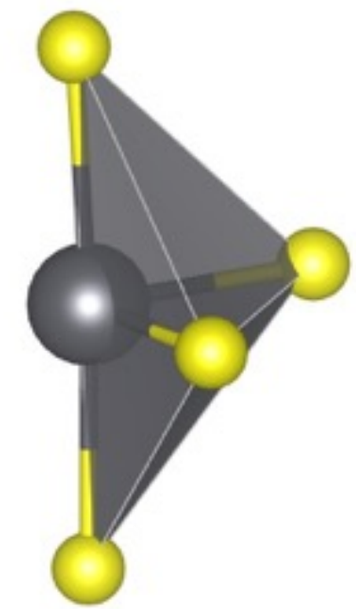
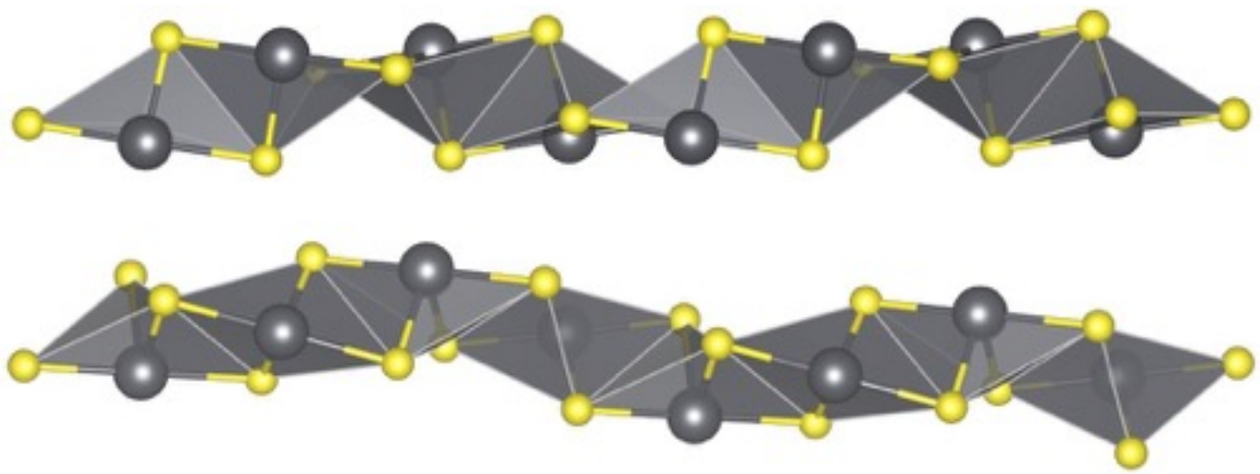
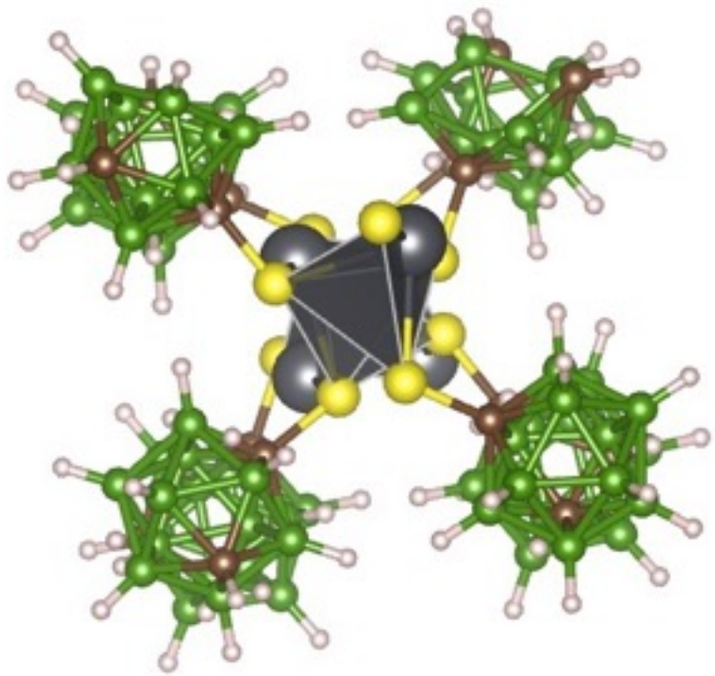
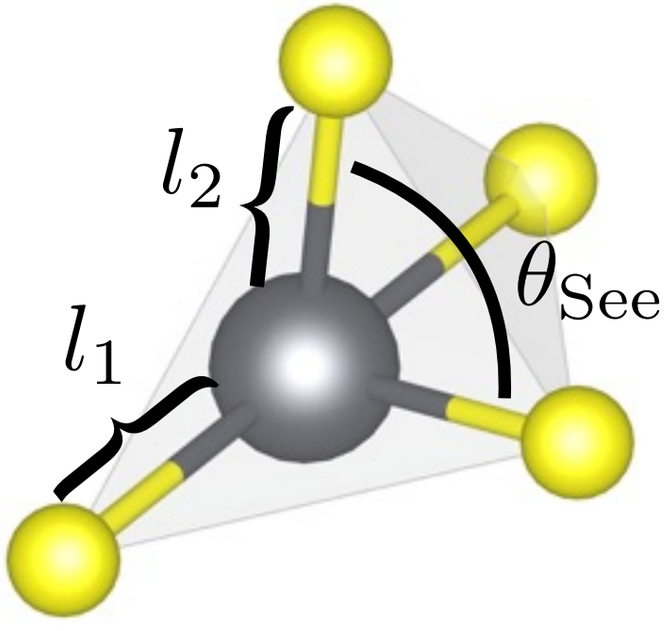


Chiral

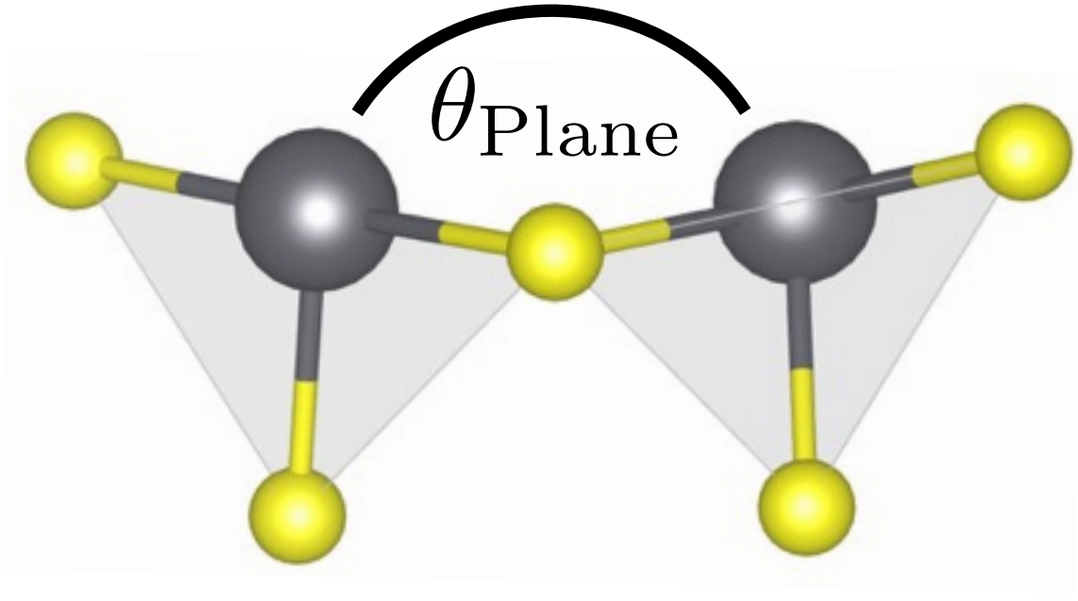




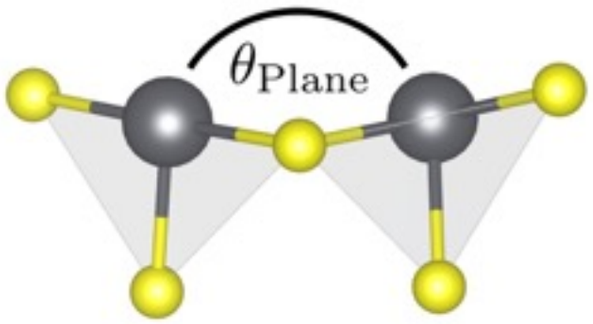
Parameterize structure by two intra-unit parameters and one inter-unit parameter.

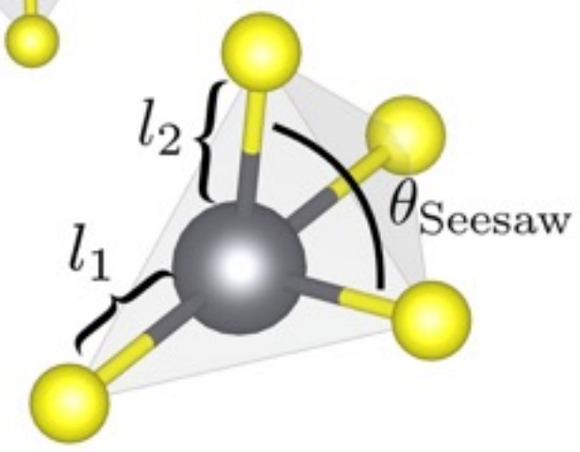


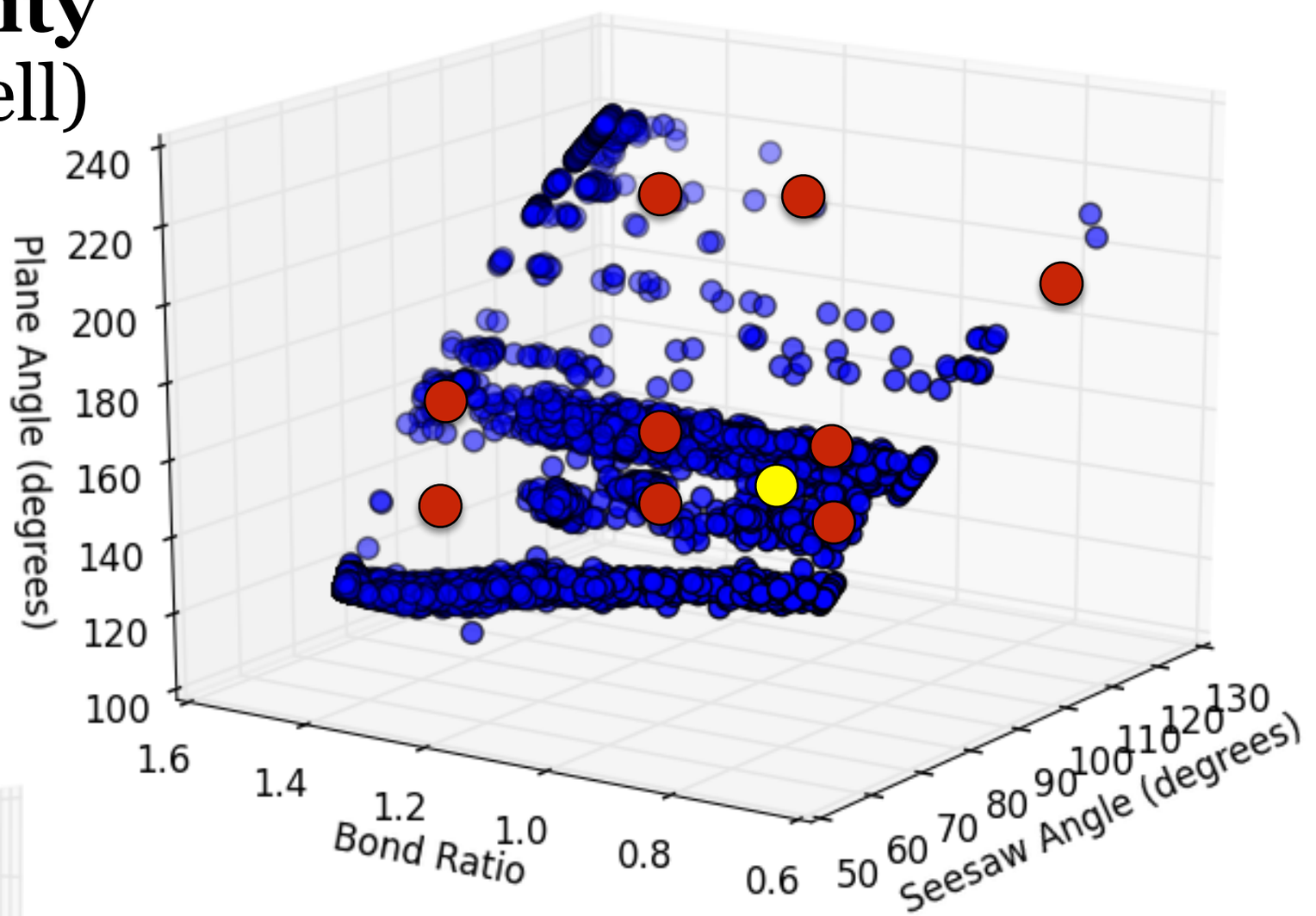
$$\frac{l_2}{l_1} = \text{bond ratio}$$

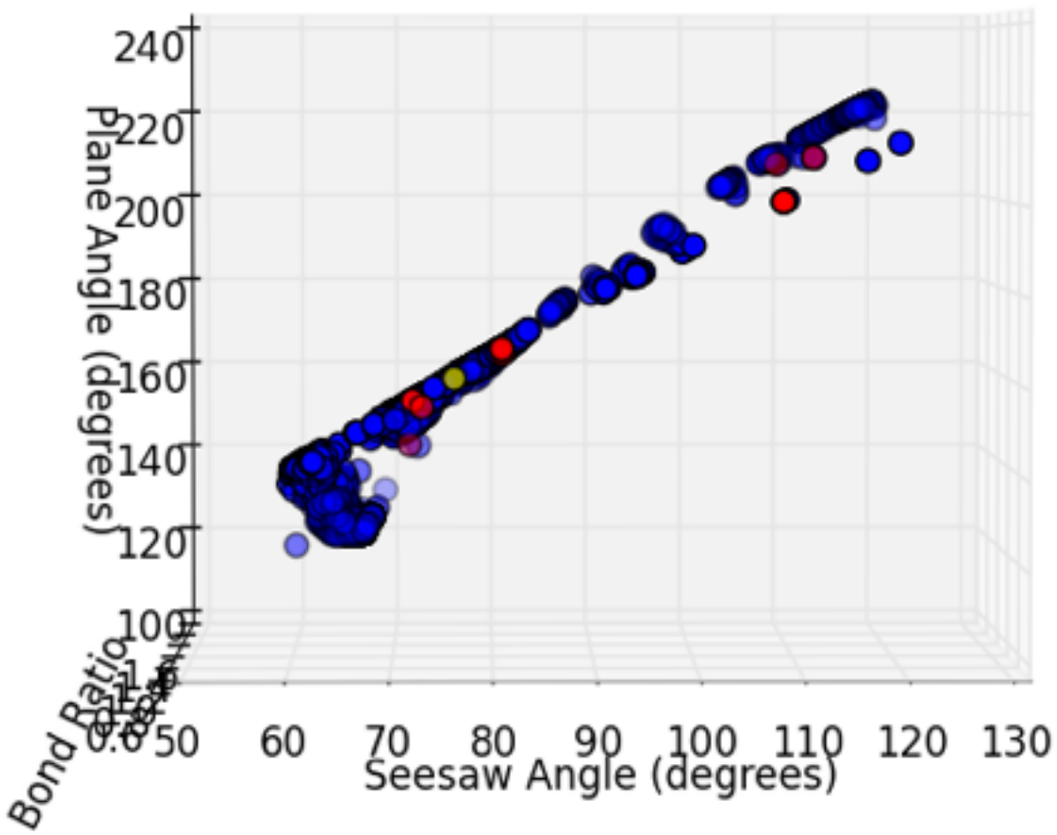


Optimize for periodicity
(ex: 4 tetrahedra / unit cell)





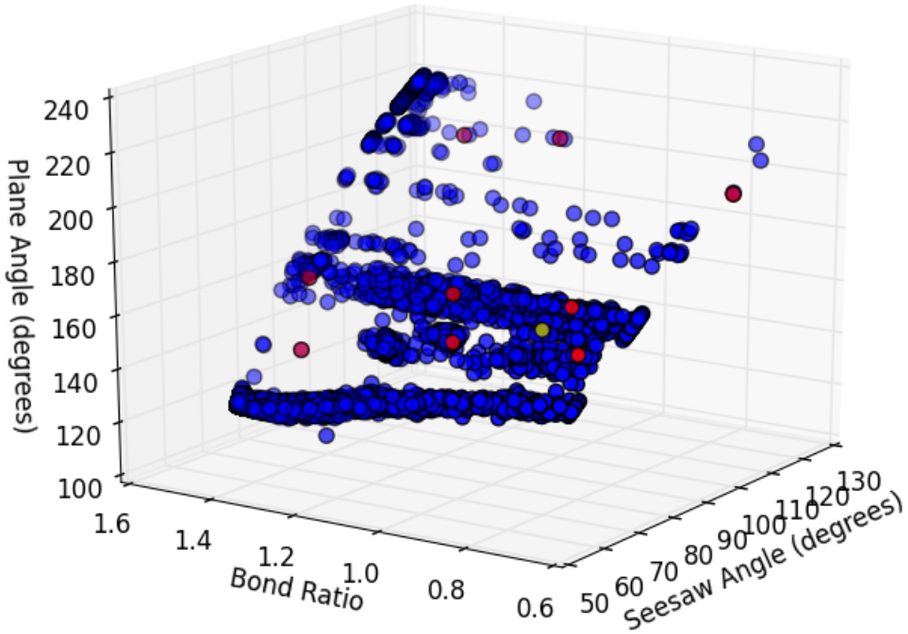




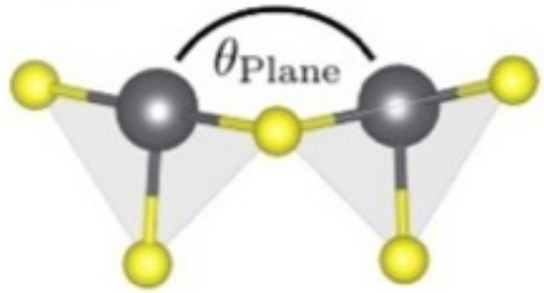
Yellow closest to exp. values

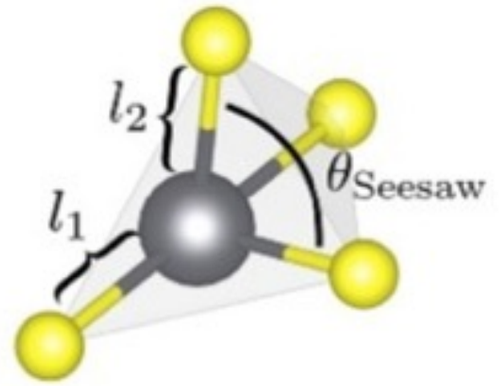
Red structures calculated

Blue other structures periodic with 4 tetrahedra

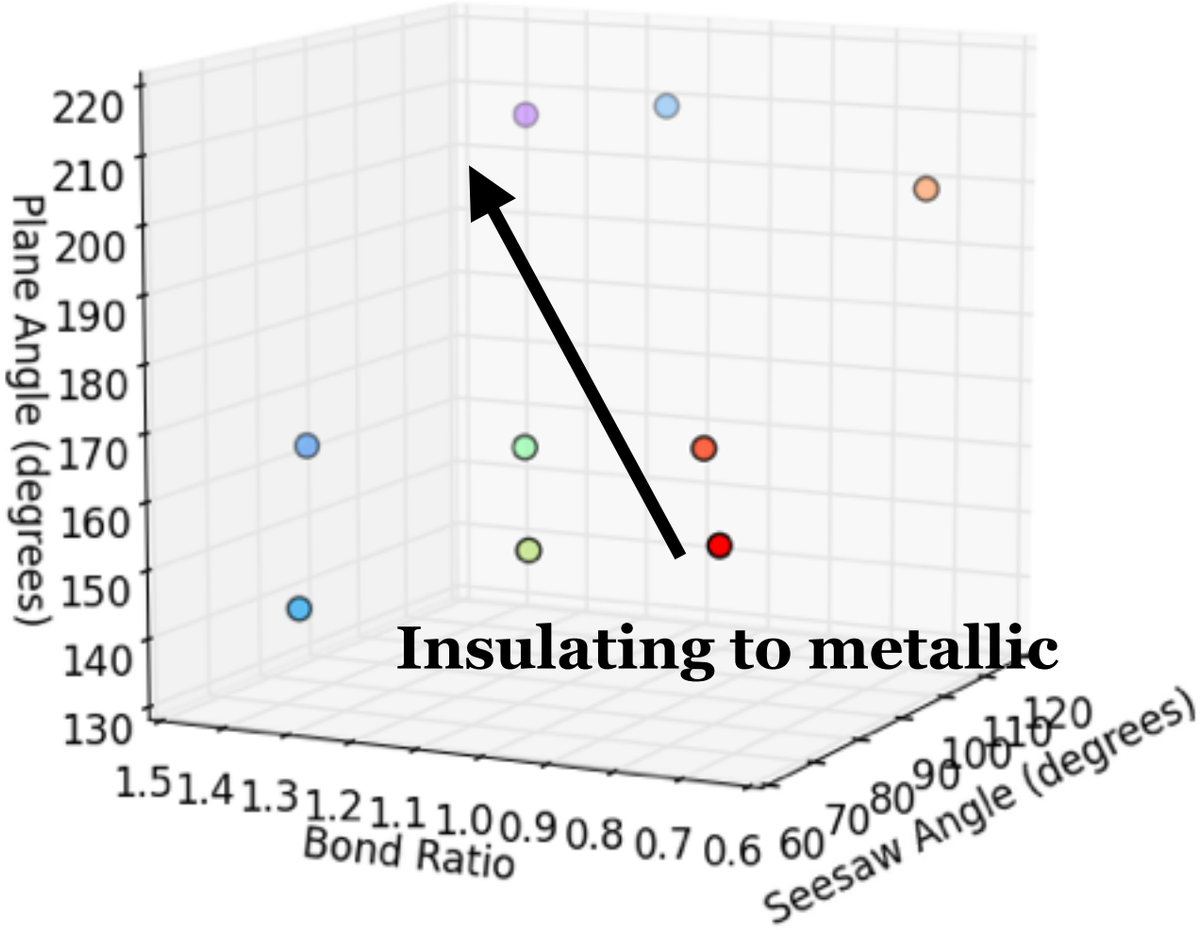


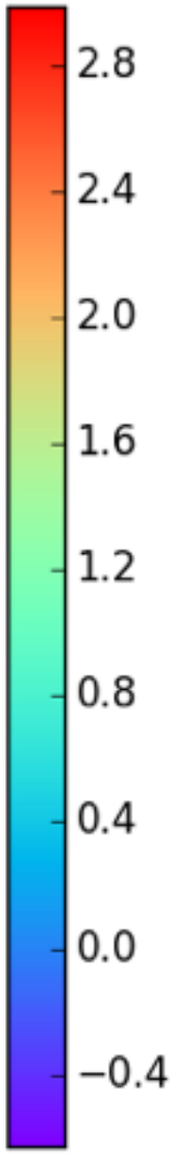
Biggest changes in electronic structure are driven by changes in bond lengths.

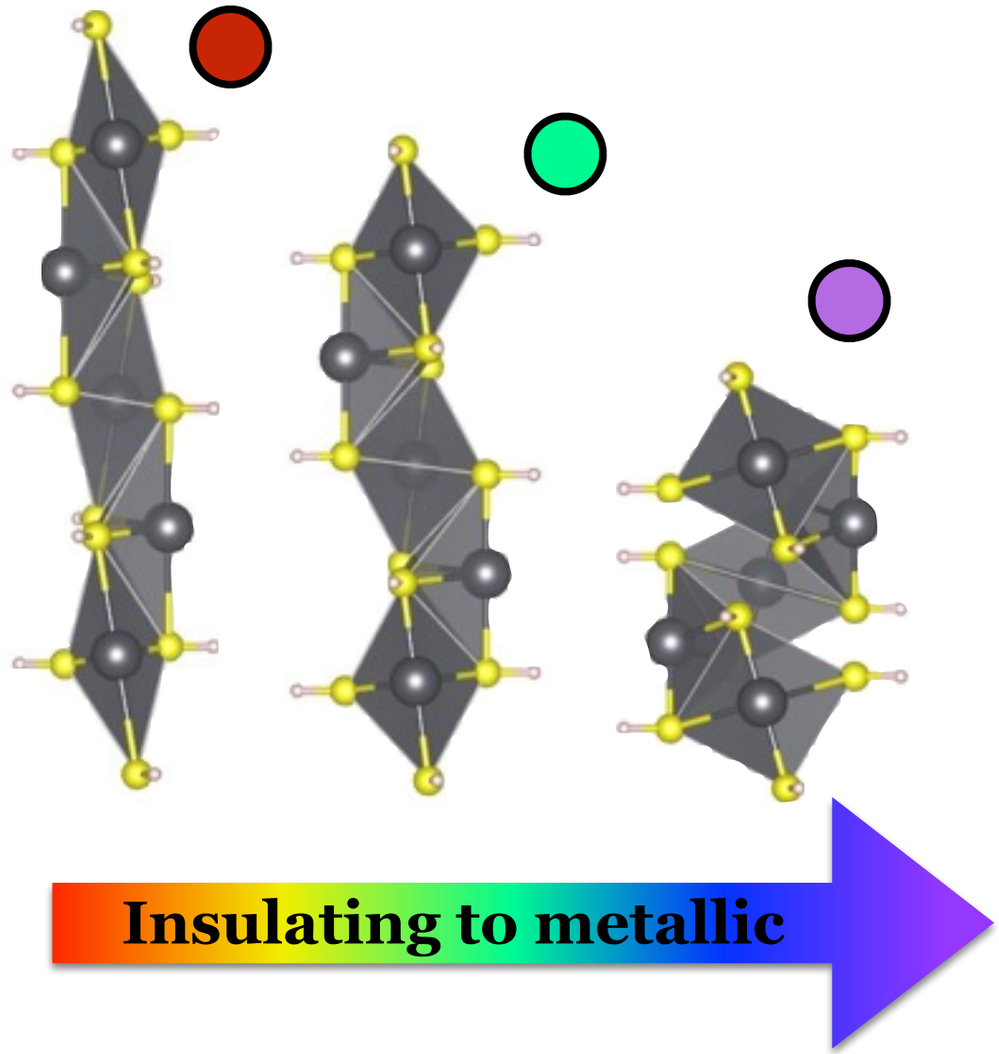




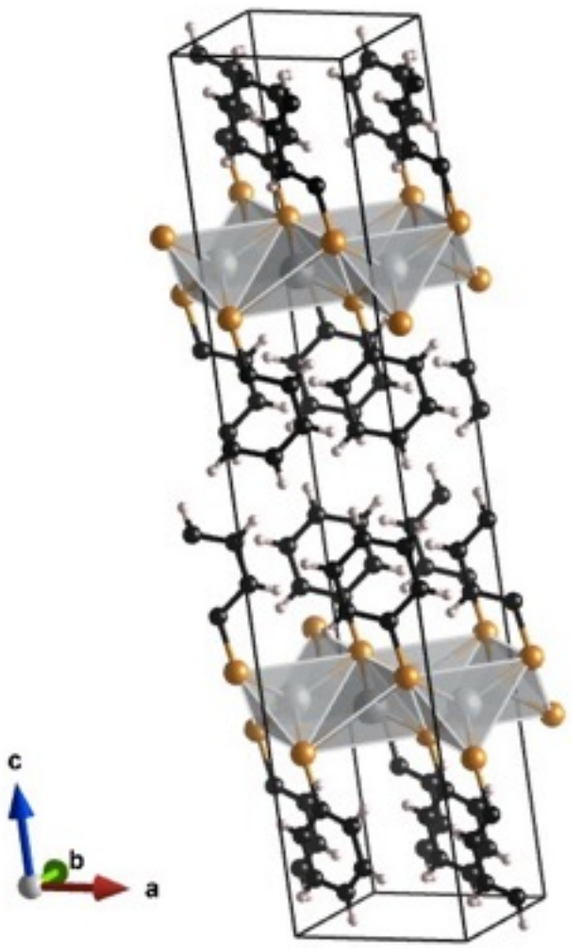
Band Gap (eV) [LDA]

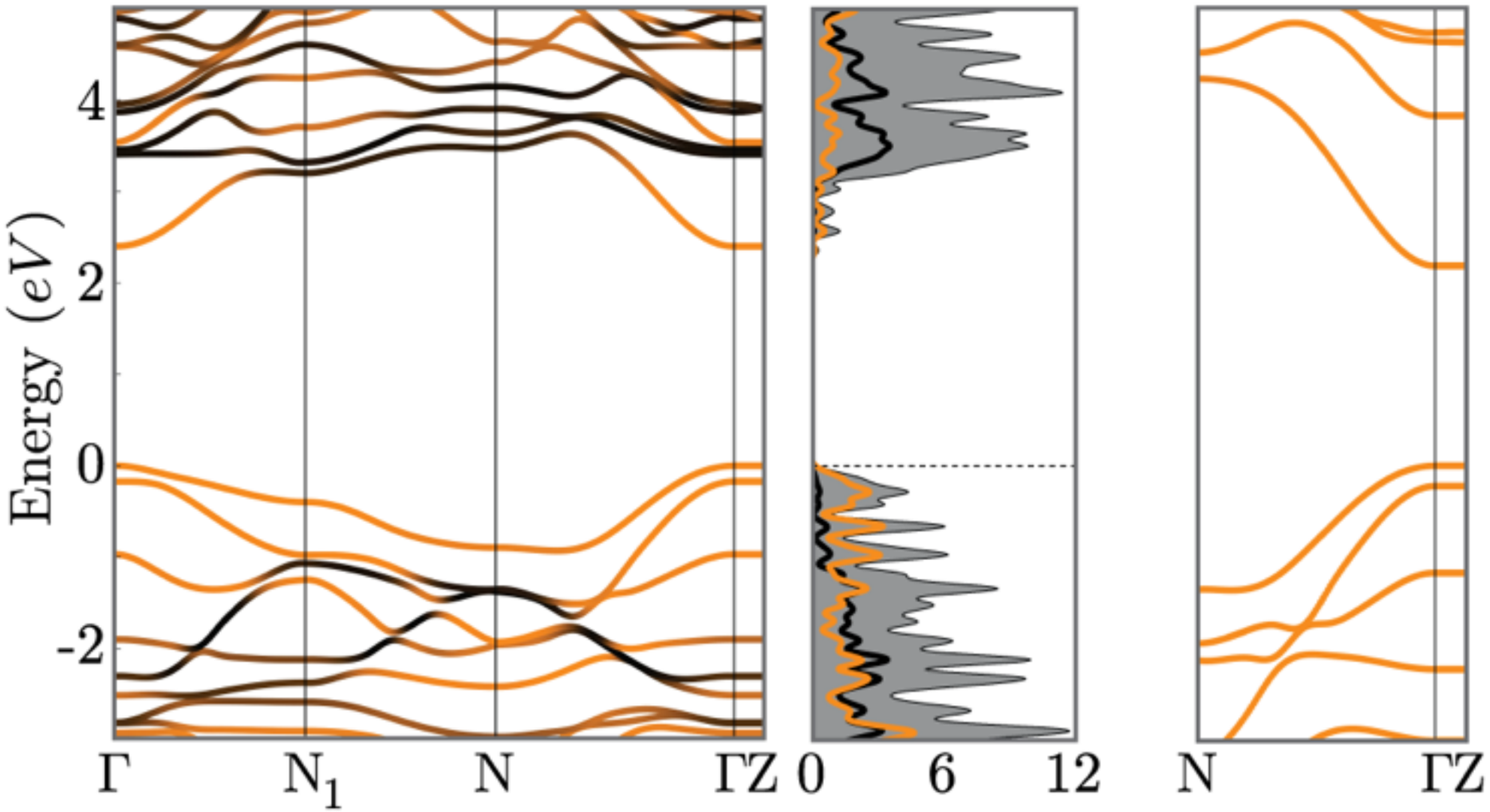


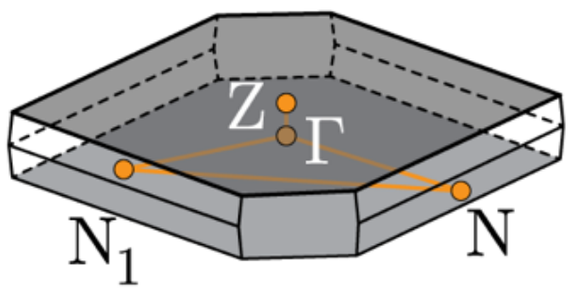




AgSePh ("Mithrene")

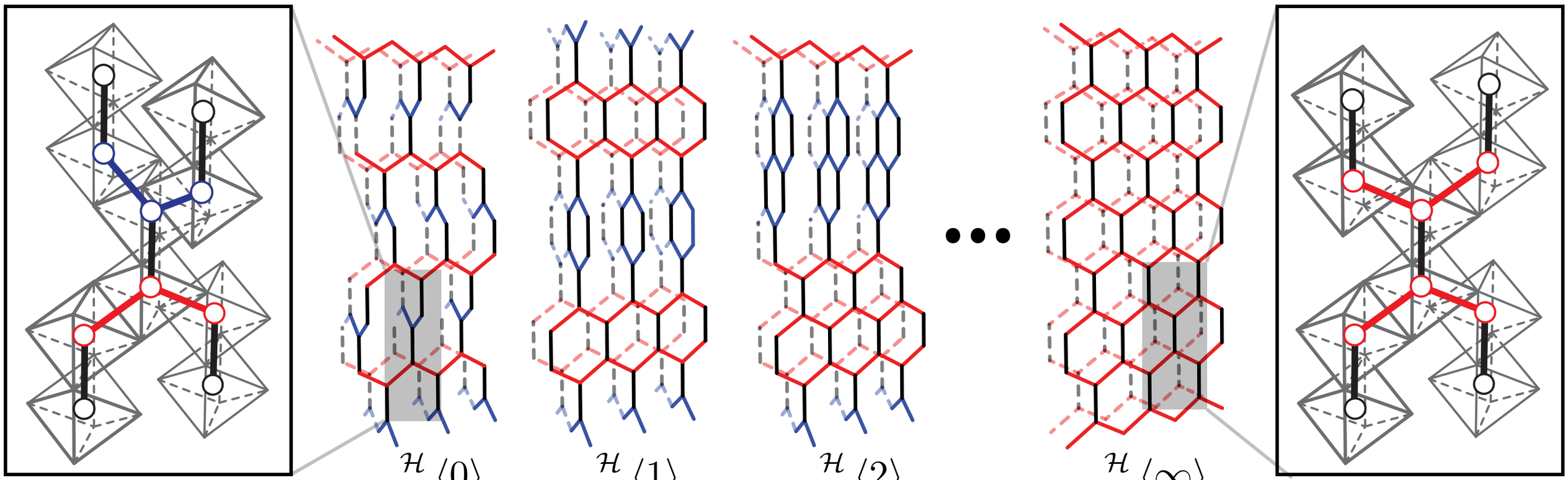






- Direct band gap at Γ.
- Organic bands and inorganic bands are well separated.
- Low mobility between layers.
- At the level of DFT with short-range exchange (HSE), layers no difference between single layer and bulk.

Ab initio Studies of Structural and Energetic Trends in the Harmonic Honeycomb Iridates: Li_2IrO_3 and Na_2IrO_3



Background

These materials host anisotropic quantum magnetism and interactions that may lead to a spin liquid.

They have complex magnetic orderings.

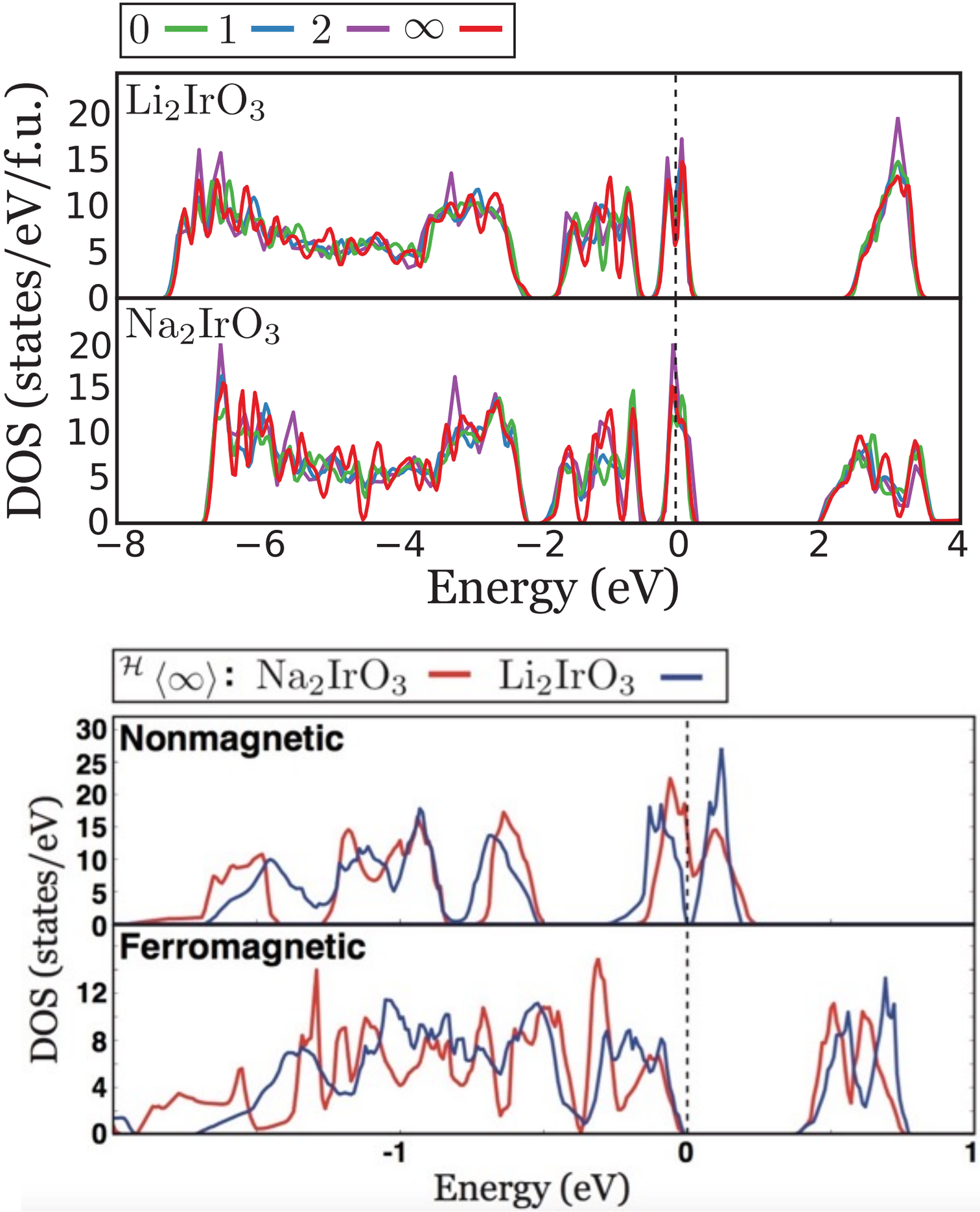
0, 1 and ∞ have been synthesized for Li_2IrO_3 and ∞ has been synthesized for Na_2IrO_3.

Results

Using DFT calculations at the level of PBE+SOC +U, we find the **homologous series is energetically degenerate**.

Furthermore, Li_2IrO_3 structure relaxations are sensitive to SOC+U while Na_2IrO_3 structures are not.

Using VCA calculations, we determine, this may be due Na inducing more distortion of the IrO_6 octahedra than Li.


0
1
2
∞
Li2IrO3
Na2IrO3
DOS (states/eV/f.u.)
Energy (eV)
$^{\mathcal{H}}\langle\infty\rangle$: Na2IrO3
Li2IrO3
Nonmagnetic
Ferromagnetic
DOS (states/eV)
Energy (eV)

Ir-Ir Bond Length (Å)

without SOC
with SOC
Ir1-Ir1 (bond 1)
Ir1-Ir1 (bond 2)

Ir-O-Ir Bond Angle (degrees)

without SOC
with SOC
Ir1-O2-Ir1
Ir1-O1-Ir1

Li (% Na) Na

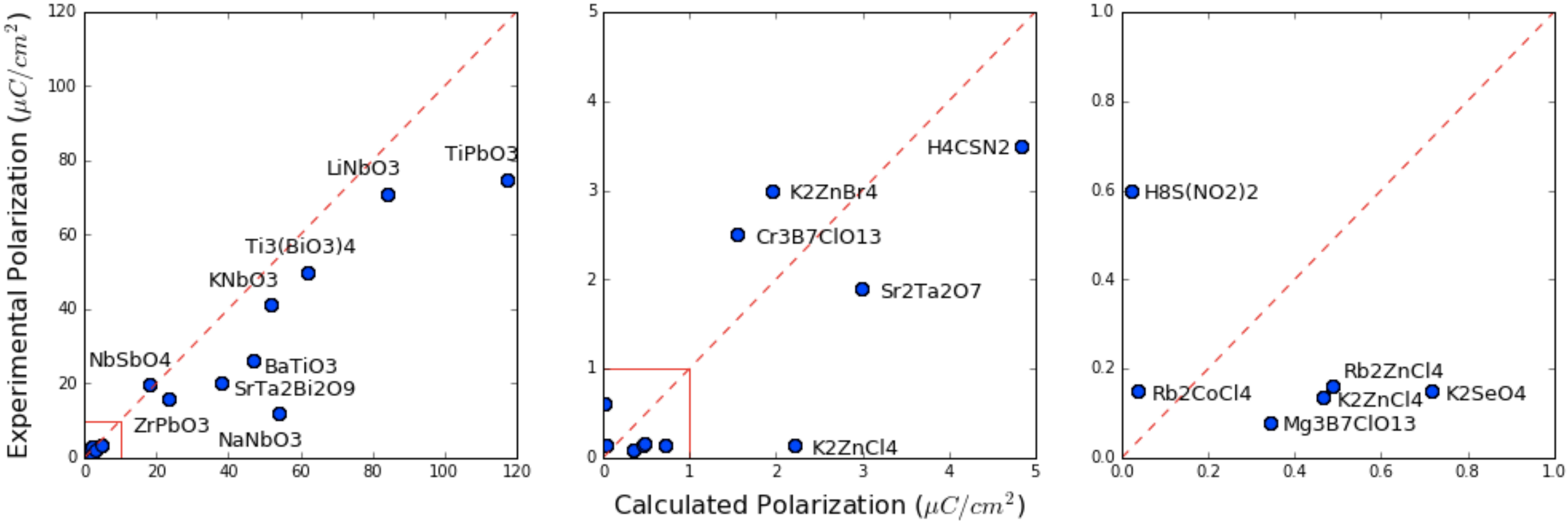
a/c

b/c

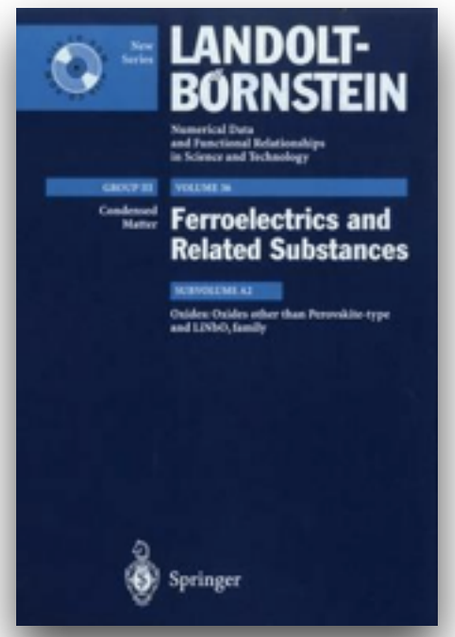
U = 0 eV
U = 1.5 eV
U = 3.0 eV
U = 6.0 eV

Li (% Na) Na

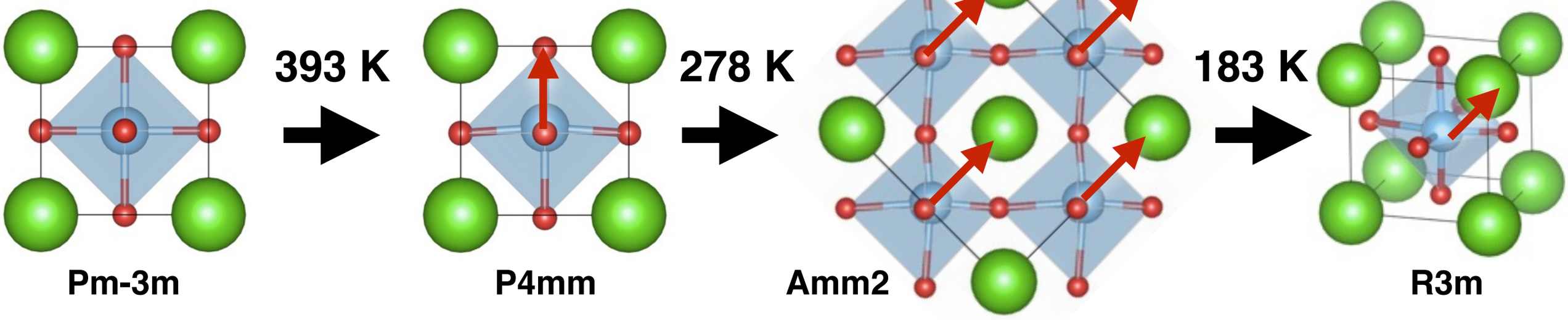
Validation: We compare our calculated polarization values to experimentally measured values.



Experimental values from Landolt-Börnstein reference.



Irreps. of BTO phase transitions



$BaTiO_3$

$\Gamma_4^-(0,0,a)$

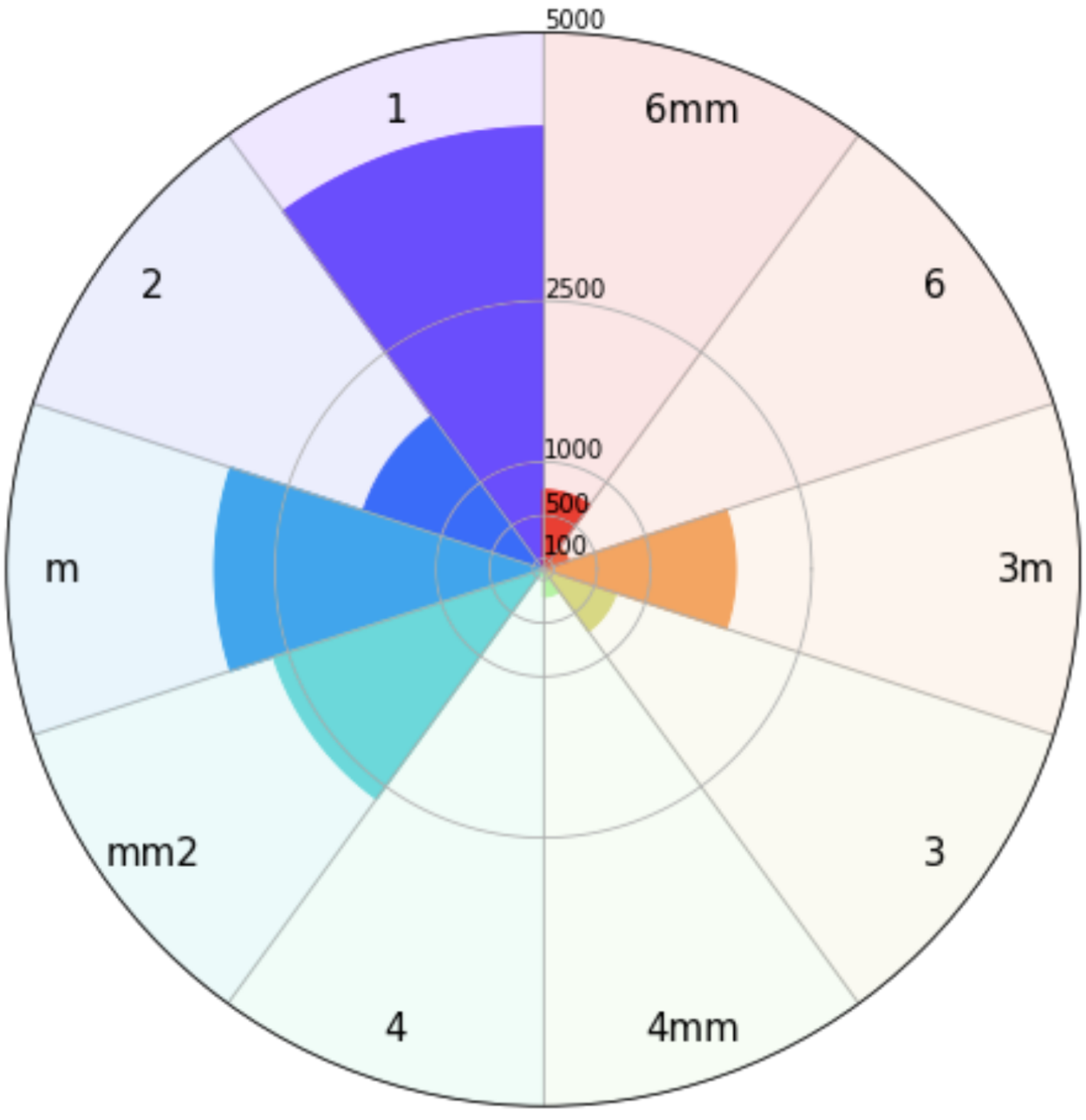
$\Gamma_4^-(a,a,0) + \Gamma_5^-(0,a,-a)$

(wrt to cubic)

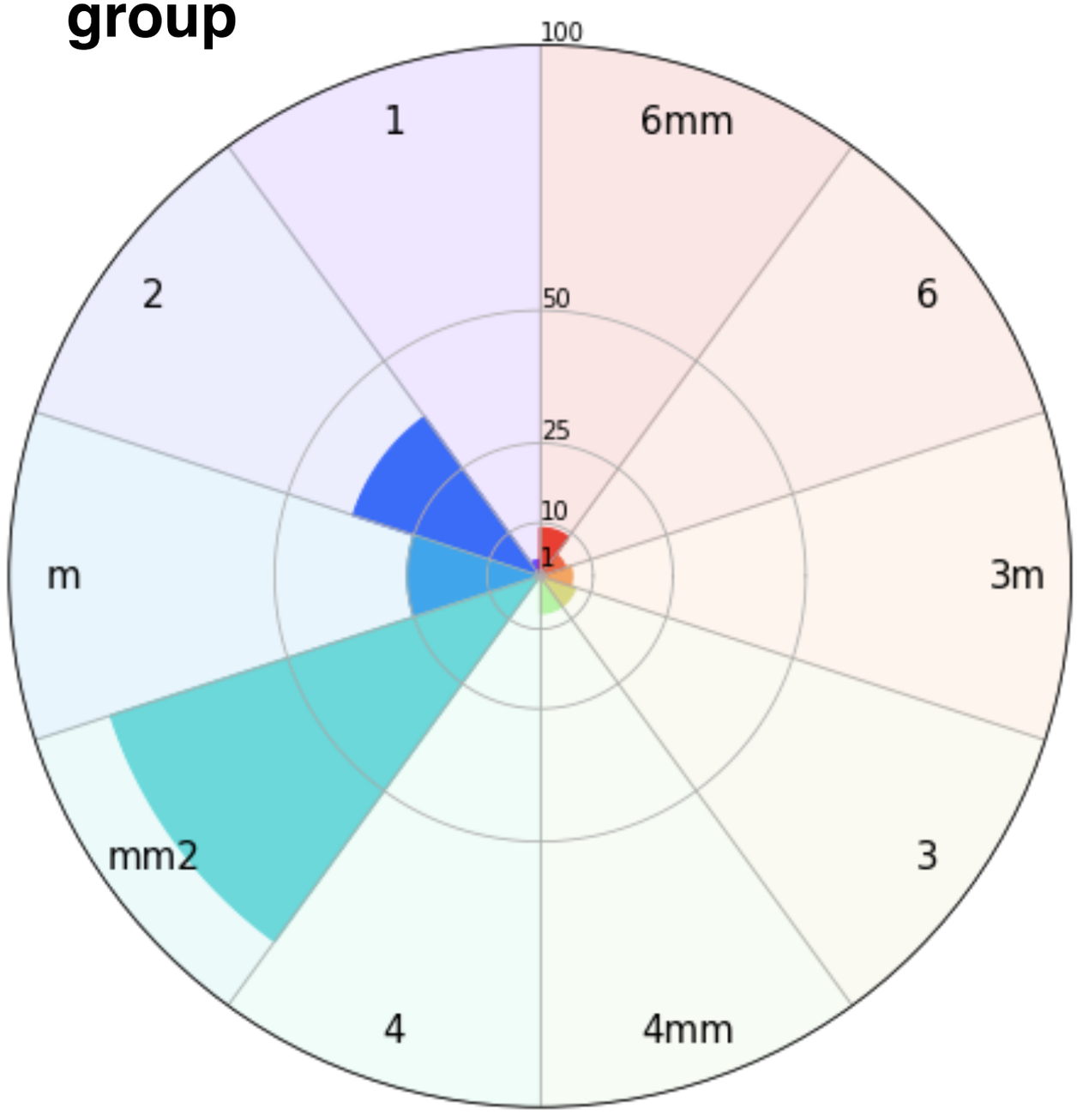
$\Gamma_4^-(a,a,a)$

(wrt to cubic)

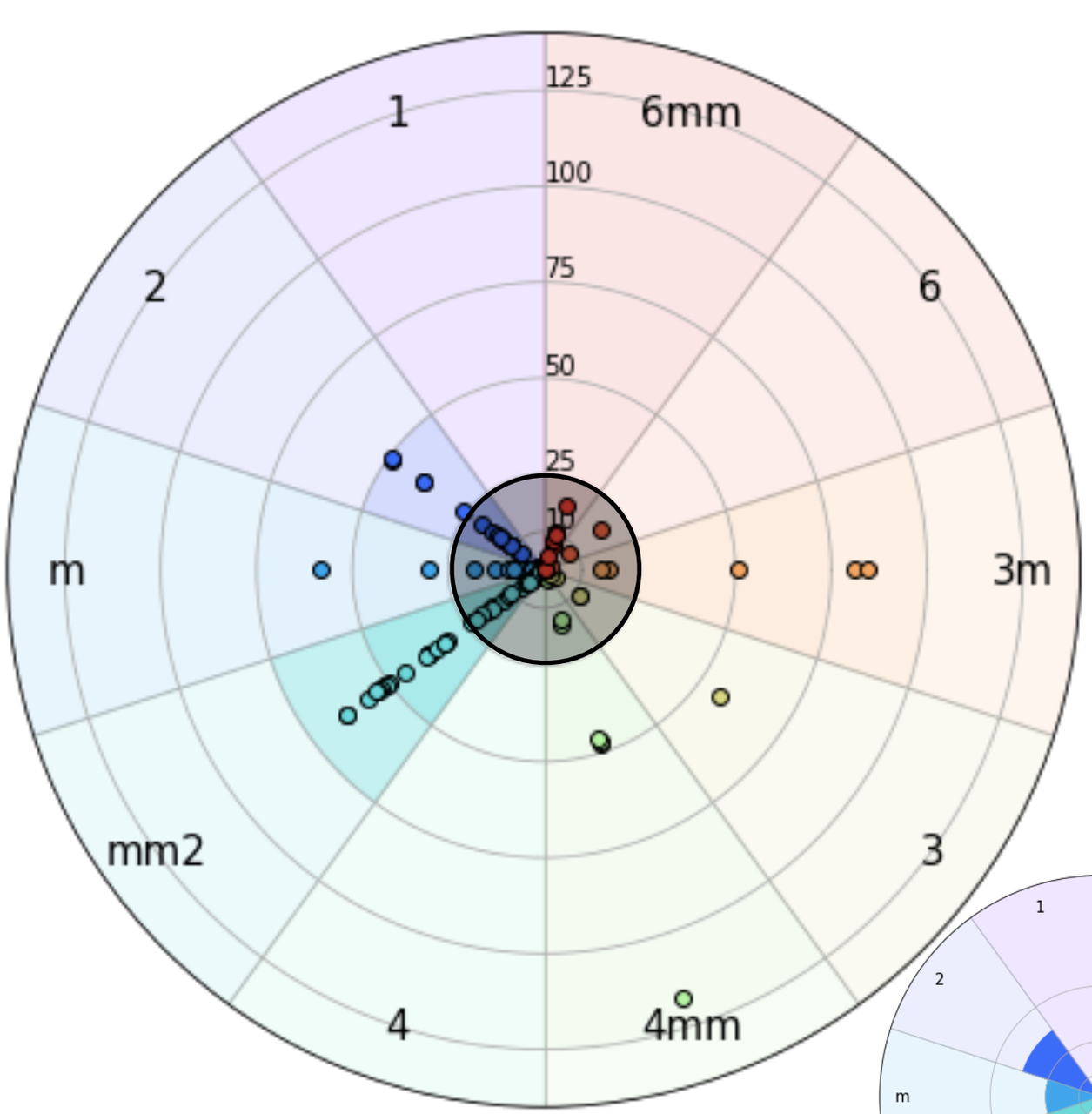
Number of polar structures in Materials Project by point group

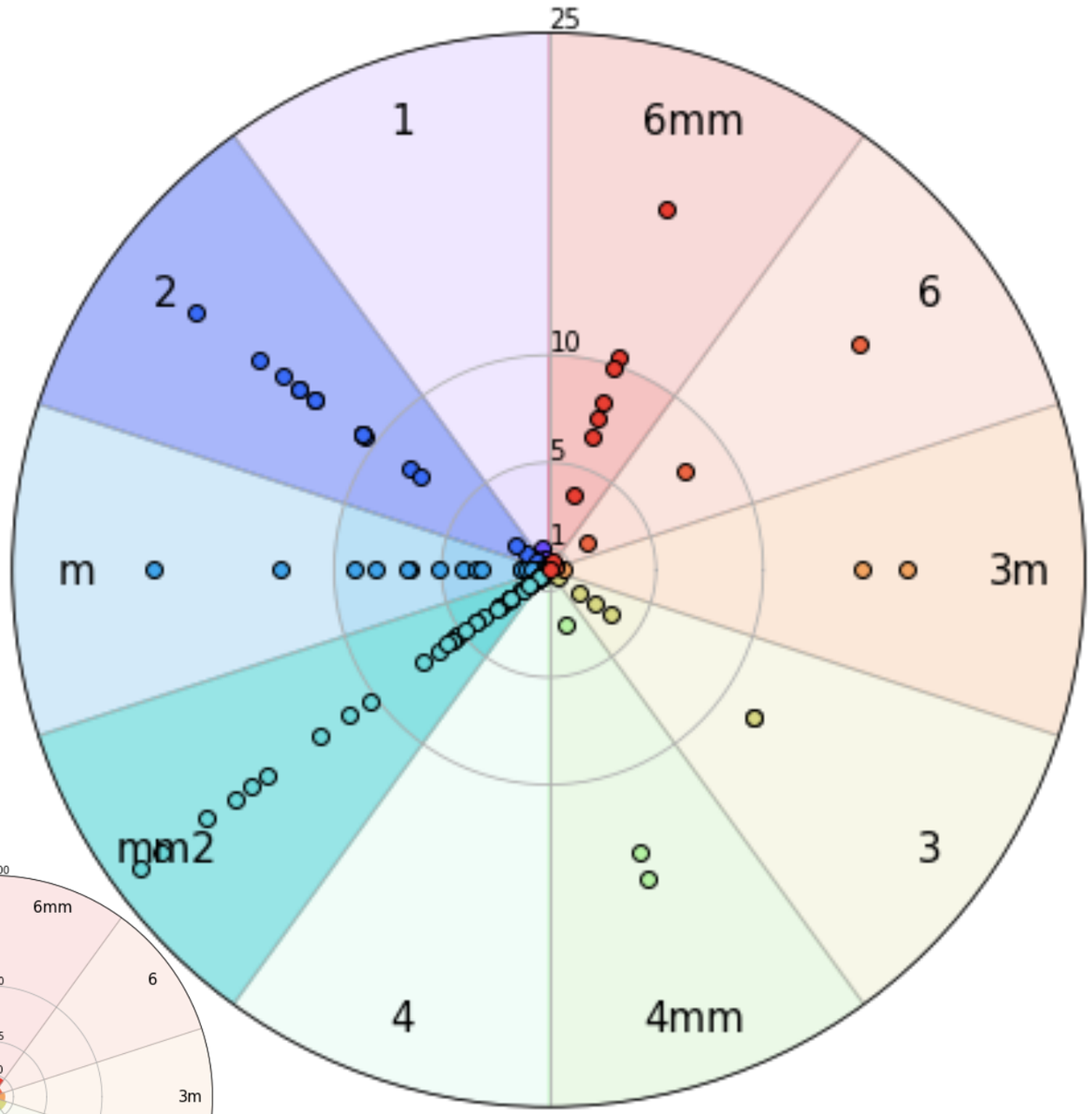


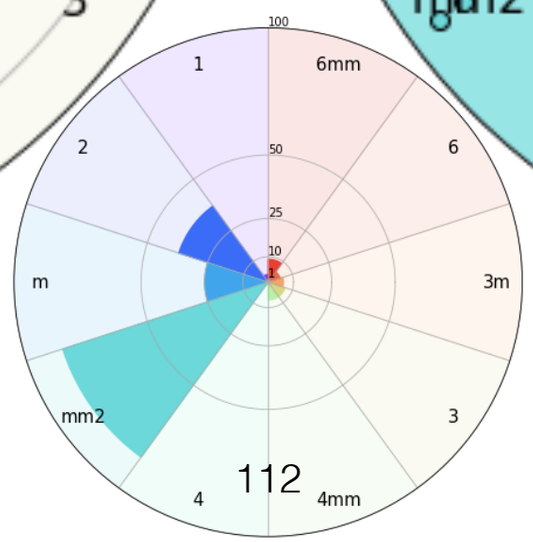
Number of ferroelectric candidates from nonpolar-polar pairs in Materials Project by point group



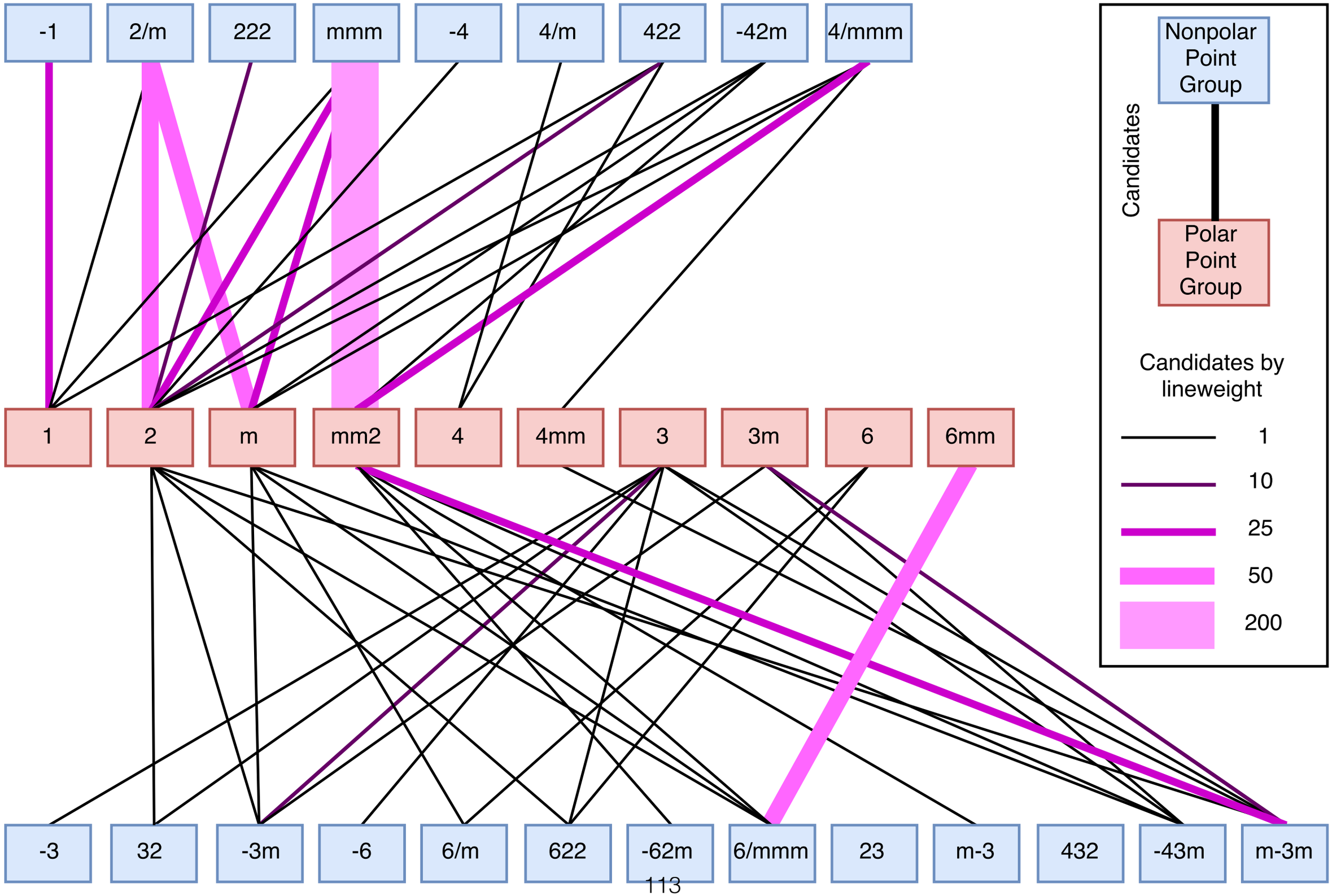
Polarization (μC/cm²) of validated ferroelectric candidates from nonpolar-polar pairs in Materials Project by point group.







Symmetry Analysis of Candidates



Symmetry Analysis

We use **pymatgen** to find nonpolar-polar structure pairs of the same composition that satisfy group-subgroup relationship.

H is a polar space group and
G is a nonpolar space group.

$$H \subset G$$

$$P(H) \in \{1, 2, m, mm2, 4, 4mm, 3, 3m, 6, 6m\}$$

$$P(G) \notin \{1, 2, m, mm2, 4, 4mm, 3, 3m, 6, 6m\}$$

point groups of H and G

polar point groups

Symmetry Analysis

We then use python scripts to interact with the **Bilbao Crystallographic Server** to determine if we can transform the high symmetry nonpolar structure to the low symmetry polar setting.

Check the following:

1. Index
2. Path
3. Wyckoff splitting
4. Lattice compatibility
5. Match atomic positions

Symmetry Analysis

We then use python scripts to interact with the **Bilbao Crystallographic Server** to determine if we can transform the high symmetry nonpolar structure to the low symmetry polar setting.

loss of translation symmetry
(change in primitive volume)

$$i = i_k \cdot i_t = \left(\begin{array}{c}\text{ratio of number of}\\ \text{formula units in primitive}\\ \text{cell polar to nonpolar}\end{array}\right) \mathbf{x} \left(\begin{array}{c}\text{ratio of point}\\ \text{group operations}\\ \text{nonpolar to polar}\end{array}\right)$$

loss of point group symmetry

Symmetry Analysis

We then use python scripts to interact with the **Bilbao Crystallographic Server** to determine if we can transform the high symmetry nonpolar structure to the low symmetry polar setting.

Check the following:

1. **Index**
2. Path
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5. Match atomic positions

loss of translation symmetry
(change in primitive volume)

number of formula units
in primitive cell

$$i = i_k \cdot i_t = \frac{Z(H)}{Z(G)} \cdot \frac{|P(G)|}{|P(H)|}$$

loss of point group symmetry

number of elements
in point group

Symmetry Analysis

We then use python scripts to interact with the **Bilbao Crystallographic Server** to determine if we can transform the high symmetry nonpolar structure to the low symmetry polar setting.

$BaTiO_3$

Check the following:

1. **Index**
2. Path
3. Wyckoff splitting
4. Lattice compatibility
5. Match atomic positions

rhombohedral

tetragonal

orthorhombic

Maximum k-index = 1

N. of subgroups (for k-index 1) found: 12

t-subgroups of space group *Pm*-3*m* (221)

N	HM Symbol	ITA	index	t-index	k-index	More info
1	*R*3*m*	160	8	8	1	show...
2	*R*3	146	16	16	1	show...
3	*P*4*mm*	099	6	6	1	show...
4	*P*4	075	12	12	1	show...
5	*Amm*2	038	12	12	1	show...
6	*Cmm*2	035	12	12	1	show...
7	*Pmm*2	025	12	12	1	show...
8	*Cm*	008	24	24	1	show...
9	*Pm*	006	24	24	1	show...
10	*C*2	005	24	24	1	show...
11	*P*2	003	24	24	1	show...
12	*P*1	001	48	48	1	show...

No change in primitive cell volume for subgroups with $i_k = 1$.

Symmetry Analysis

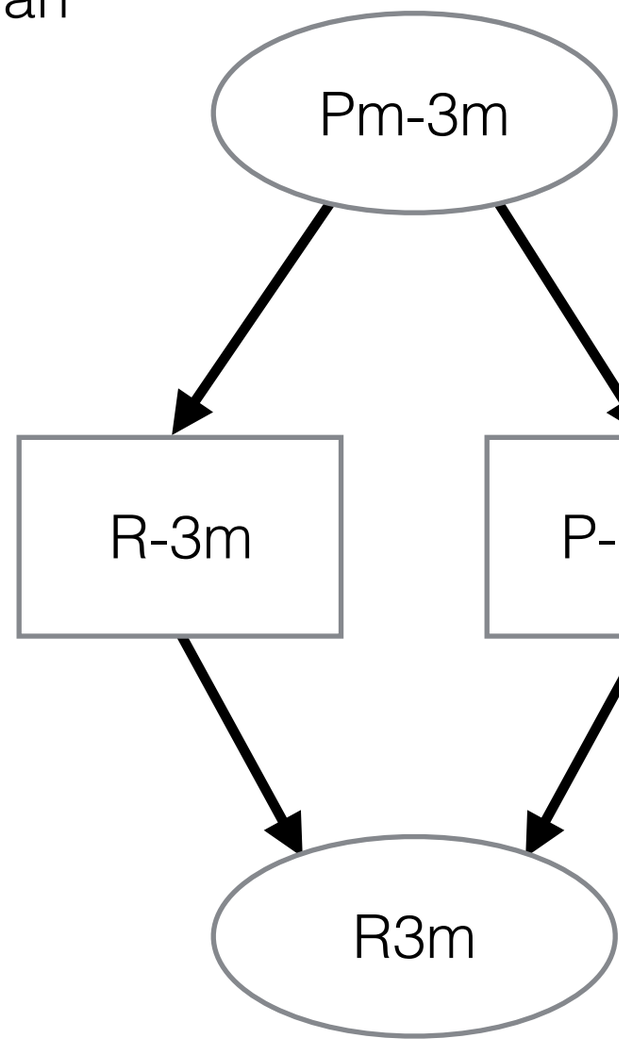
We then use python scripts to interact with the **Bilbao Crystallographic Server** to determine if we can transform the high symmetry nonpolar structure to the low symmetry polar setting.

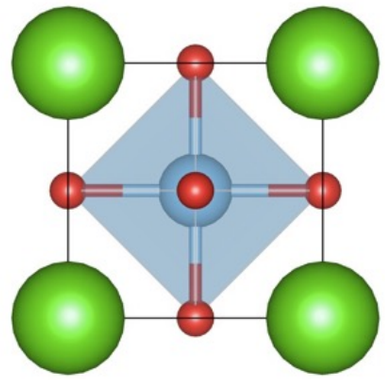
$BaTiO_3$

Different paths can lead to different transformations.

Check the following:

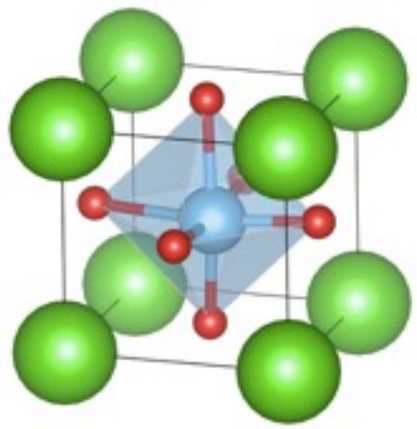
1. Index
2. **Path**
3. Wyckoff splitting
4. Lattice compatibility
5. Match atomic positions





cubic

rhombohedral



Symmetry Analysis

We then use python scripts to interact with the **Bilbao Crystallographic Server** to determine if we can transform the high symmetry nonpolar structure to the low symmetry polar setting.

$BaTiO_3$

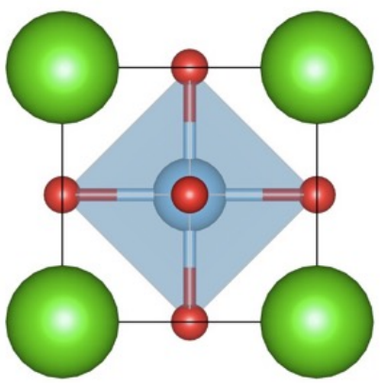
Check the following:

1. Index
2. Path
3. **Wyckoff splitting**
4. Lattice compatibility
5. Match atomic positions

Wyckoff positions

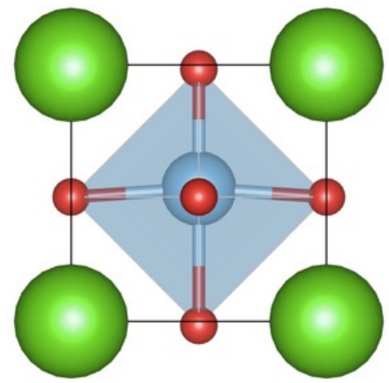
Pm-3m	P4mm
48n	8g 8g 8g 8g 8g 8g
24m	4d 4d 8g 8g
24l	4f 4f 4f 4f 8g
24k	4e 4e 4e 4e 8g
12j	4f 4f 4d
12i	4e 4e 4d
12h	4f 4e 2c 2c
8g	4d 4d
6f	4f 1b 1b
6e	4e 1a 1a
3d	2c 1a
3c	2c 1b
1b	1b
1a	1a

cubic



3 symmetrically unique positions

tetragonal



4 symmetrically unique positions

Symmetry Analysis

We then use python scripts to interact with the **Bilbao Crystallographic Server** to determine if we can transform the high symmetry nonpolar structure to the low symmetry polar setting.

$BaTiO_3$ **cubic → orthorhombic**

transformation matrix | high symmetry lattice vectors | low symmetry setting

$$\begin{pmatrix} 0 & 1 & 1 \\ 0 & -1 & 1 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 4.04 & 0 & 0 \\ 0 & 4.04 & 0 \\ 0 & 0 & 4.04 \end{pmatrix} = \begin{pmatrix} 0 & 4.04 & 4.04 \\ 0 & -4.04 & 4.04 \\ 4.04 & 0 & 0 \end{pmatrix}$$

Check the following:

1. Index
2. Path
3. Wyckoff splitting
4. **Lattice compatibility**
5. Match atomic positions

nonpolar

$a = 4.04, b = 5.71, c = 5.71$

$\alpha = \beta = \gamma = 90°$

polar

$a = 3.99, b = 5.81, c = 5.89$

$\alpha = \beta = \gamma = 90°$

Want:

$$a_{np} - a_p < \delta_{vector}$$

$$\dots$$

$$\alpha_{np} - \alpha_p < \delta_{angle}$$

$$\dots$$

tolerances

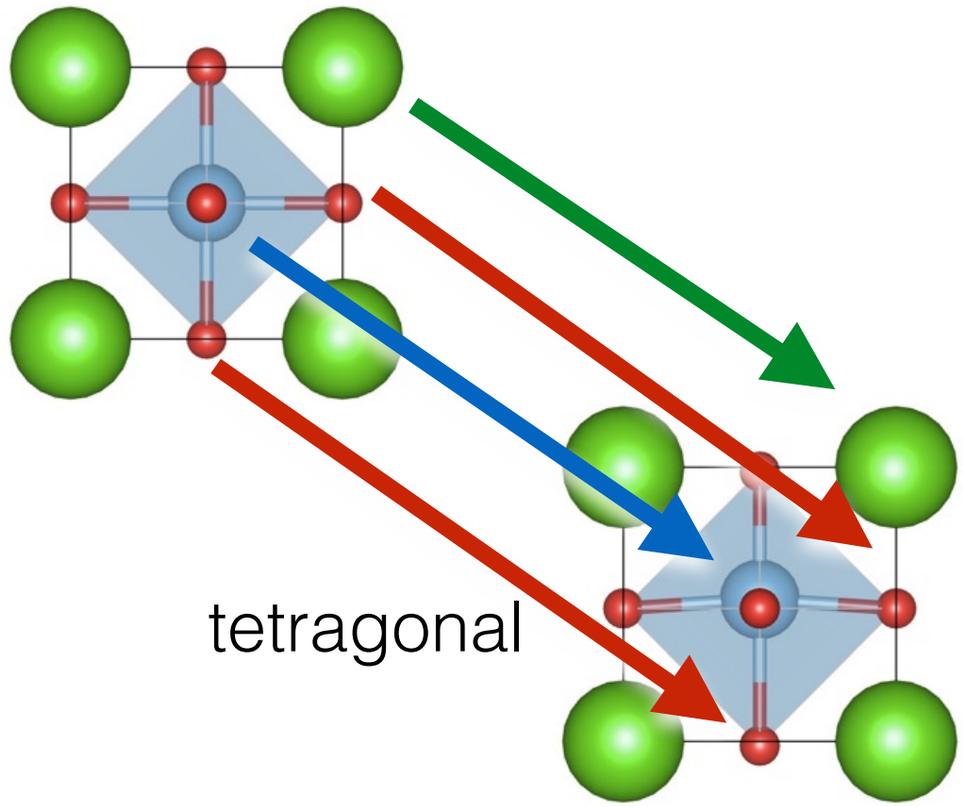
Symmetry Analysis

We then use python scripts to interact with the **Bilbao Crystallographic Server** to determine if we can transform the high symmetry nonpolar structure to the low symmetry polar setting.

$BaTiO_3$

Check the following:

1. Index
2. Path
3. Wyckoff splitting
4. Lattice compatibility
5. **Match atomic positions**



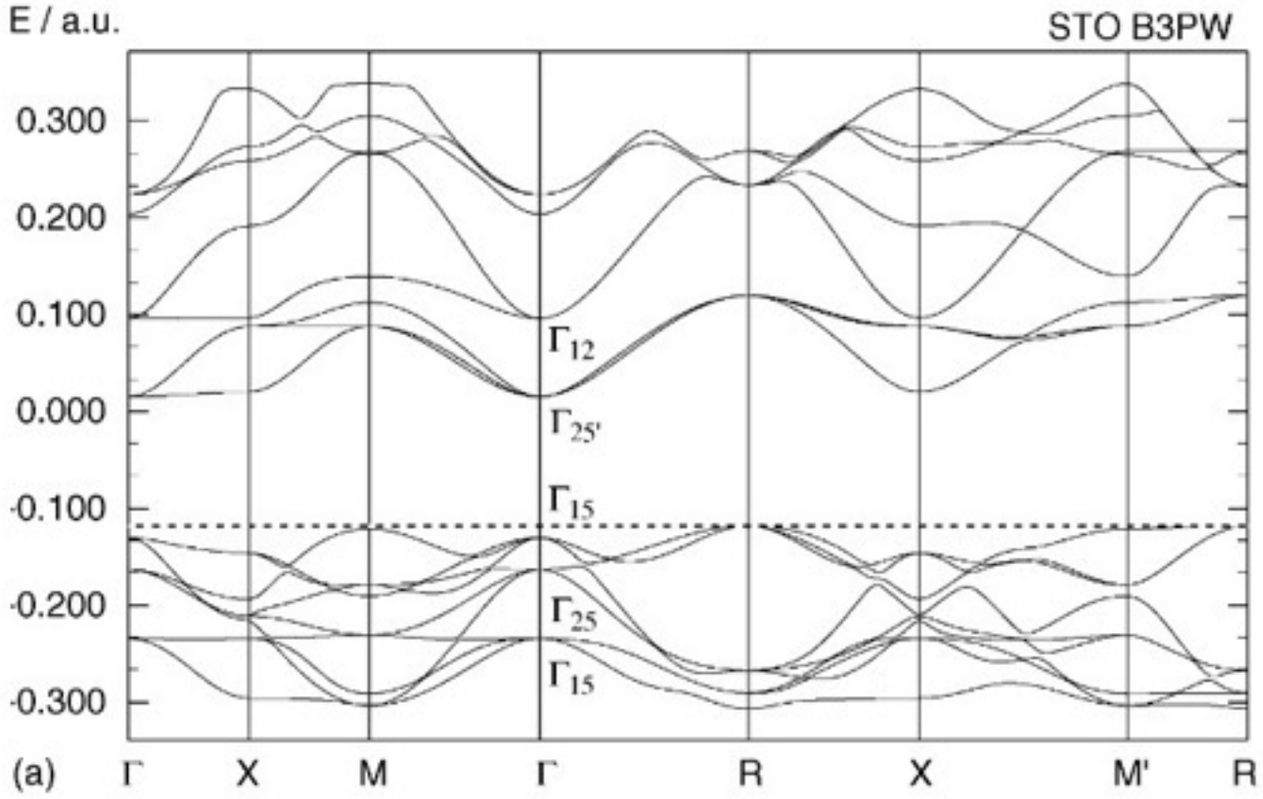
Max displacement < 1.5 Å

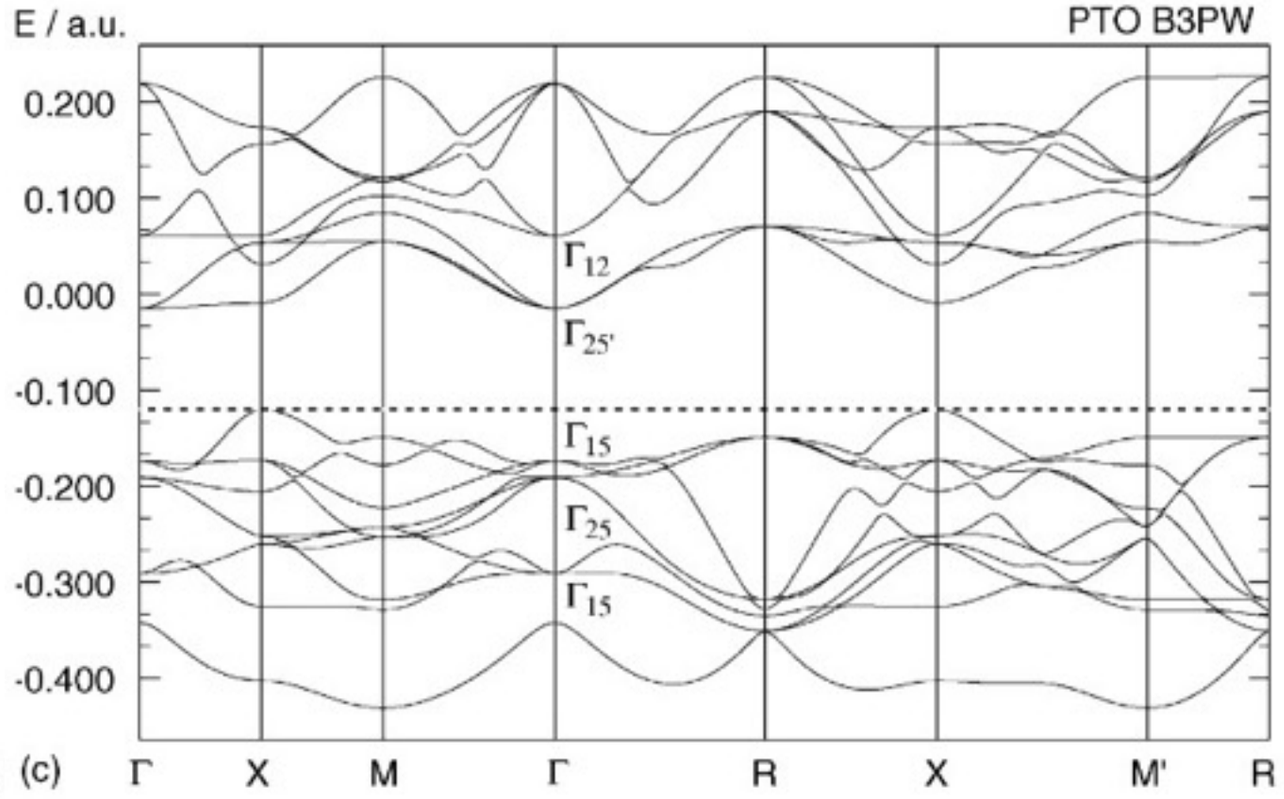
Table 4
The calculated optical band gap (eV)

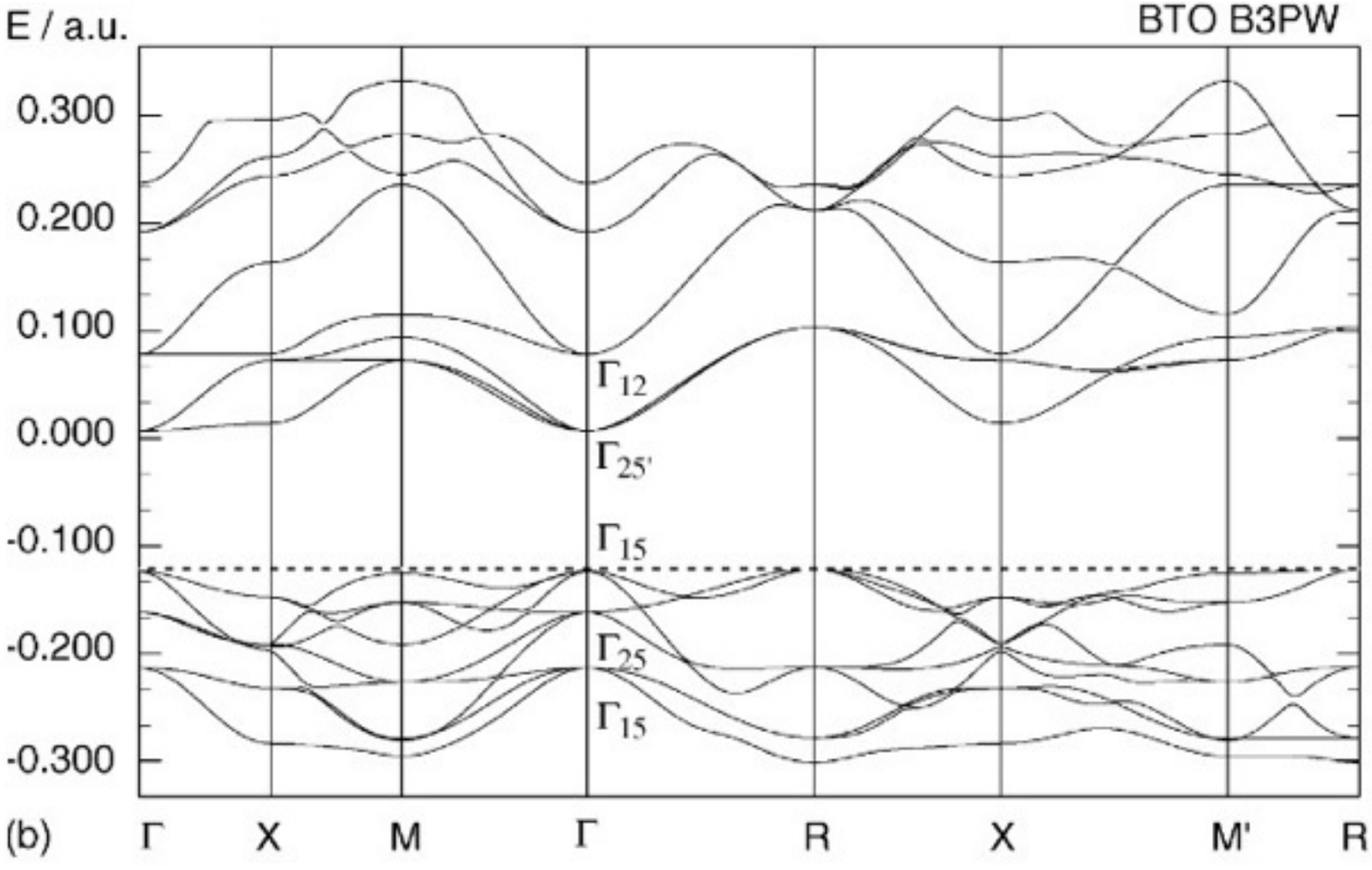
	Optical gap	LDA	PWGGA	PBE	BLYP	P3PW	B3LYP	HF	Experiment
STO	Γ–Γ	2.36	2.31	2.35	2.27	3.96 (4.43)	3.89	12.33	3.75—direct gap
	X–X	2.94	2.79	2.84	2.72	4.53 (5.08)	4.42	13.04	3.25—indirect gap (Ref. [46])
	M–M	4.12	3.69	3.74	3.56	5.70 (6.45)	5.50	14.45	
	R–R	4.77	4.25	4.31	4.09	6.47 (7.18)	6.23	15.72	
	X–Γ	2.78	2.69	2.73	2.63	4.39	4.31	12.86	
	M–Γ	2.15	2.06	2.08	2.03	3.71 (4.23)	3.66	12.02	
	R–Γ	2.04	1.97	1.99	1.94	3.63 (4.16)	3.57	11.97	
BTO	Γ–Γ	1.98	1.97	1.99	1.91	3.55	3.49	11.73	3.2 (Ref. [47])
	X–X	2.85	2.73	2.74	2.57	4.39	4.26	12.83	
	M–M	3.81	3.47	3.50	3.24	5.39	5.19	14.11	
	R–R	4.45	4.03	4.07	3.76	6.12	5.89	15.22	
	X–Γ	2.64	2.55	2.57	2.44	4.20	4.10	12.57	
	M–Γ	2.01	1.93	1.95	1.84	3.60	3.51	11.95	
	R–Γ	1.92	1.84	1.86	1.76	3.50	3.42	11.85	
PTO	Γ–Γ	2.65	2.61	2.65	2.48	4.32	4.15	12.74	3.4 (Ref. [48])
	X–X	1.54	1.68	1.70	1.77	3.02	3.05	10.24	
	M–M	3.78	3.58	3.61	3.33	5.55	5.33	13.76	
	R–R	4.16	3.91	3.94	3.65	5.98	5.78	15.07	
	X–Γ	1.40	1.56	1.58	1.67	2.87	2.92	10.01	
	M–Γ	2.01	1.98	2.00	1.88	3.66	3.53	11.43	
	R–Γ	2.03	1.98	2.00	1.89	3.66	3.52	12.03	

The results of previous CRYSTAL calculations [15] are given in the brackets.

Piskunov, S., et al. "Bulk properties and electronic structure of SrTiO 3, BaTiO 3, PbTiO 3 perovskites: an ab initio HF/DFT study." Computational Materials Science 29.2 (2004): 165-178.







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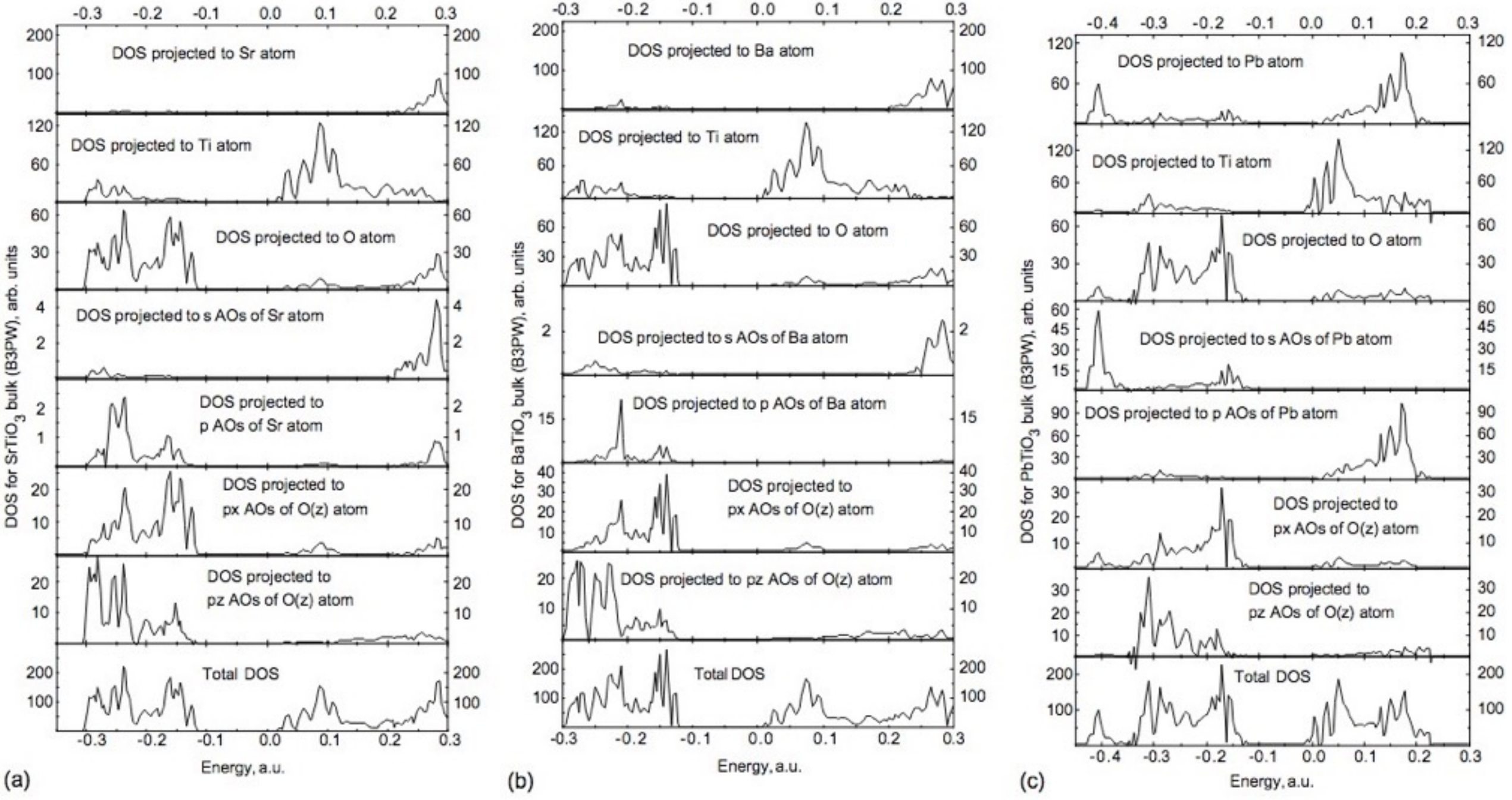

Piskunov, S., et al. "Bulk properties and electronic structure of SrTiO 3, BaTiO 3, PbTiO 3 perovskites: an ab initio HF/DFT study." Computational Materials Science 29.2 (2004): 165-178.

Table 11.1. Characters for Γ_{equiv} for perovskite. The atoms that remain unchanged under each symmetry operation are indicated

	E	$8C_3$	$3C_4^2$	$6C_2'$	$6C_4$	i	$8iC_3$	$3iC_4^2$	$6iC_2'$	$6iC_4$
$\Gamma^{\text{equiv.}}$	5	2	5	3	3	5	2	5	3	3
	all	Ba,Ti	all	Ba,Ti	Ba,Ti	all	Ba,Ti	all	Ba,Ti	Ba,Ti
				one O	one O				one O	one O

Table A.31. Character table for the cubic group O_h (cubic)†

repr.	basis functions	E	$3C_4^2$	$6C_4$	$6C_2'$	$8C_3$	i	$3iC_4^2$	$6iC_4$	$6iC_2'$	$8iC_3$
A_1^+	1	1	1	1	1	1	1	1	1	1	1
A_2^+	$x^4(y^2-z^2)+$ $y^4(z^2-x^2)+$ $z^4(x^2-y^2)$	1	1	−1	−1	1	1	1	−1	−1	1
E^+	x^2-y^2 $2z^2-x^2-y^2$	2	2	0	0	−1	2	2	0	0	−1
T_1^-	x, y, z	3	−1	1	−1	0	−3	1	−1	1	0
T_2^-	$z(x^2-y^2)\ldots$	3	−1	−1	1	0	−3	1	1	−1	0
A_1^-	$xyz[x^4(y^2-z^2)+$ $y^4(z^2-x^2)+$ $z^4(x^2-y^2)]$	1	1	1	1	1	−1	−1	−1	−1	−1
A_2^-	xyz	1	1	−1	−1	1	−1	−1	1	1	−1
E^-	$xyz(x^2-y^2)\ldots$	2	2	0	0	−1	−2	−2	0	0	1
T_1^+	$xy(x^2-y^2)\ldots$	3	−1	1	−1	0	3	−1	1	−1	0
T_2^+	xy, yz, zx	3	−1	−1	1	0	3	−1	−1	1	0

† The basis functions for T_2^- are $z(x^2-y^2)$, $x(y^2-z^2)$, $y(z^2-x^2)$, for E^- are $xyz(x^2-y^2)$, $xyz(3z^2-s^2)$ and for T_1^+ are $xy(x^2-y^2)$, $yz(y^2-z^2)$, $zx(z^2-x^2)$

Dresselhaus, Mildred S., Gene Dresselhaus, and Ado Jorio. Group theory: application to the physics of condensed matter. Springer Science & Business Media, 2007.

Important for many applications of group theory is the number of atoms within the primitive cell (for example for calculation of $\chi^{\text{a.s.}}$). For example, in Fig. 9.7(a) there is one atom per unit cell. This can be obtained from Fig. 9.7(a) by considering that only one eighth of each of the eight atoms shown in the figure is inside the cubic primitive cell. In Fig. 9.7(b) there are two distinct atoms per unit cell but for each $\Gamma^{\text{a.s.}} = \Gamma_1$ to give a total $\Gamma^{\text{a.s.}} = 2\Gamma_1$. In Fig. 9.7(c), there are one Ti, six half O, and eight 1/8 parts of Ba inside the primitive cell, giving altogether five atoms, i.e., one unit of $BaTiO_3$ per unit cell. Here $\Gamma^{\text{a.s.}}$ for each of the Ba and Ti sublattices we have $\Gamma^{\text{a.s.}} = \Gamma_1$ but for the three oxygens $\Gamma^{\text{a.s.}} = \Gamma_1 + \Gamma_{12}$ to give a total of $\Gamma^{\text{a.s.}} = 3\Gamma_1 + \Gamma_{12}$ for the whole $BaTiO_3$ molecule (see Sect. 11.3.2).

Dresselhaus, Mildred S., Gene Dresselhaus, and Ado Jorio. Group theory: application to the physics of condensed matter. Springer Science & Business Media, 2007.

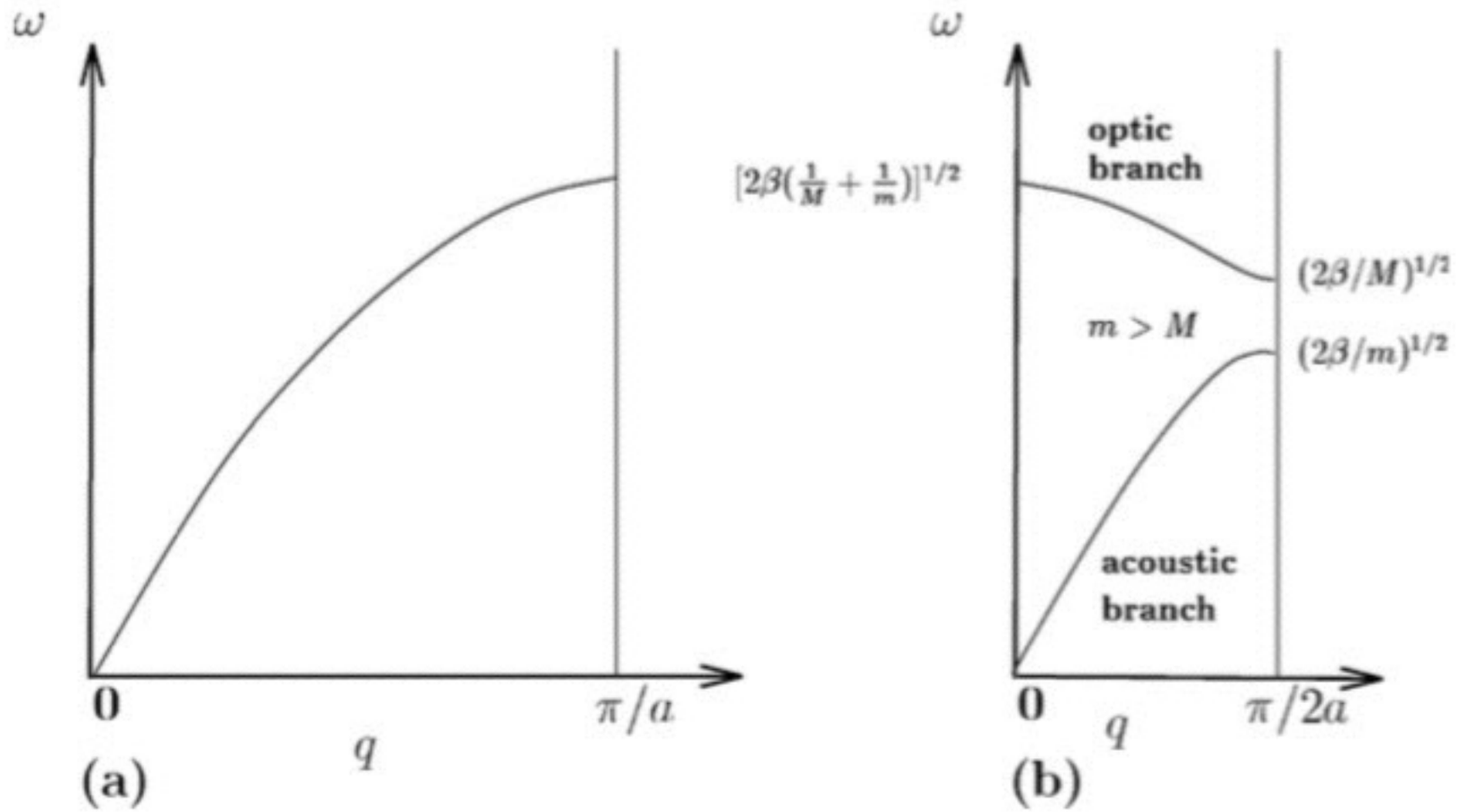

Fig. 11.1. Phonon dispersion curves for a one-dimensional line of atoms with (**a**) a single mass and (**b**) two different masses m and M

Dresselhaus, Mildred S., Gene Dresselhaus, and Ado Jorio. Group theory: application to the physics of condensed matter. Springer Science & Business Media, 2007.

The polarization is the dipole moment per unit cell.
It is not uniquely defined; polarization is a lattice vector.

$$\vec{P} = \vec{P}_0 + \sum_{i \in 1,2,3} \frac{\mathrm{e}\vec{R}_i}{\Omega}$$

e is the electron charge,
R is a lattice vector, and
Ω is the unit cell volume.

Spaldin, Nicola A. "A beginner's guide to the modern theory of polarization." Journal of Solid State Chemistry 195 (2012): 2-10.

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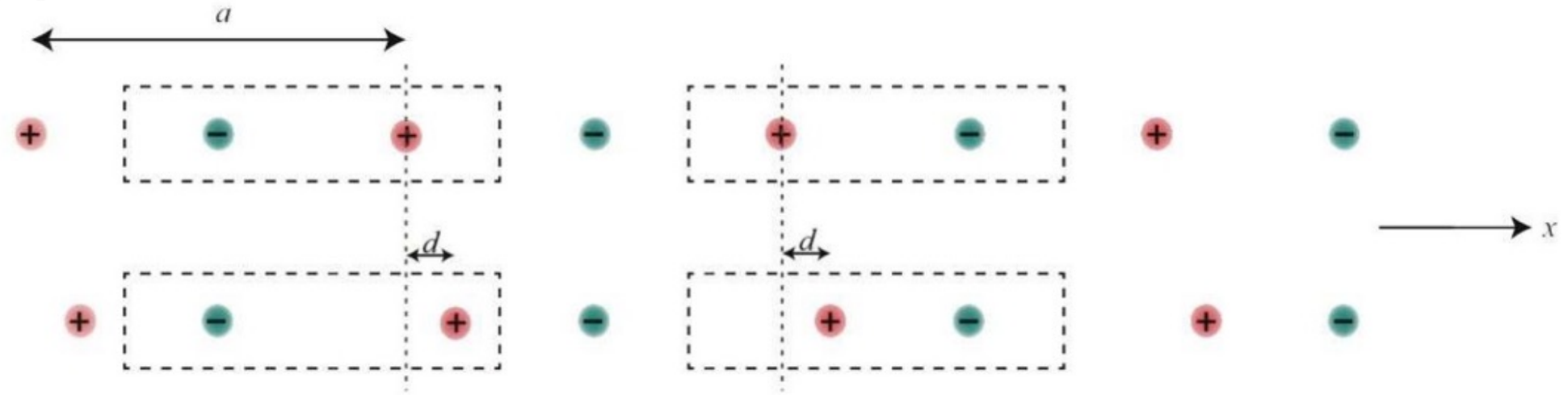
Periodic 1D example:

$$p = \frac{1}{a} \sum_i q_i x_i$$



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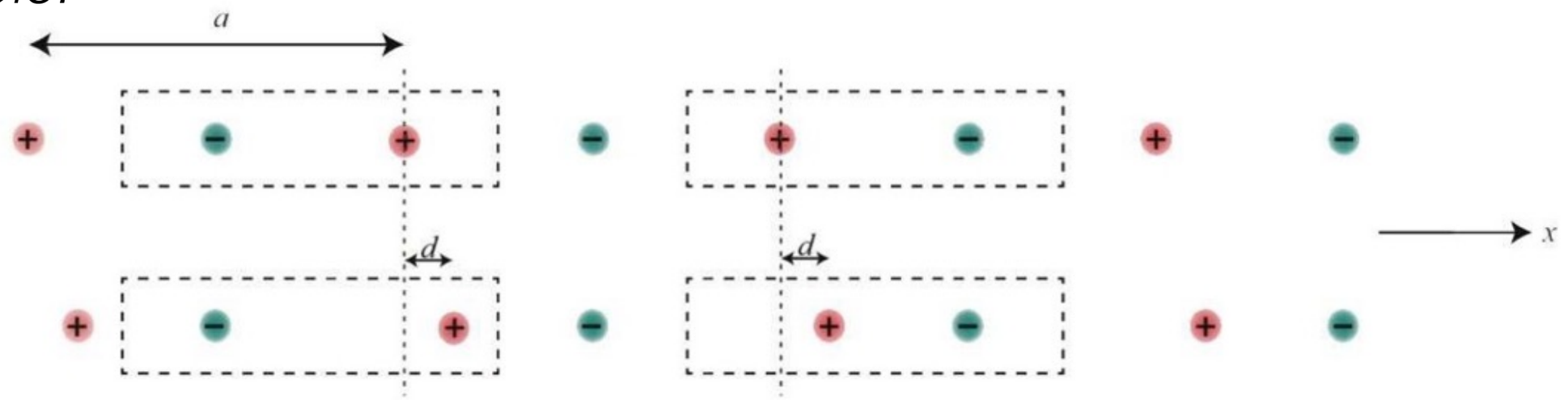

$$p_{R(0)} = \frac{1}{a}\left(-\frac{a}{4} + \frac{3a}{4}\right) = \frac{1}{2} \rightarrow p_{R(1)} = \frac{1}{a}\left(-\frac{a}{4} + \left(\frac{3a}{4} + d\right)\right) = \frac{1}{2} + \frac{d}{a}$$

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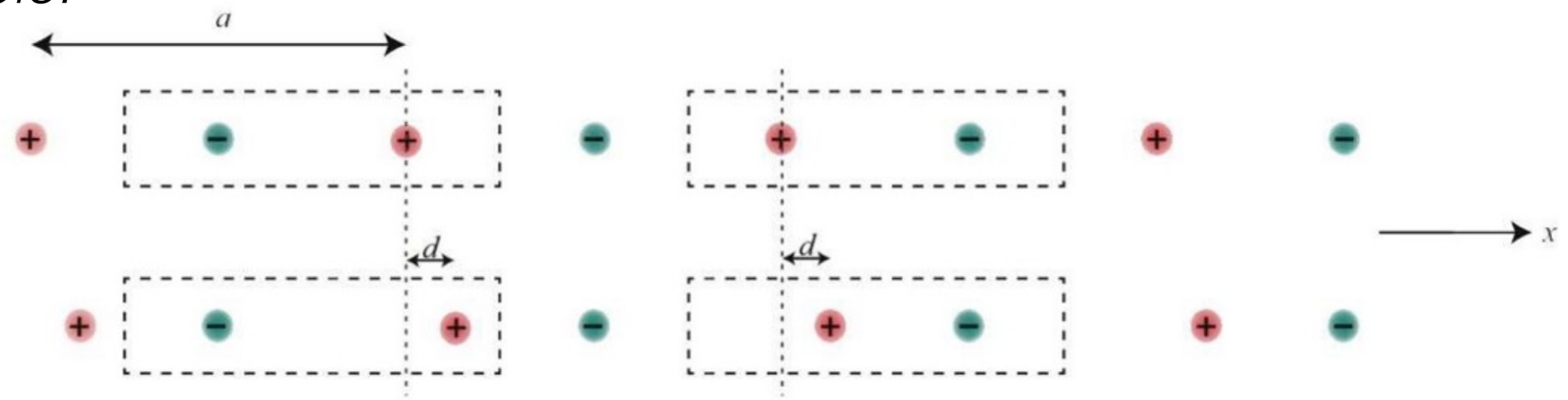

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$$p_{L(0)} = \frac{1}{a}\left(\frac{a}{4} - \frac{3a}{4}\right) = -\frac{1}{2} \rightarrow p_{L(1)} = \frac{1}{a}\left(\left(\frac{a}{4} + d\right) - \frac{3a}{4}\right) = -\frac{1}{2} + \frac{d}{a}$$

Spaldin, Nicola A. "A beginner's guide to the modern theory of polarization." Journal of Solid State Chemistry 195 (2012): 2-10.

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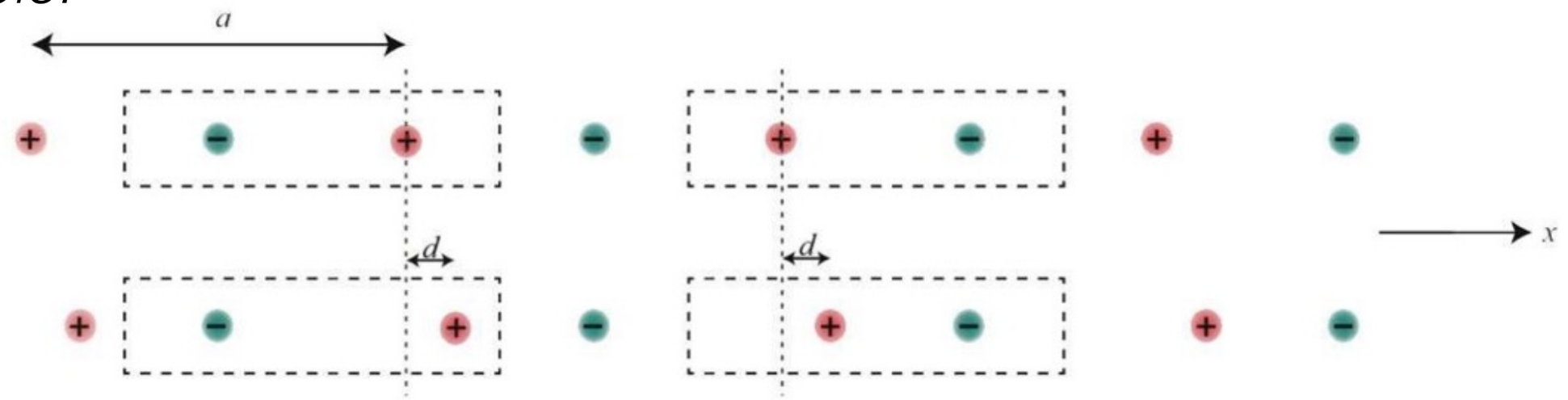

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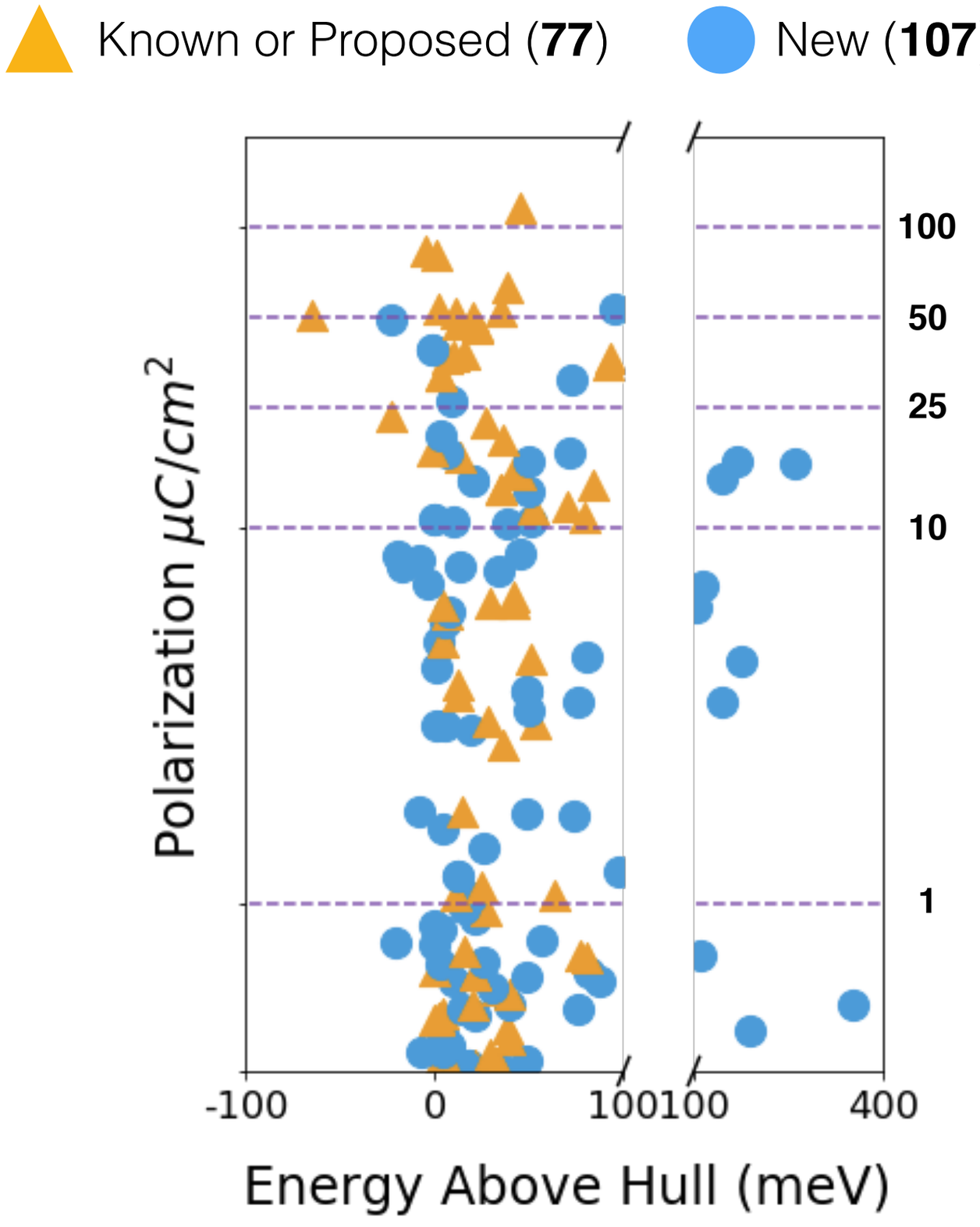
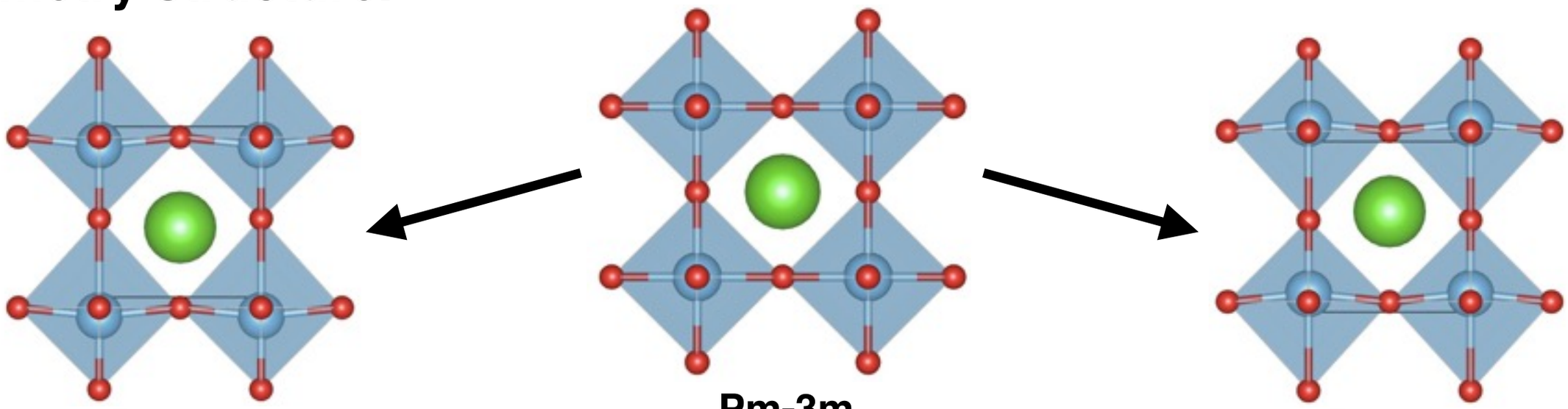
$$\delta p_L = \delta p_R = \frac{d}{a}$$

Spaldin, Nicola A. "A beginner's guide to the modern theory of polarization." Journal of Solid State Chemistry 195 (2012): 2-10.


Known or Proposed (77)
New (107)
100
50
25
10
1
-100
0
100
100
400
Energy Above Hull (meV)
Polarization $\mu C/cm^2$

Ferroelectrics are products of spontaneous symmetry breaking of a high symmetry structure.



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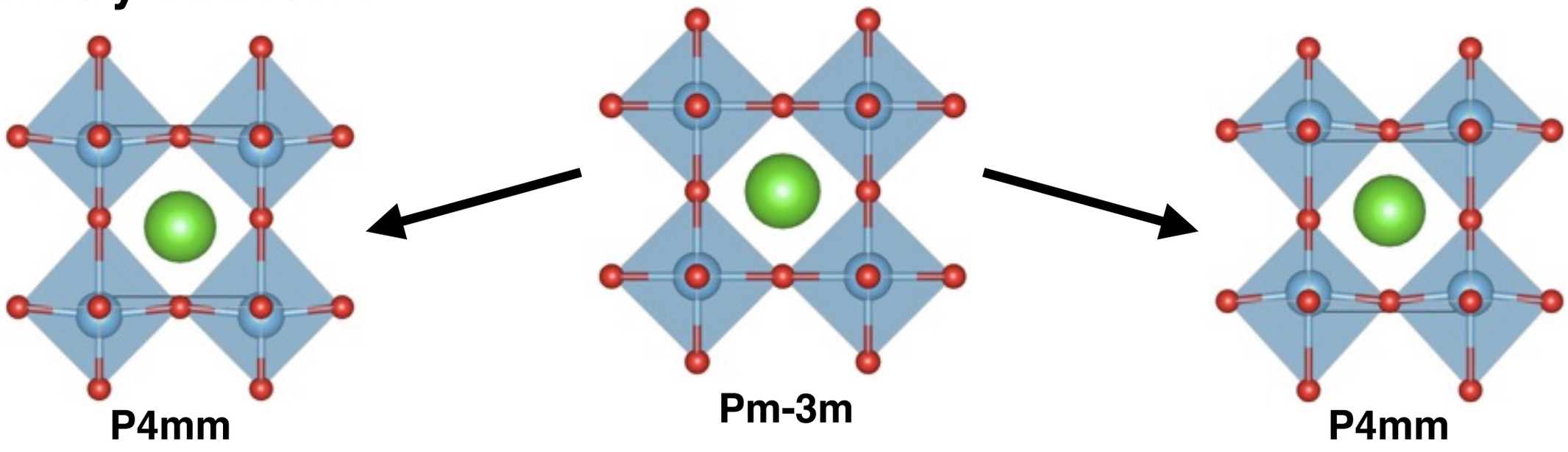

We can write the Landau expansion of the free energy of a ferroelectric material (1D polarization) near its transition temperature as:

$$F = \frac{1}{2}a(T - T_0)P_z^2 + \frac{1}{4}bP_z^4 + \frac{1}{6}cP_z^6 - EP_z$$

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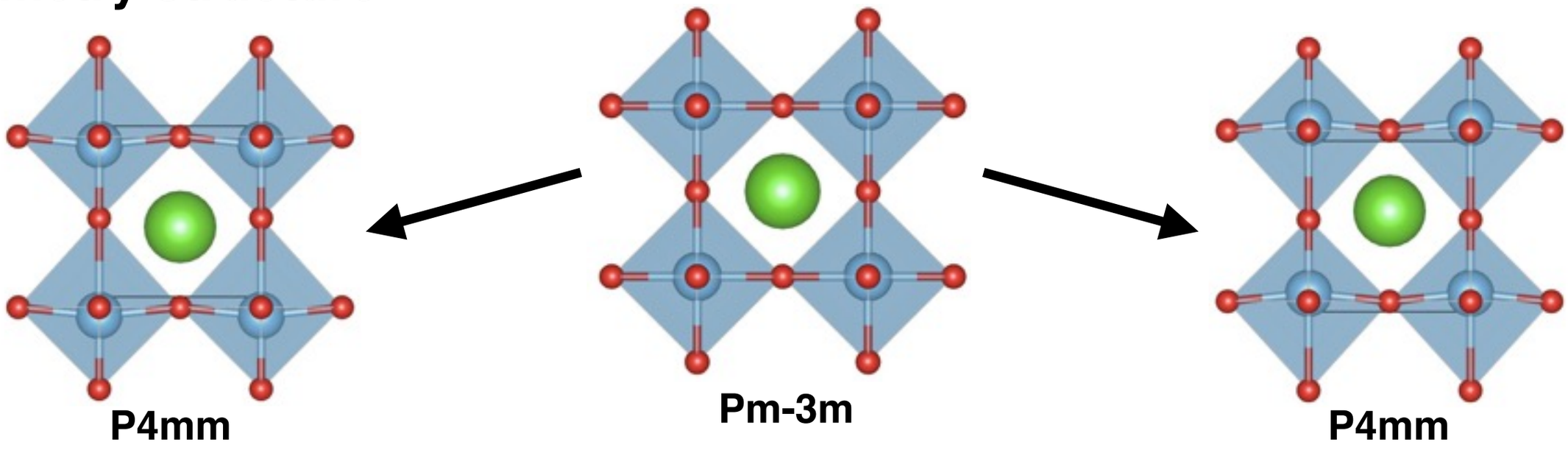

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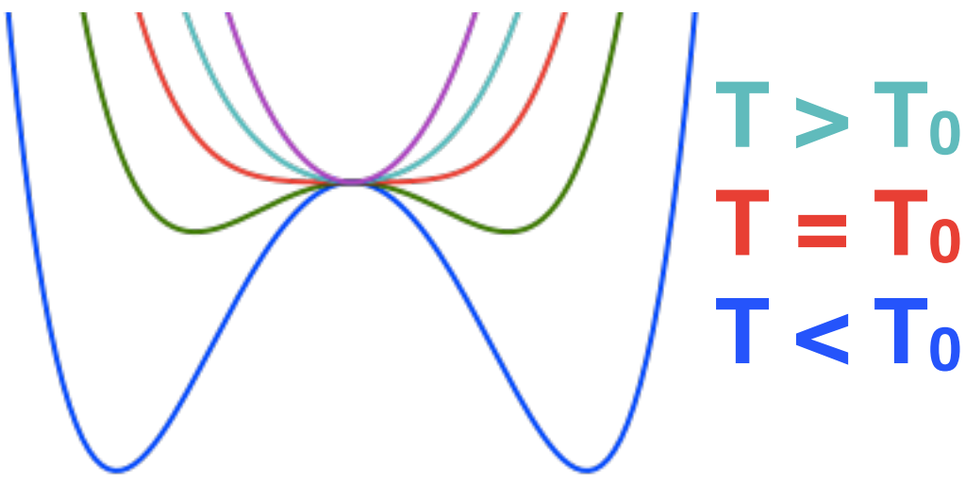
2nd order: b > 0



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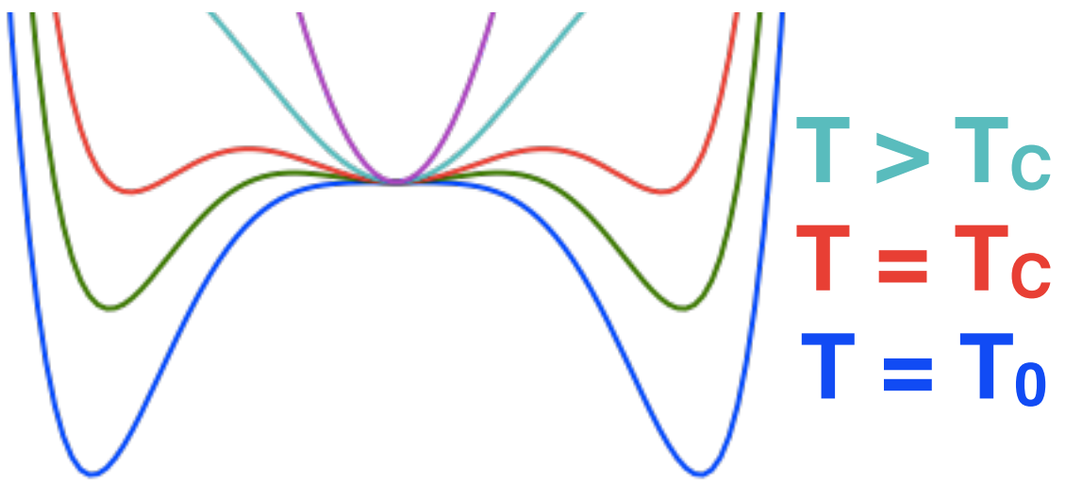


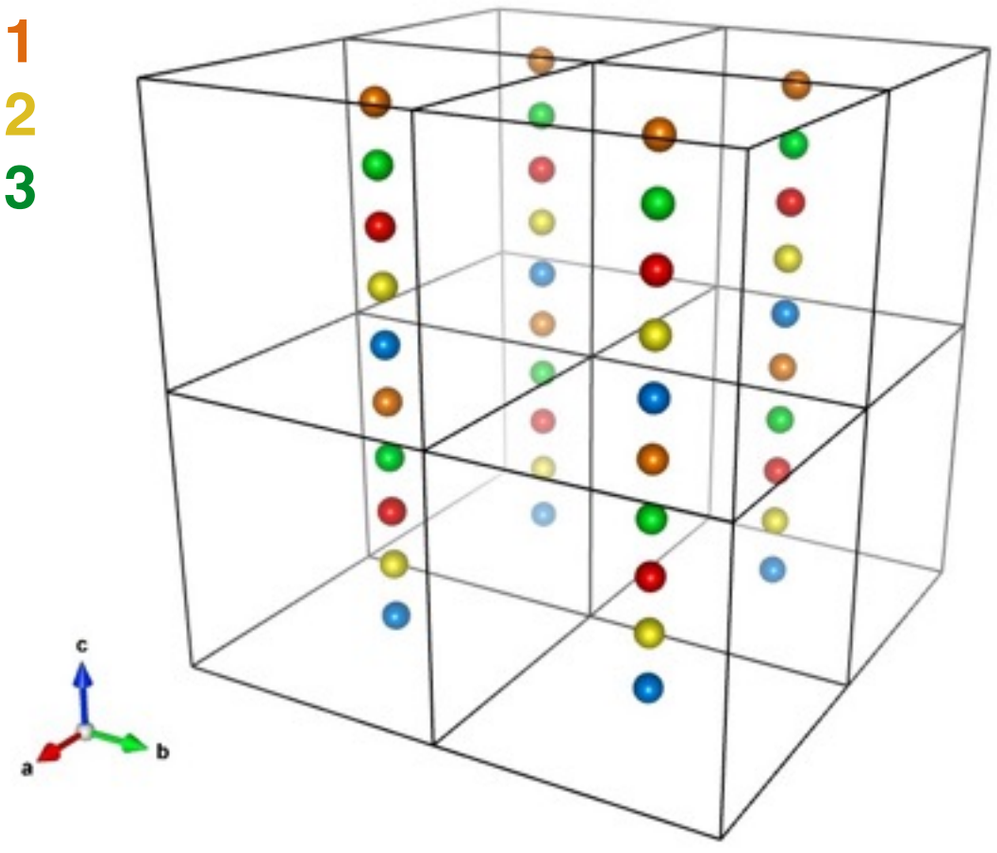
Post-processing: Algorithm for adjusting to the same branch polarization

Polarization is defined on a lattice

$$\vec{P} = \vec{P}_0 + \sum_{i \in 1,2,3} \frac{e\vec{R}_i}{\Omega}$$

e is the electron charge,
R is a lattice vector, and
Ω is the unit cell volume.

Nonpolar
Interpolation 1
Interpolation 2
Interpolation 3
Polar



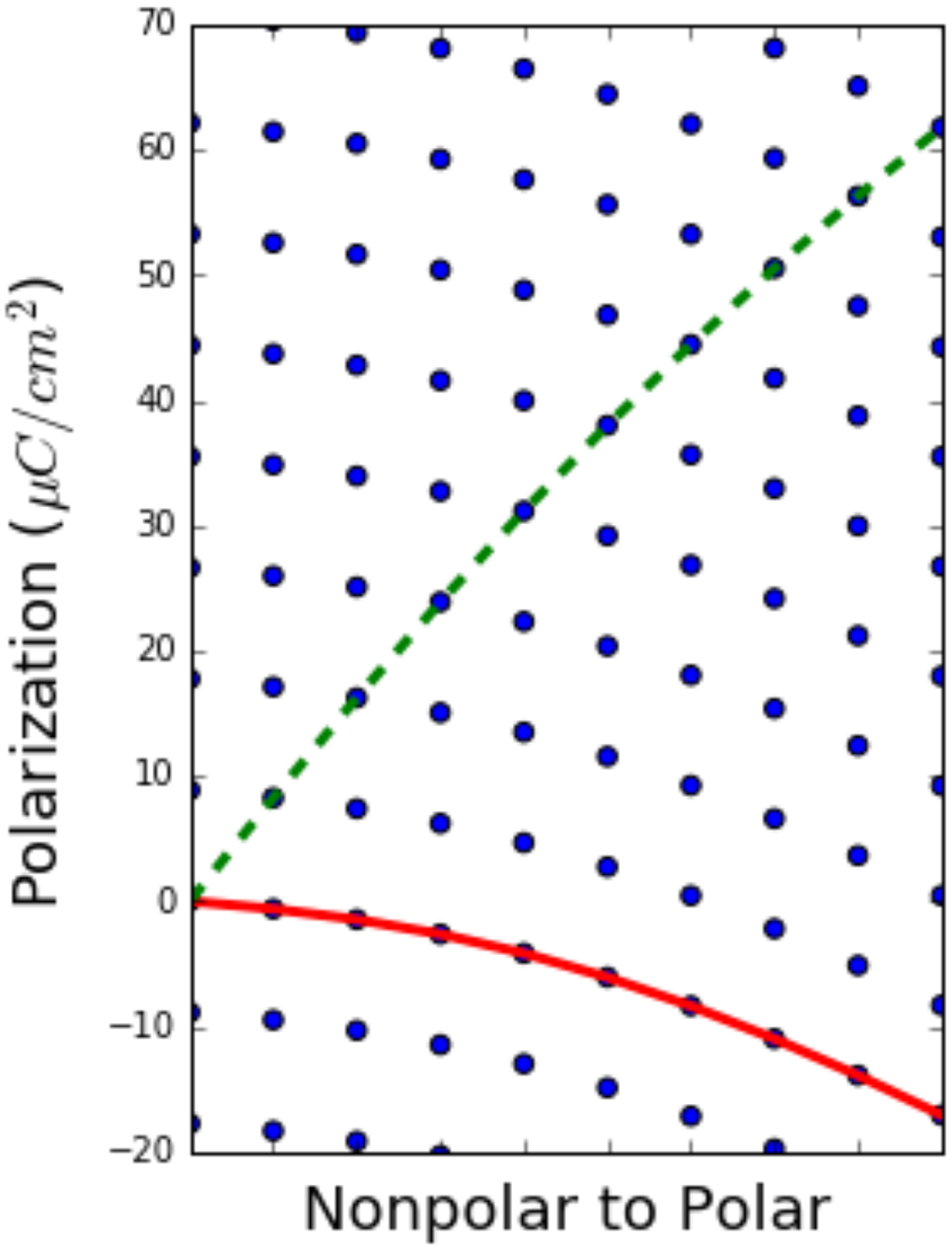
Polarization changes are observables and must be uniquely defined.

We use tools implemented in pymatgen for periodic structures to find the closest “image” to a given Cartesian coordinate.

We start with the nonpolar polarization closest to zero and iteratively find the closest polarization image of subsequent interpolations.

Algorithm for adjusting to the same branch polarization

This method can fail if there are insufficient interpolations to distinguish seemingly continuous branches. For example, large unit cells have smaller polarization quanta.



Ti3(BiO)4

To prevent this, the number interpolations should satisfy the following condition.

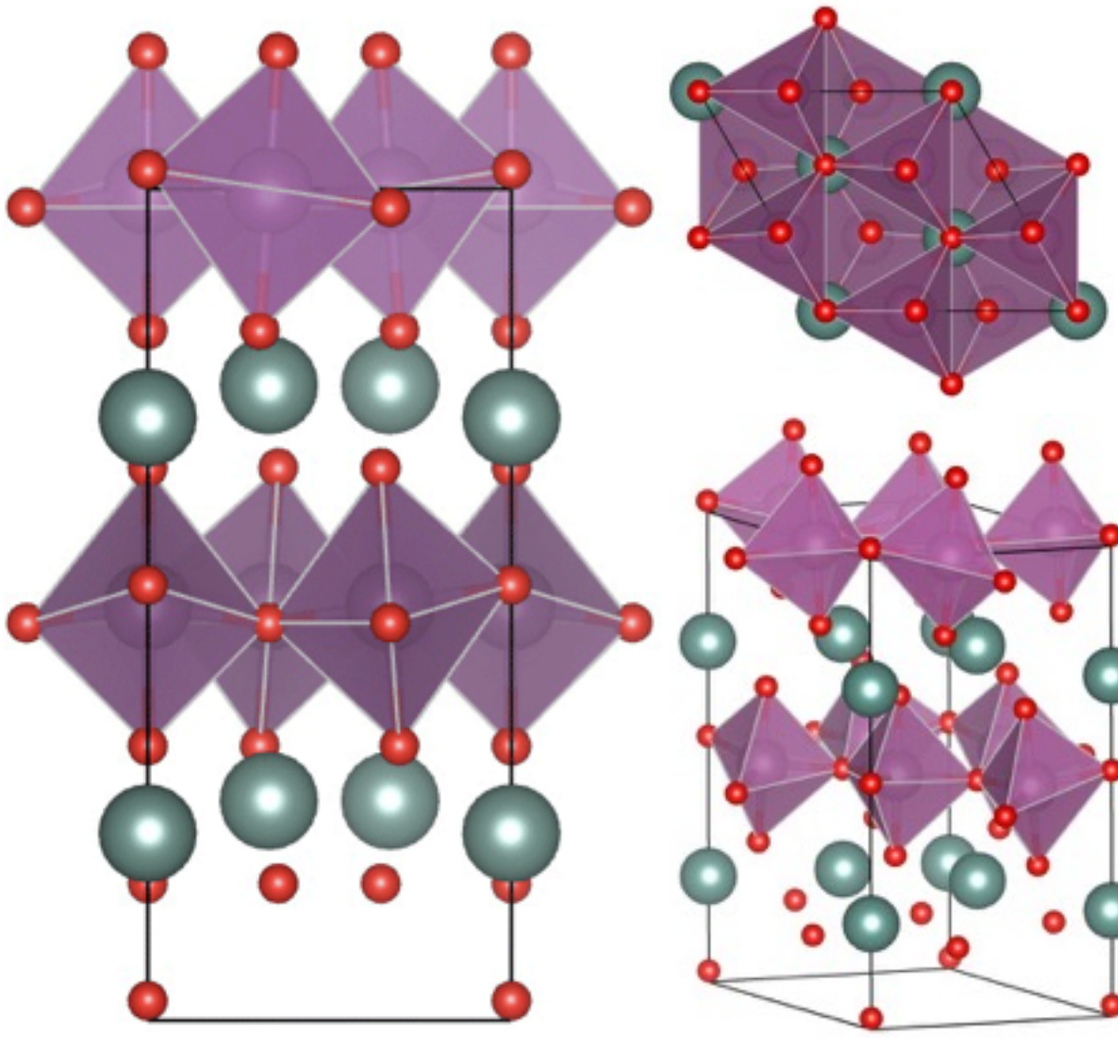
$$\frac{P_S}{N_I} << \min\left(\frac{eR_a}{\Omega}, \frac{eR_b}{\Omega}, \frac{eR_c}{\Omega}\right)$$

One can estimate the spontaneous polarization to be ~100 μC/cm^2 to find a conservative number of interpolations needed.

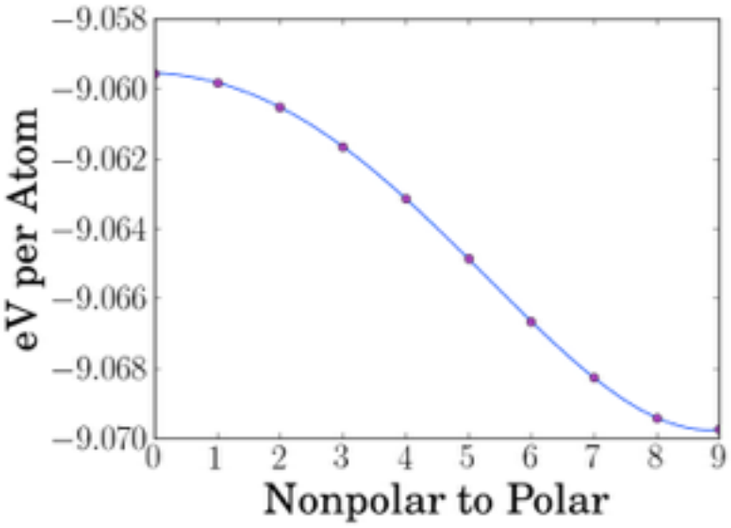
Algorithm chooses lowest consistent polarization.

LuGaO3, YSbO3, ScGaO3, YScO3
Non-magnetic hexagonal manganite-like

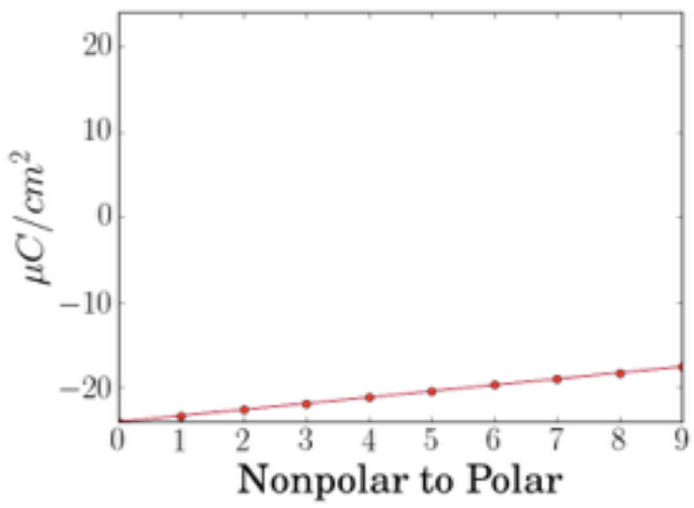
From the MIT matgen database.
Hypothetical structures.



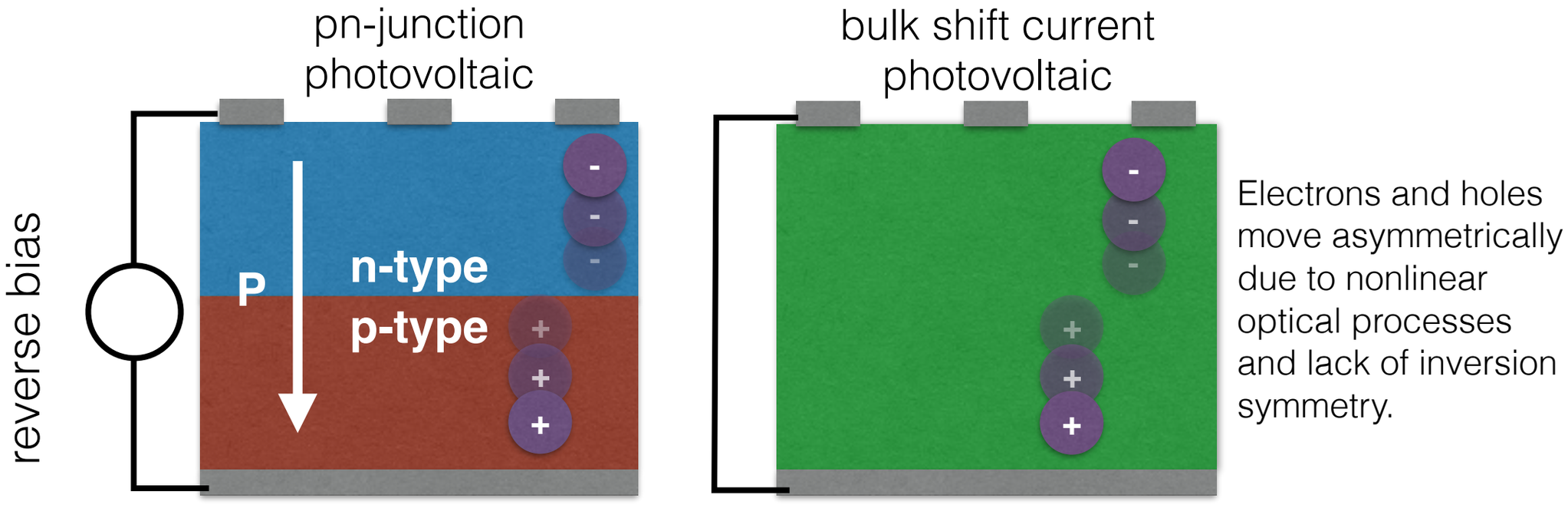
YScO3



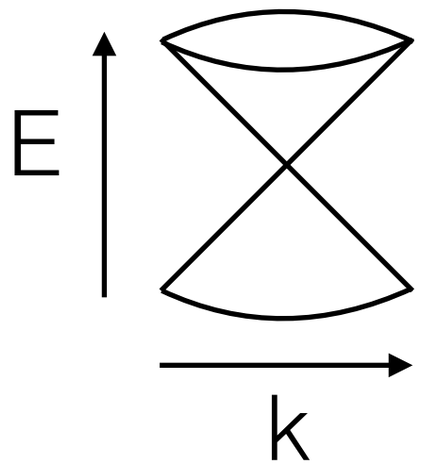
All have half-quantum polarizations for nonpolar structure.



Ferroelectrics can be used to make non-volatile RAM and possibly bulk shift current photovoltaics.



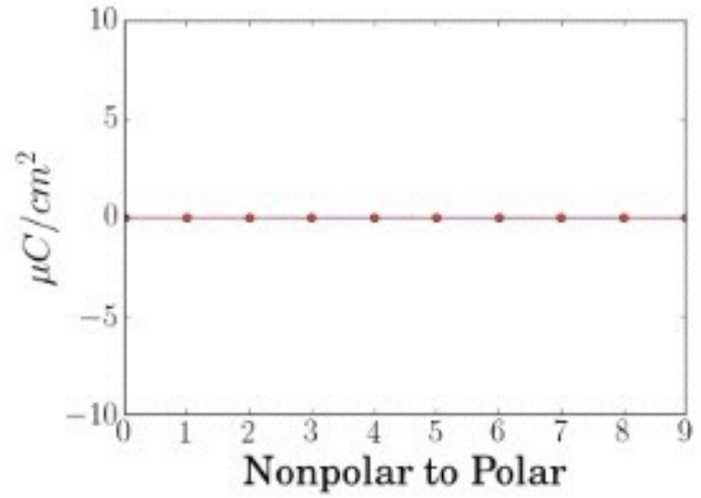
Ferroelectrics can serve as a testbed for new physics: e.g. topological ferroelectrics and ferroaxial ferroelectrics.

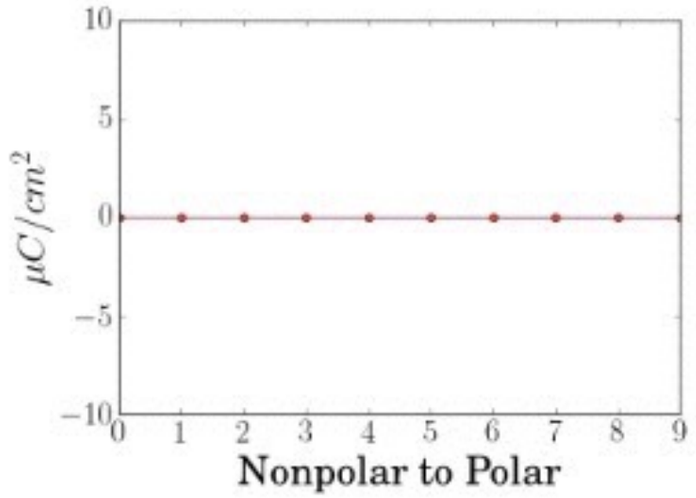


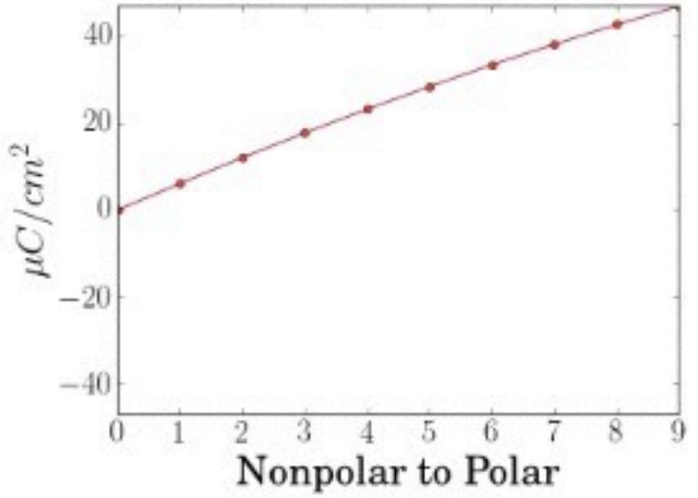
$$\mathbf{P}_{tot} = \mathbf{P} + \mathrm{curl}\mathbf{T}^{e}$$

wfid_1476040947.794782

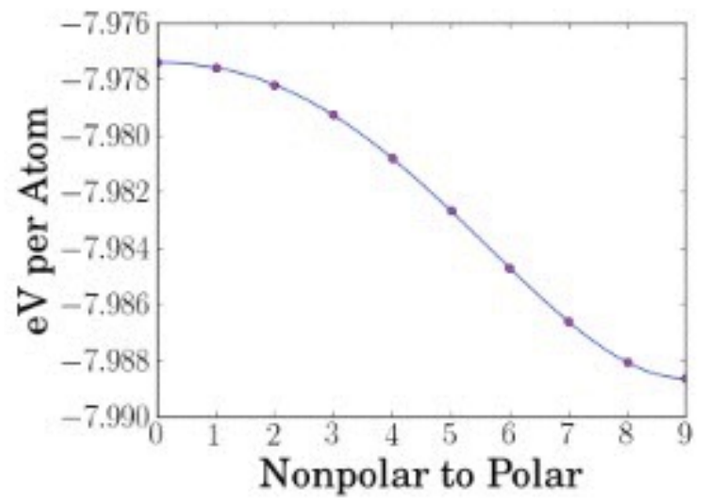
Polarization Adjusted (a,b,c)



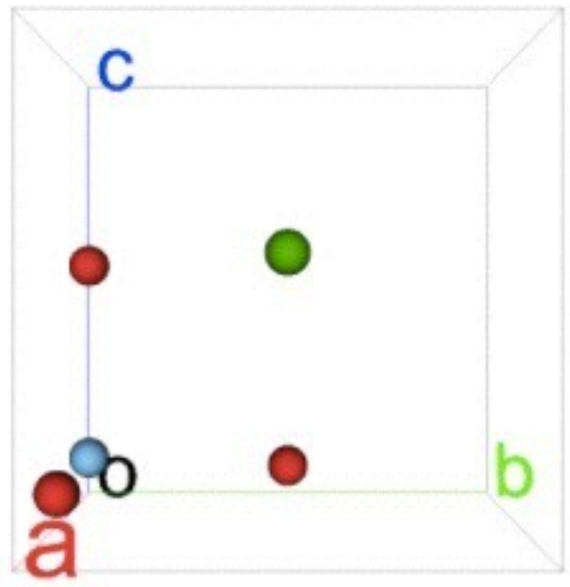




Energy



Distortion



Formula: BaTiO3

Polar SG: 99

Nonpolar SG: 221

PBE Gap: 1.7312

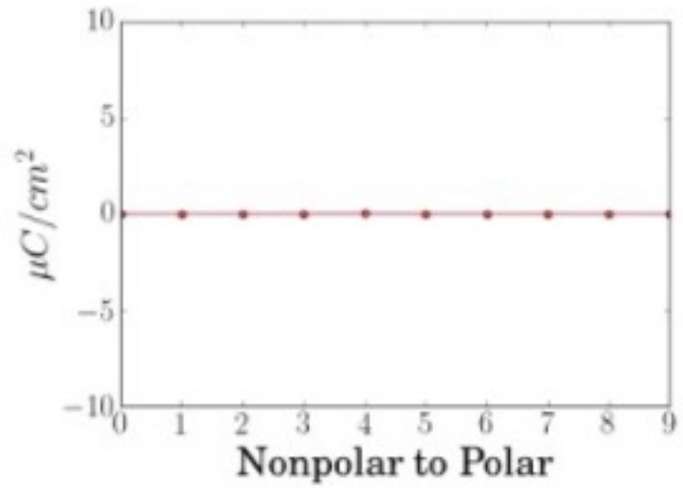
HSE Gap: None

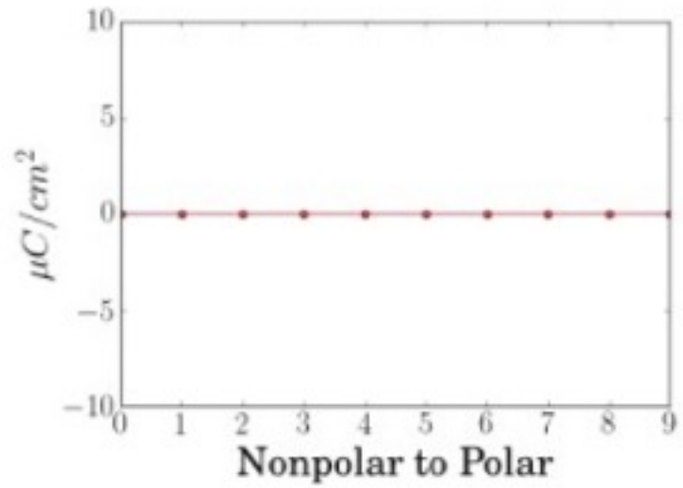
Local minima for charge density (~30 candidates)

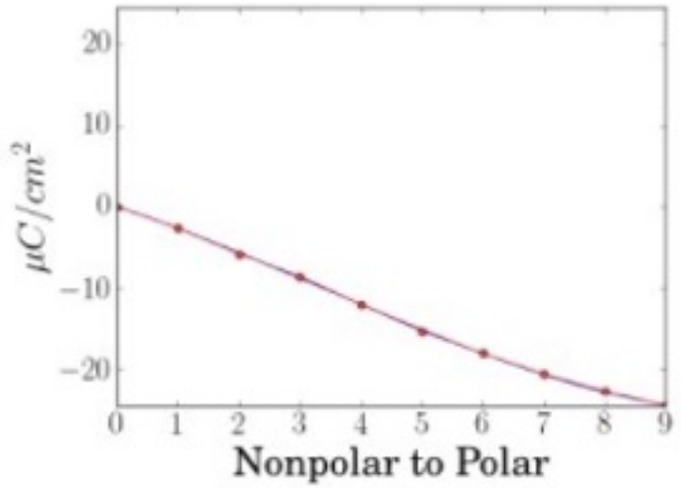
Typically have transition metal that can take multiple oxidation states.

wfid_1476040802.838448

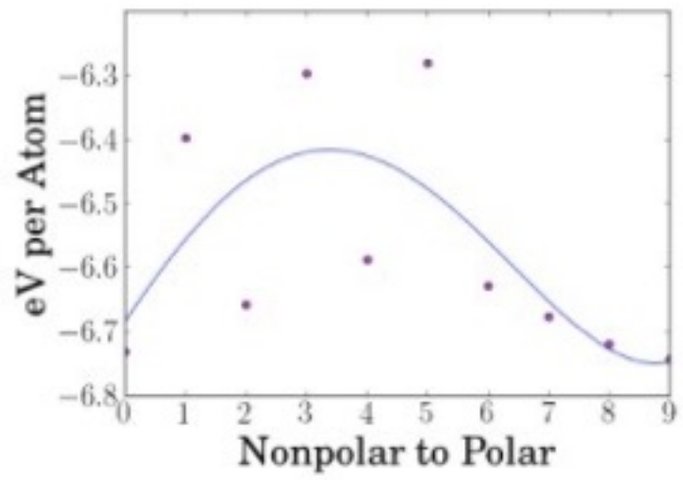
Polarization Adjusted (a,b,c)



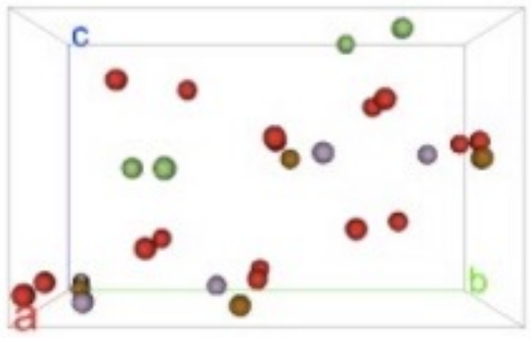




Energy



Distortion



Formula: LiFePO4

Polar SG: 33

Nonpolar SG: 63

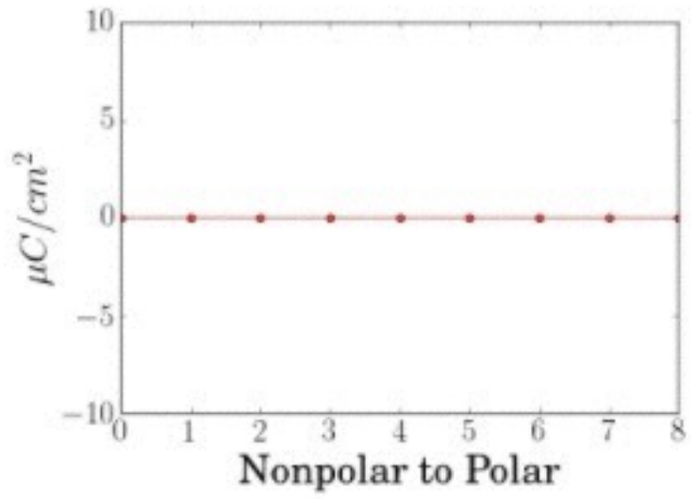
PBE Gap: 3.2893

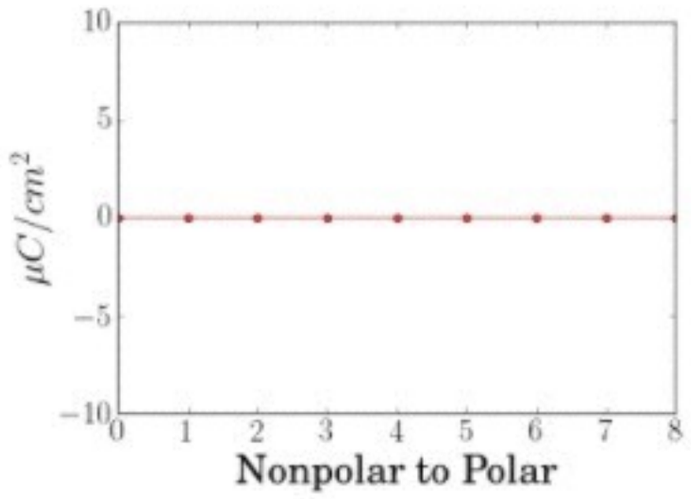
HSE Gap: None

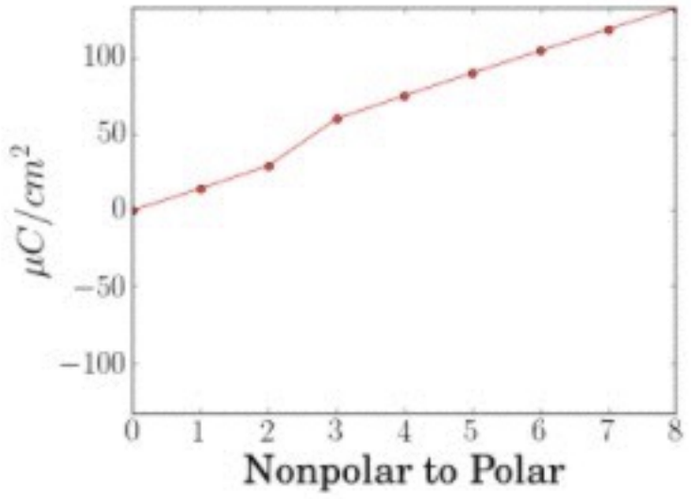
Metallic interpolation (38 candidates)

wfid_1476041018.244845

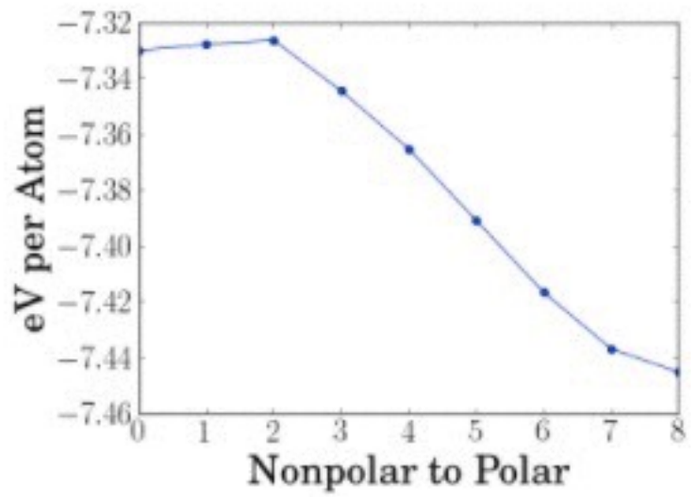
Polarization Adjusted (a,b,c)



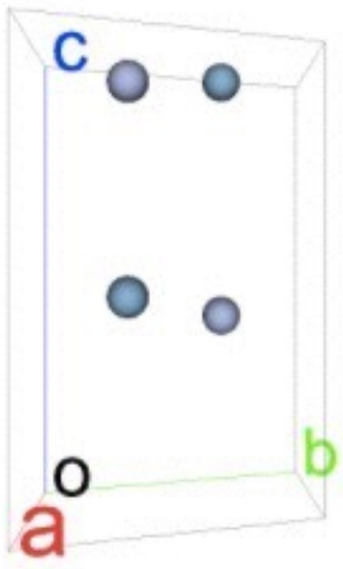




Energy



Distortion



Formula: AlN

Polar SG: 186

Nonpolar SG: 194

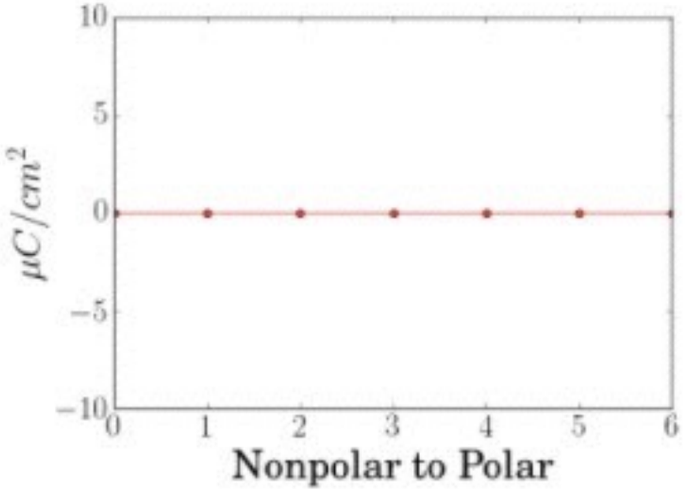
PBE Gap: 4.0544

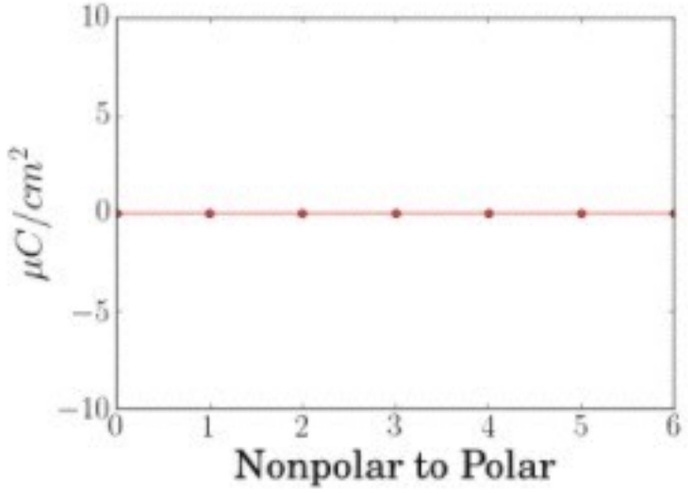
HSE Gap: None

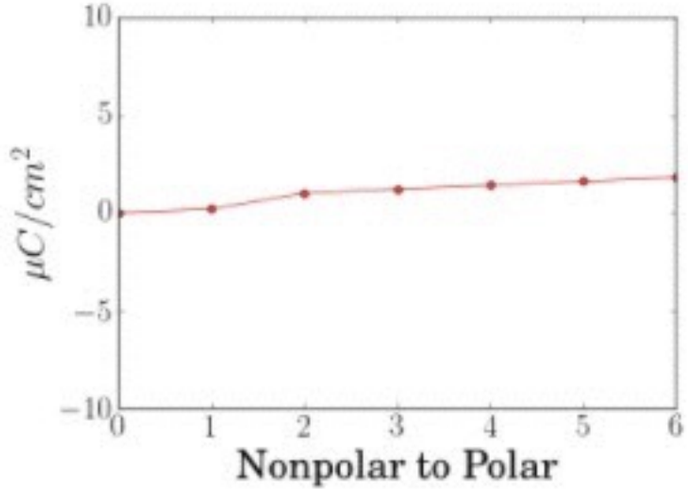
Metallic interpolation (38 candidates)

wfid_1476041054.047338

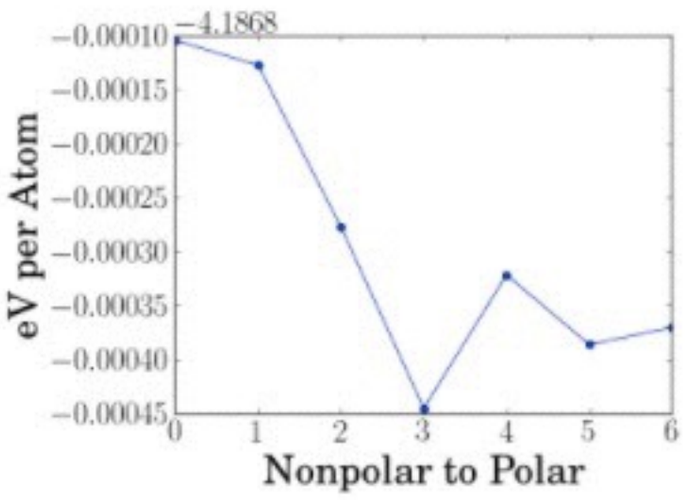
Polarization Adjusted (a,b,c)



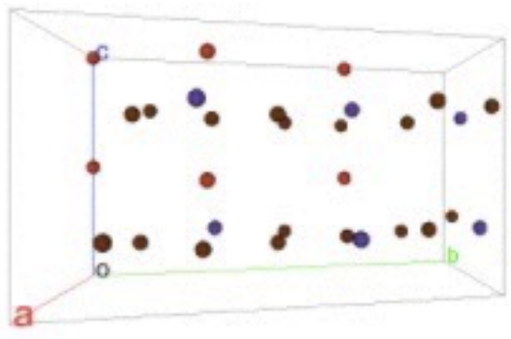




Energy



Distortion



Formula: RbVBr3

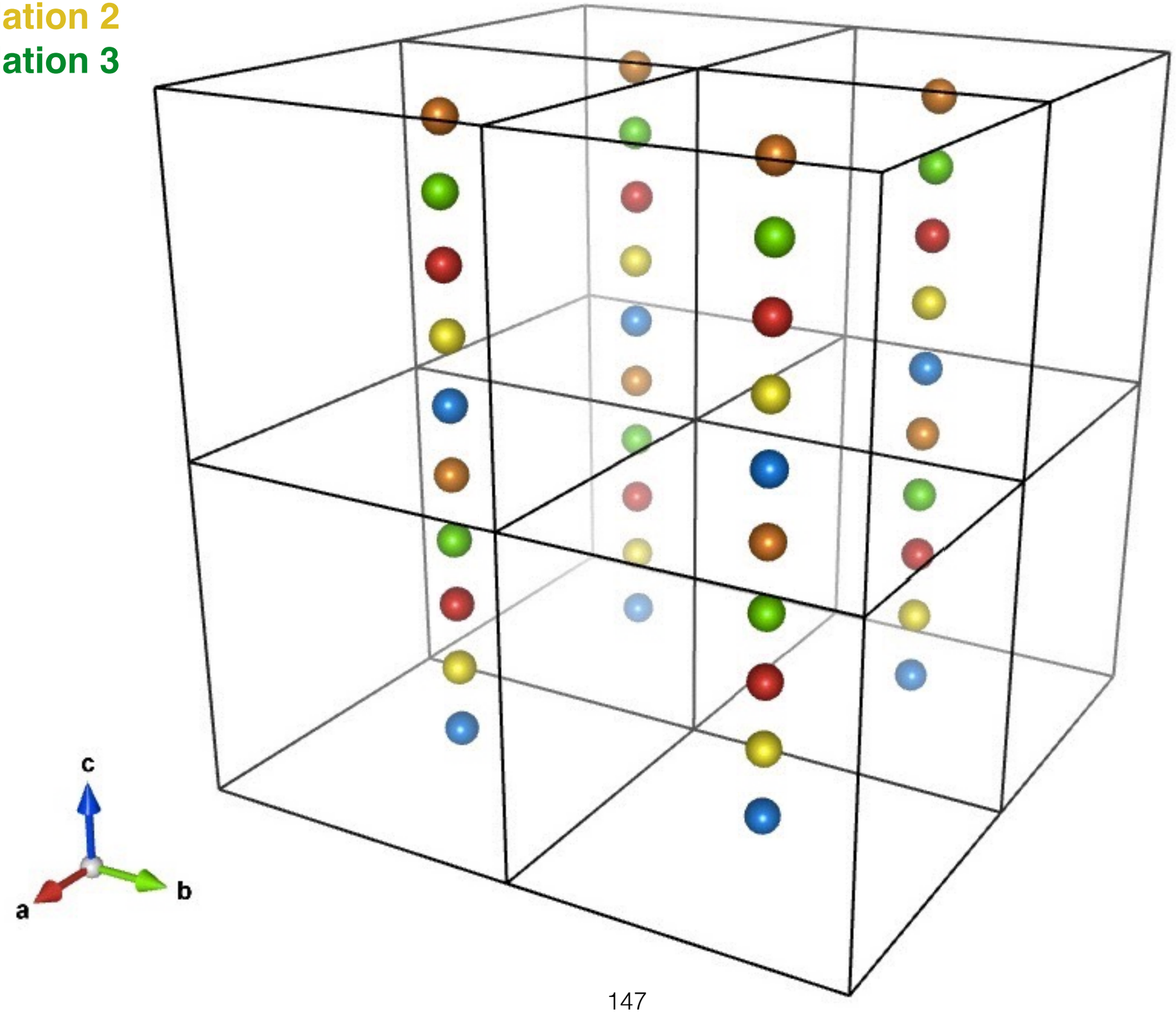
Polar SG: 185

Nonpolar SG: 194

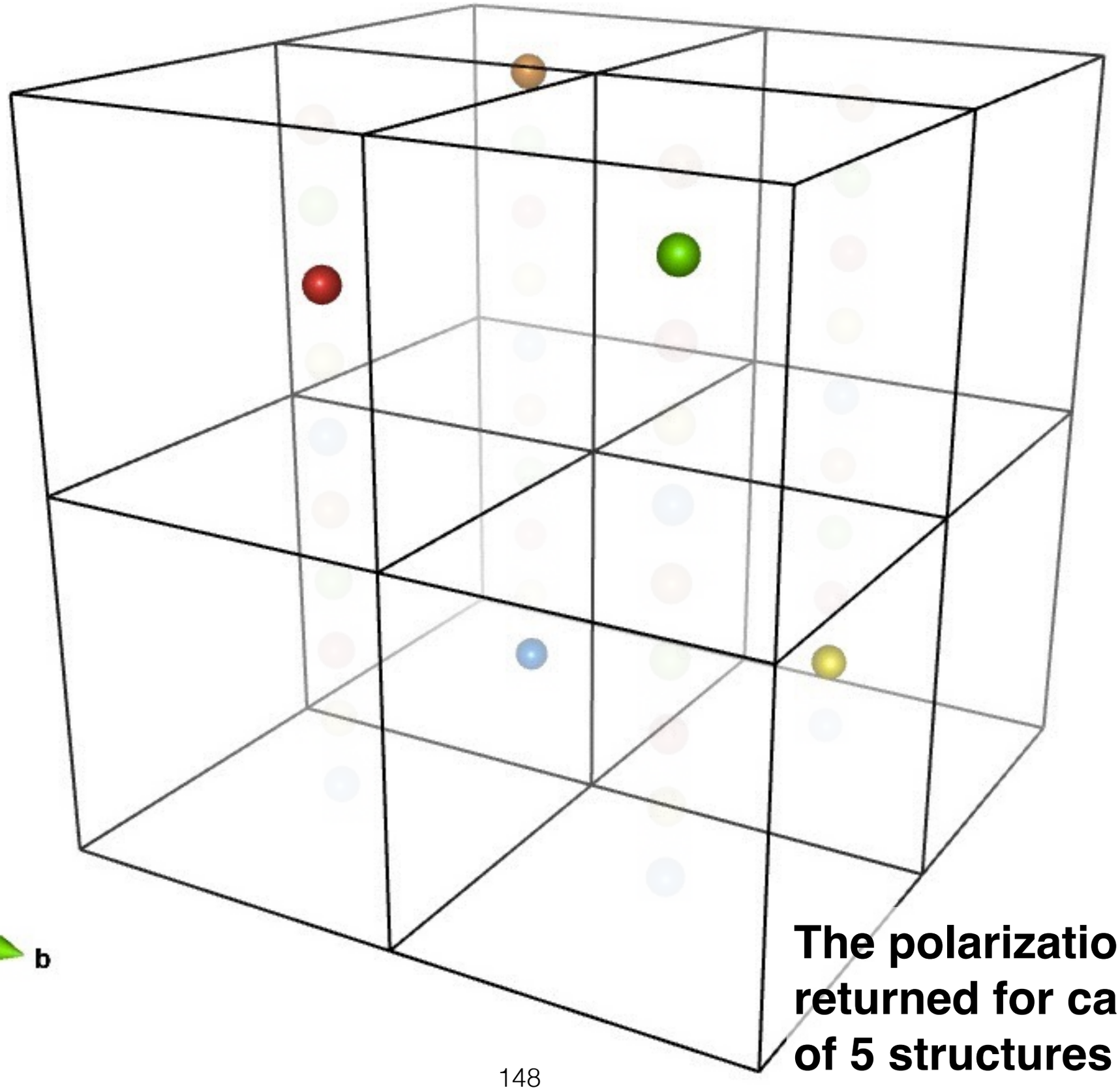
PBE Gap: 0.6221

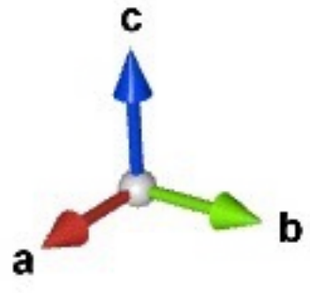
HSE Gap: None

Nonpolar
Interpolation 1
Interpolation 2
Interpolation 3
Polar



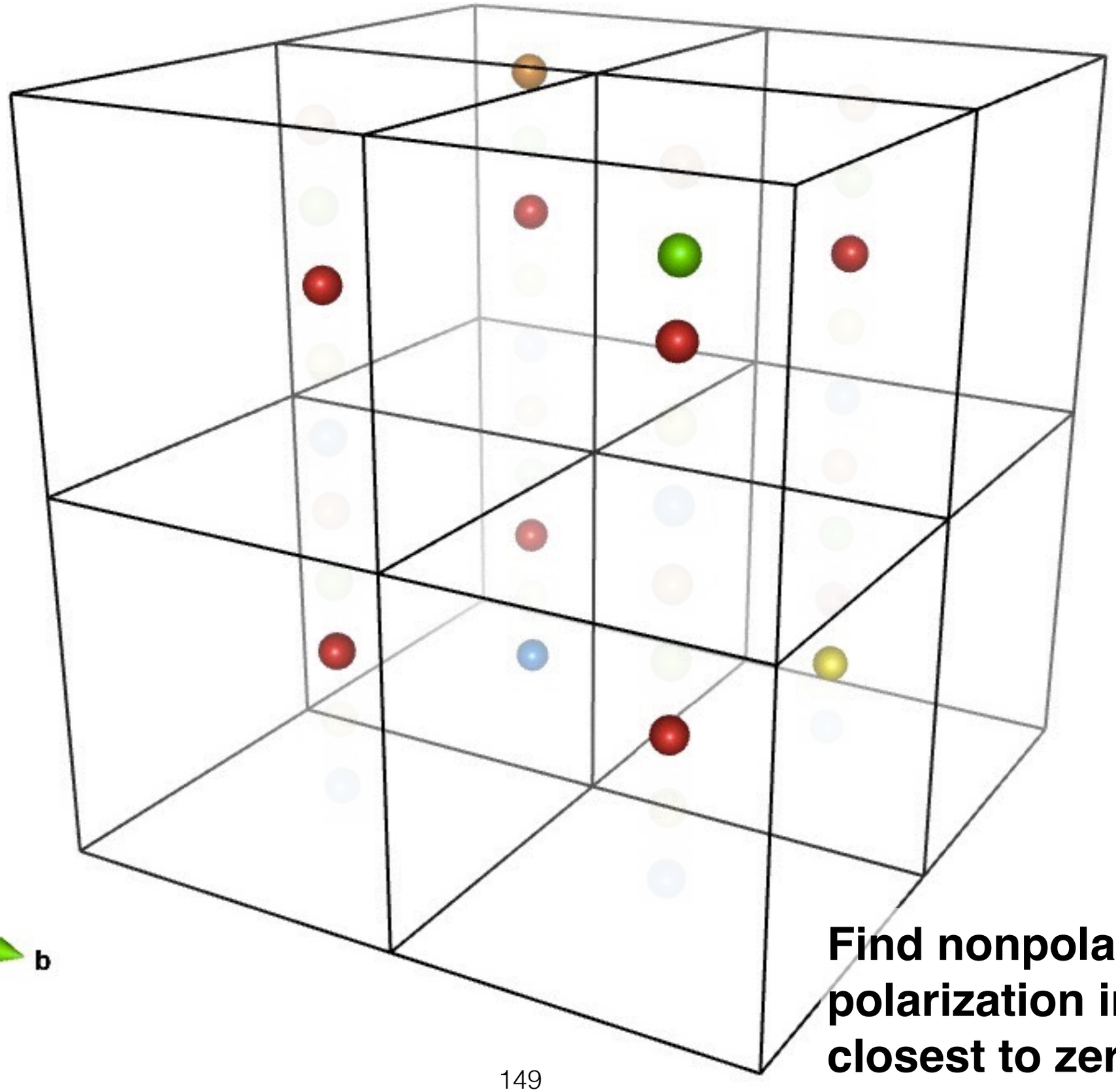
Nonpolar
Interpolation 1
Interpolation 2
Interpolation 3
Polar

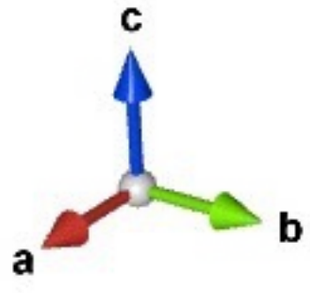




The polarization values returned for calculations of 5 structures along distortion.

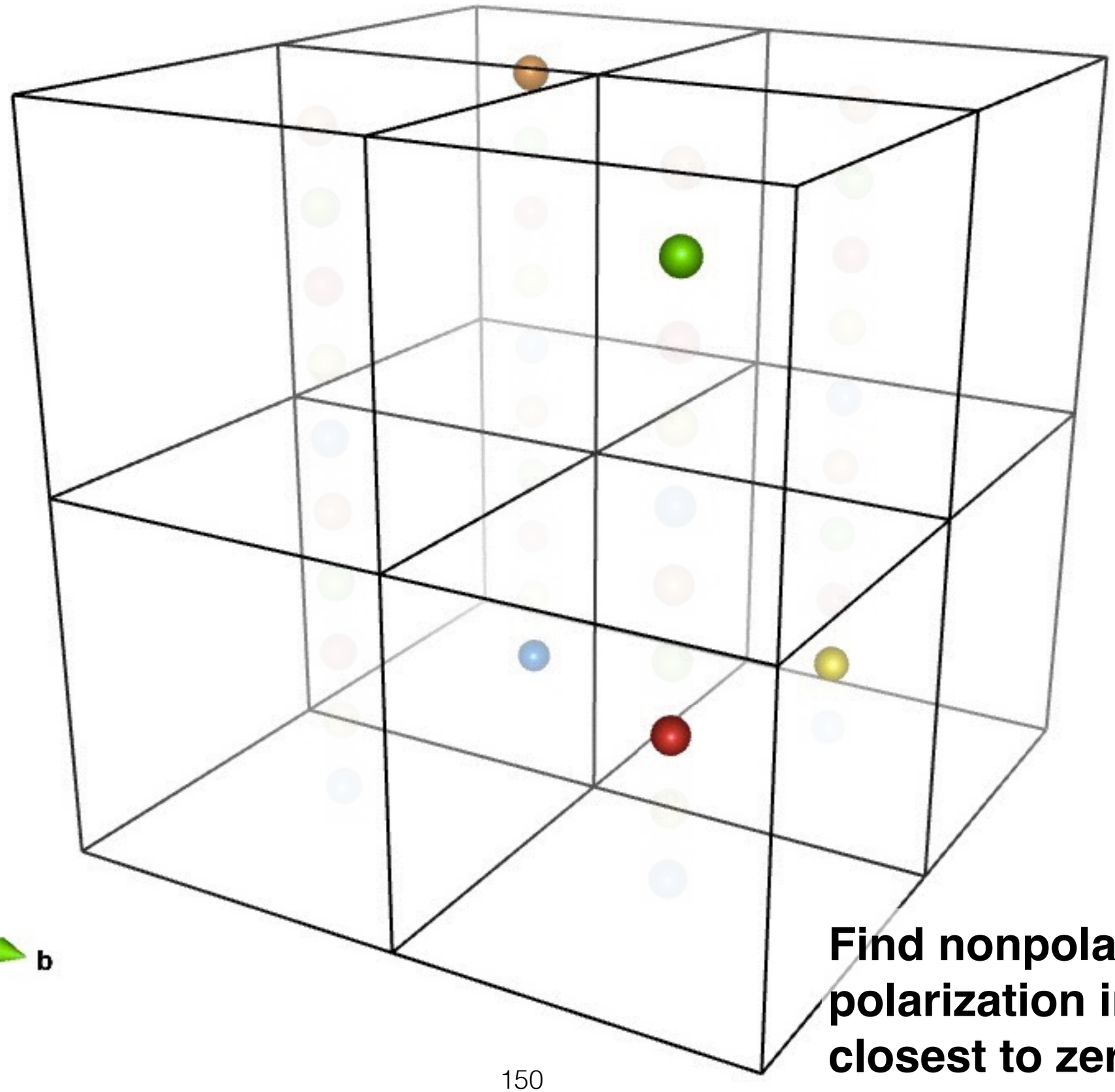
Nonpolar
Interpolation 1
Interpolation 2
Interpolation 3
Polar

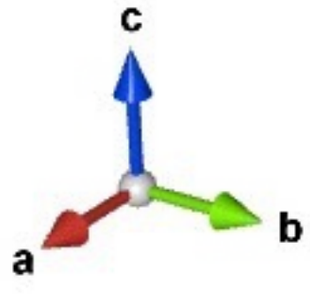




Find nonpolar polarization image closest to zero.

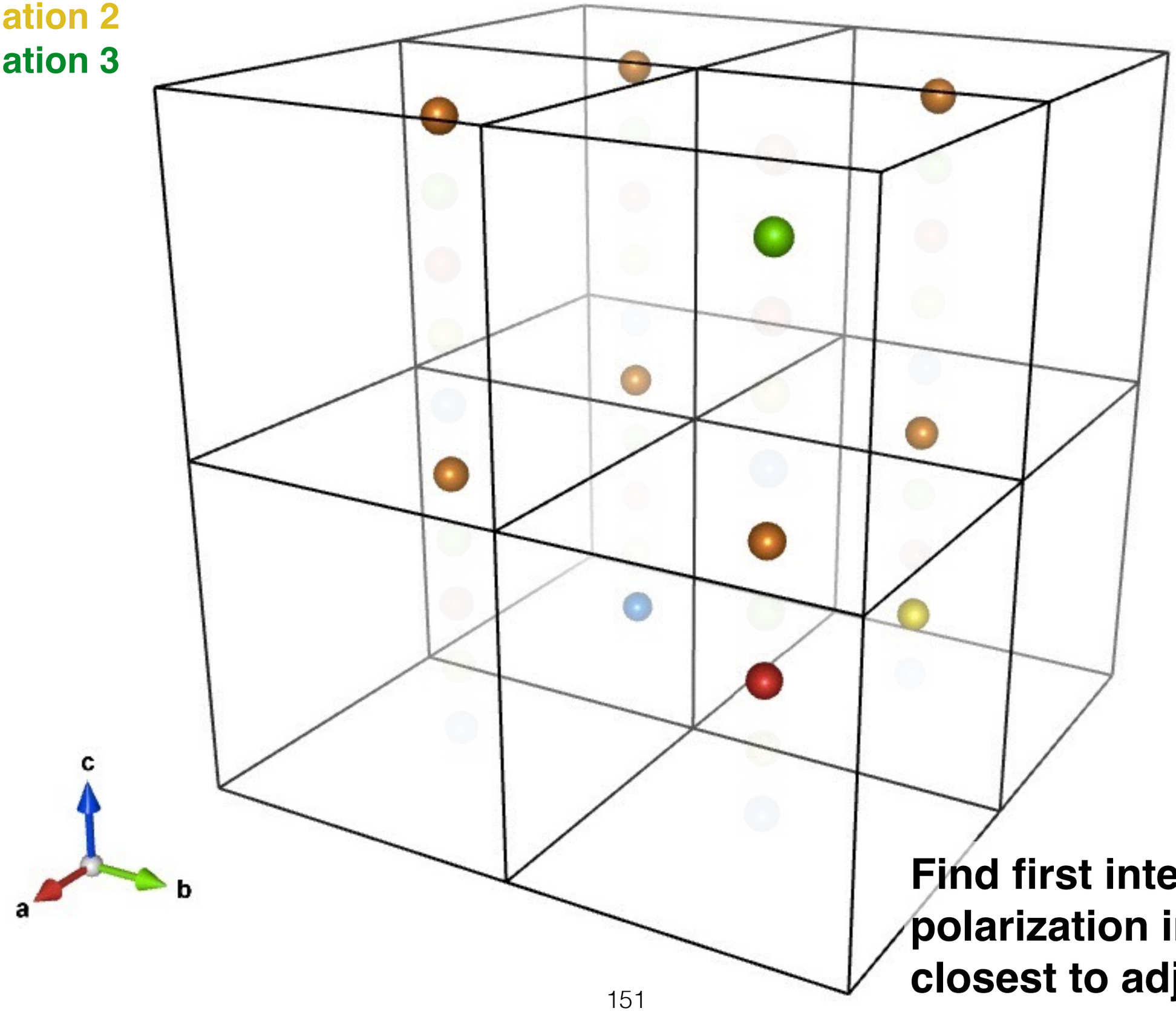
Nonpolar
Interpolation 1
Interpolation 2
Interpolation 3
Polar





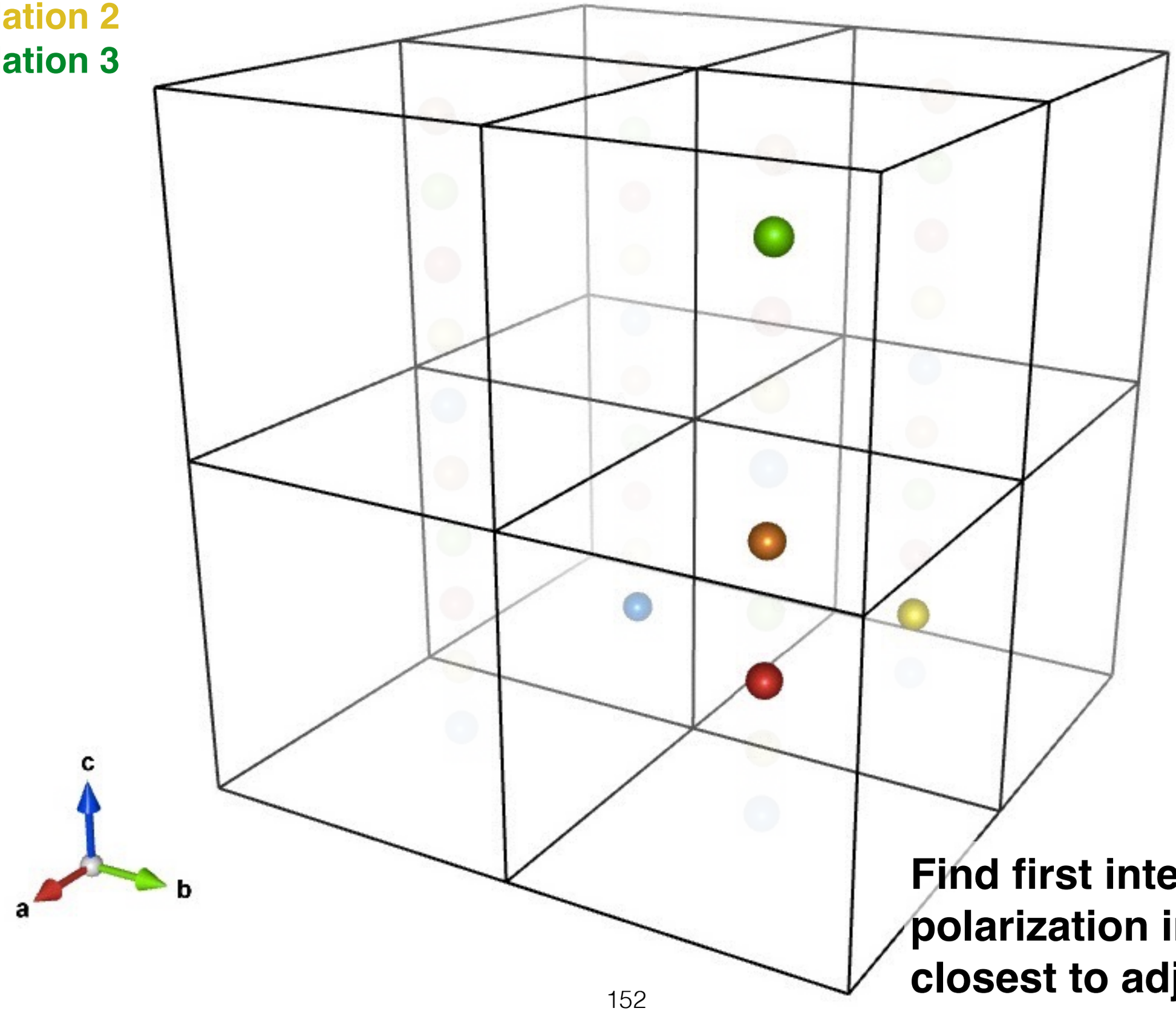
Find nonpolar polarization image closest to zero.

Nonpolar
Interpolation 1
Interpolation 2
Interpolation 3
Polar



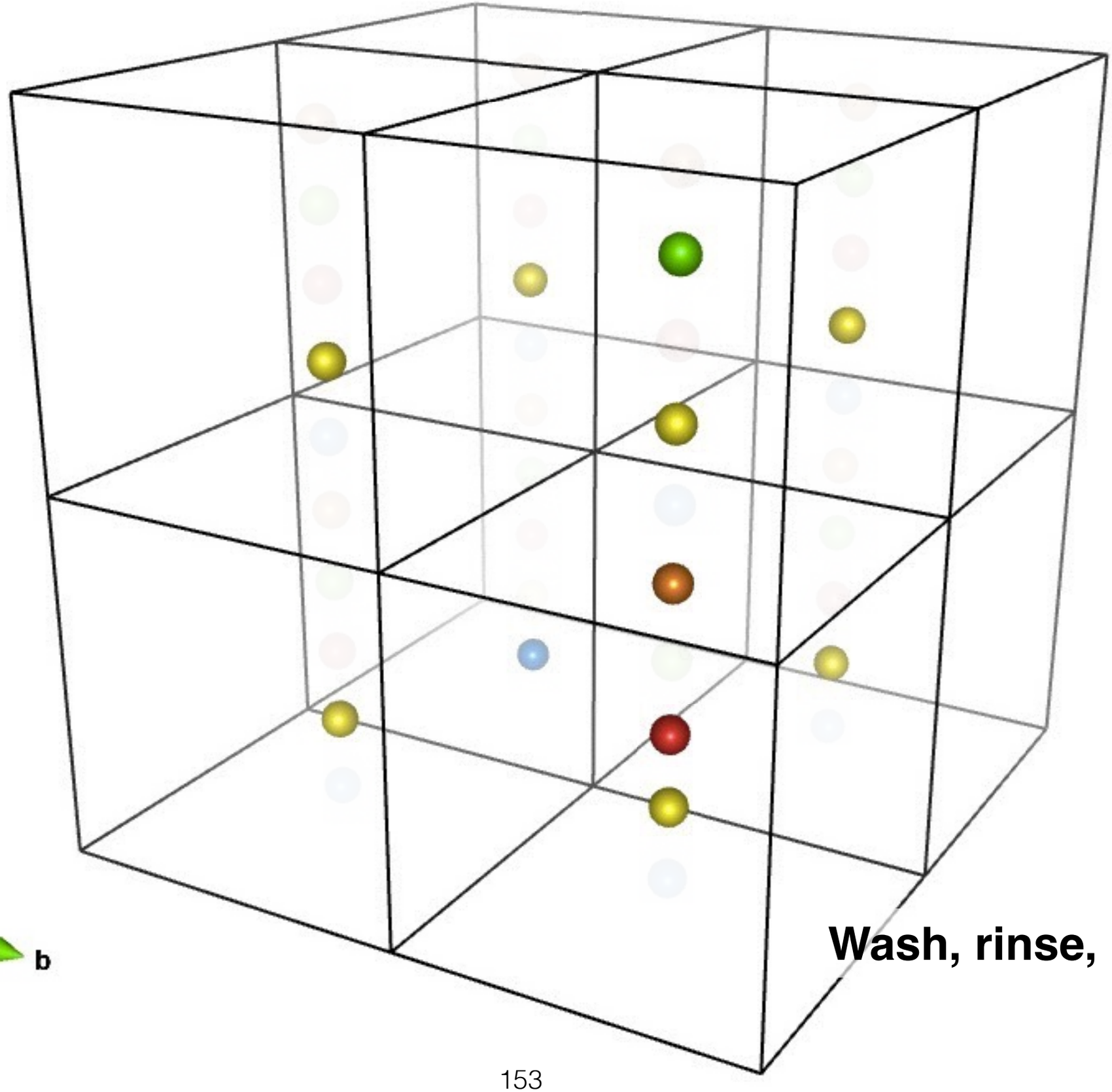
Find first interpolation polarization image closest to adjusted nonpolar polarization.

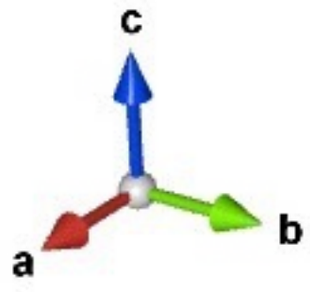
Nonpolar
Interpolation 1
Interpolation 2
Interpolation 3
Polar



Find first interpolation polarization image closest to adjusted nonpolar polarization.

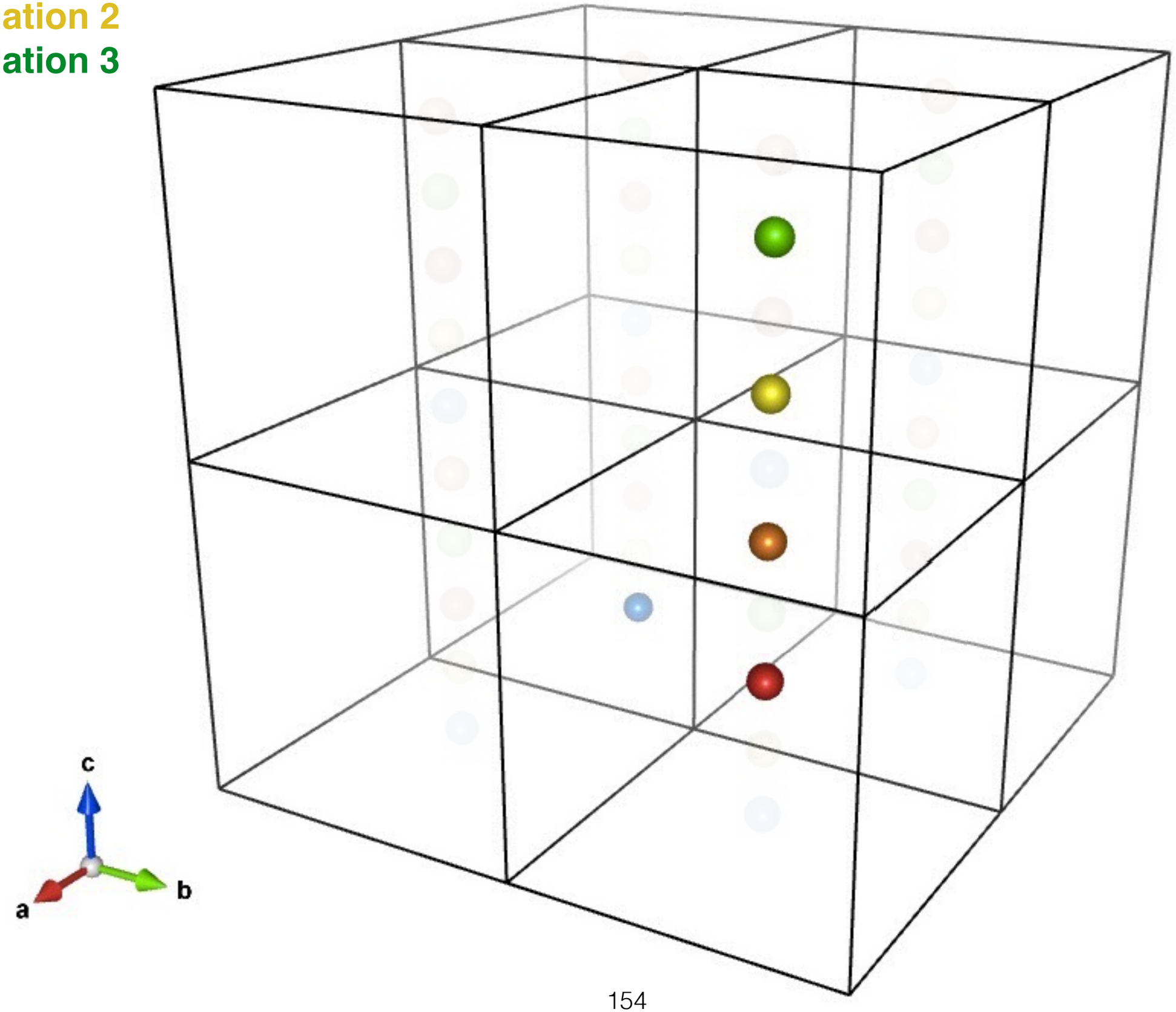
Nonpolar
Interpolation 1
Interpolation 2
Interpolation 3
Polar



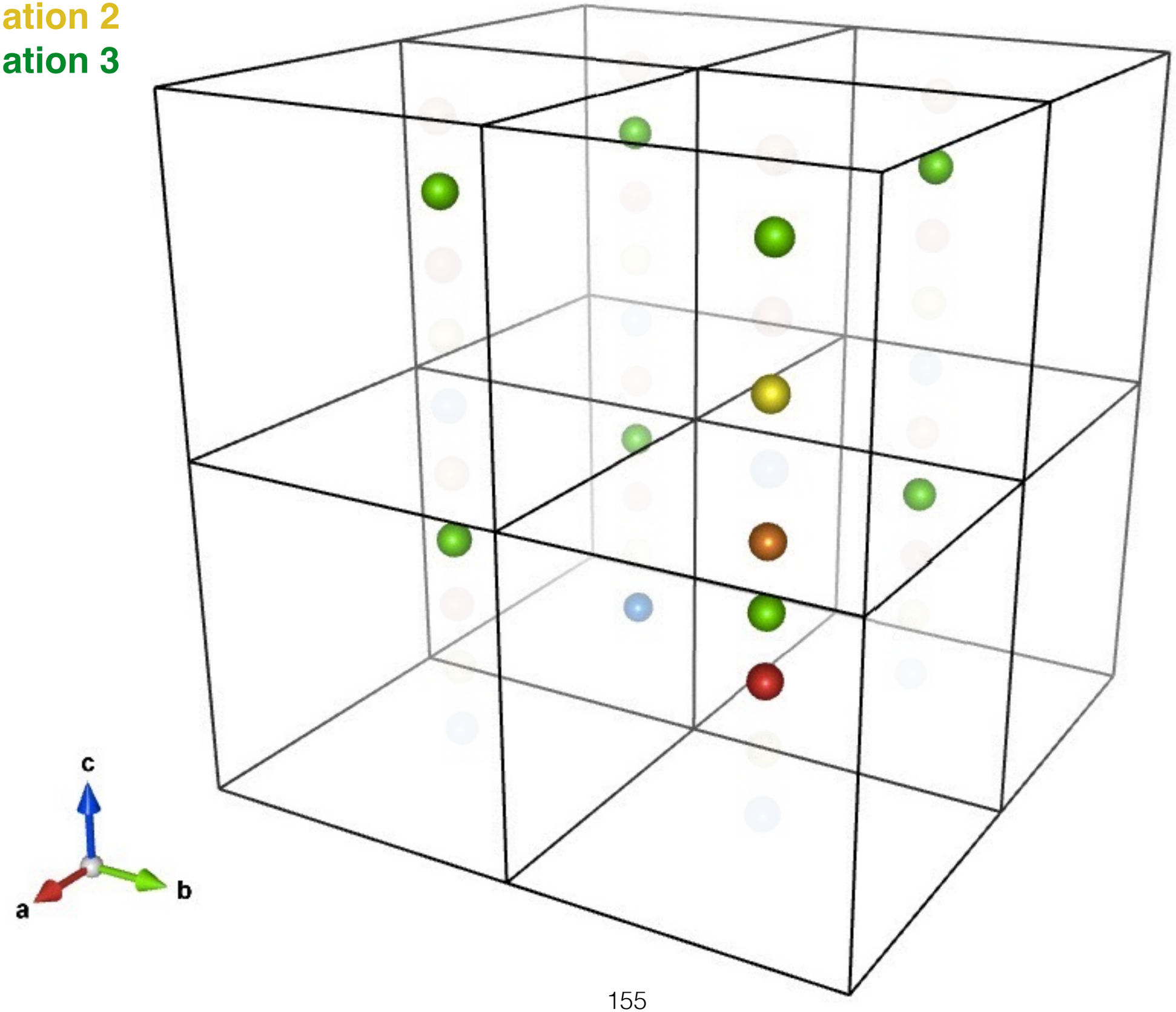


Wash, rinse, repeat…

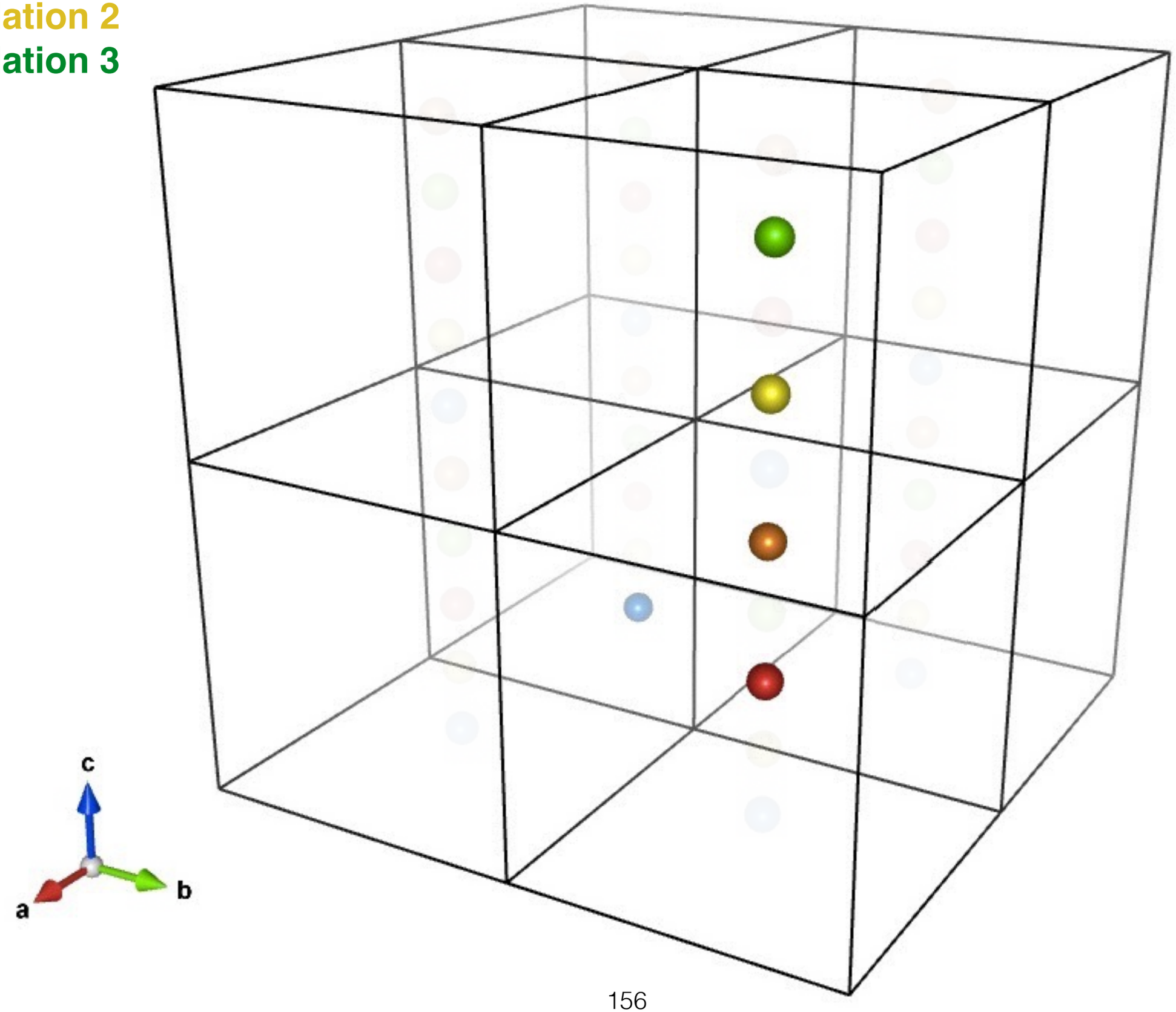
Nonpolar
Interpolation 1
Interpolation 2
Interpolation 3
Polar



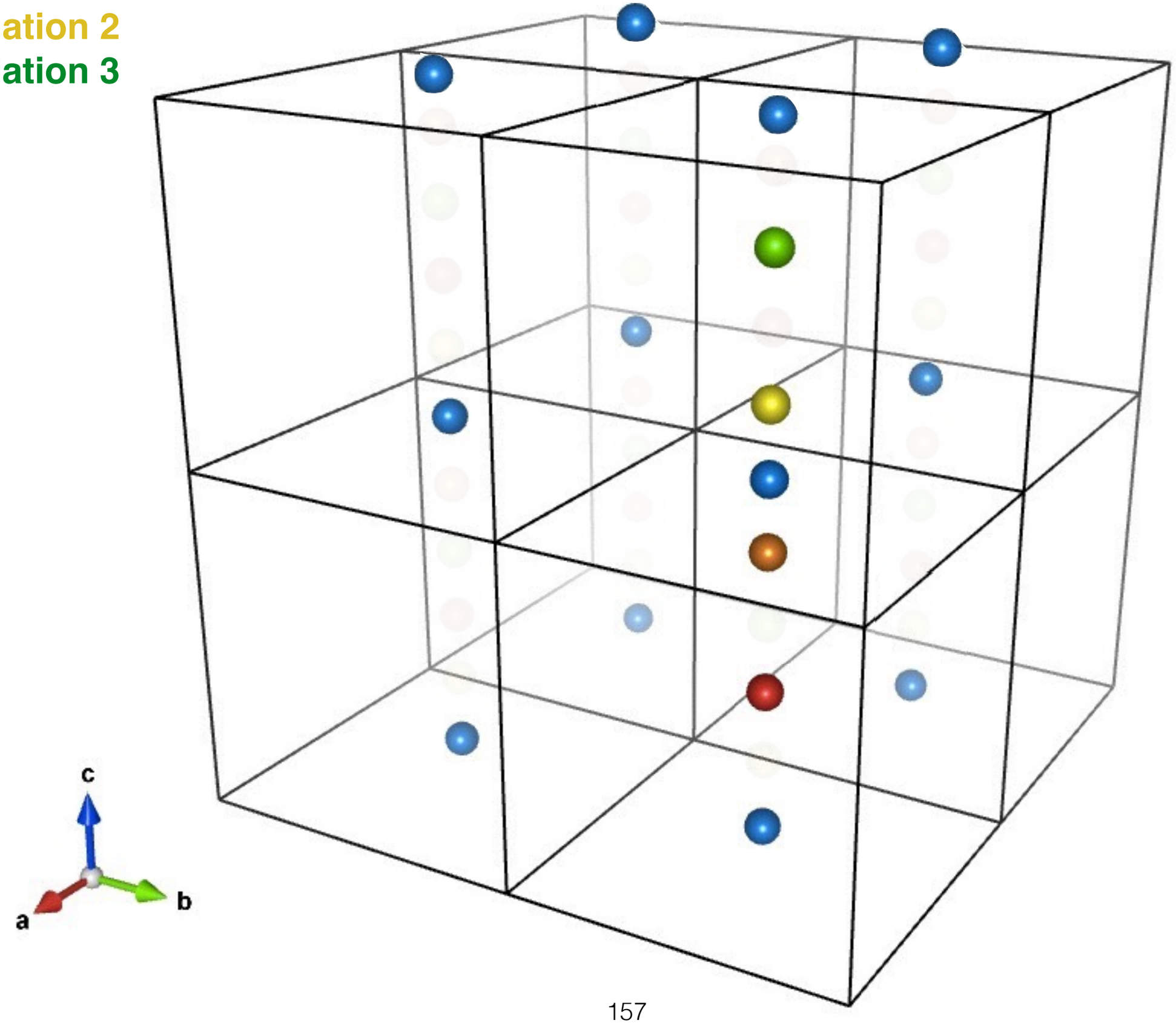
Nonpolar
Interpolation 1
Interpolation 2
Interpolation 3
Polar



Nonpolar
Interpolation 1
Interpolation 2
Interpolation 3
Polar



Nonpolar
Interpolation 1
Interpolation 2
Interpolation 3
Polar



Nonpolar
Interpolation 1
Interpolation 2
Interpolation 3
Polar