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New classes of piezoelectrics, ferroelectrics, and antiferroelectrics by first-principles high-throughput materials design

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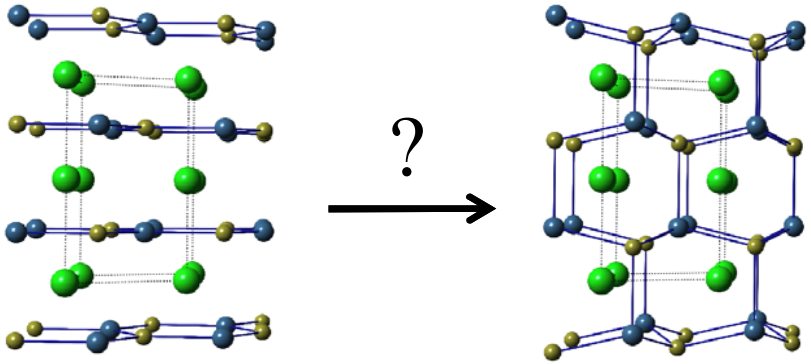
New Classes of Piezoelectrics, Ferroelectrics, and Antiferroelectrics by First-Principles High-Throughput Materials Design



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Emerging Technologies…

In order to solve the problems facing us in the 21st century there arises a critical need for new technologies based on multifunctional materials.

High speed, low power computation
Improved communications
High yield energy conversion and storage

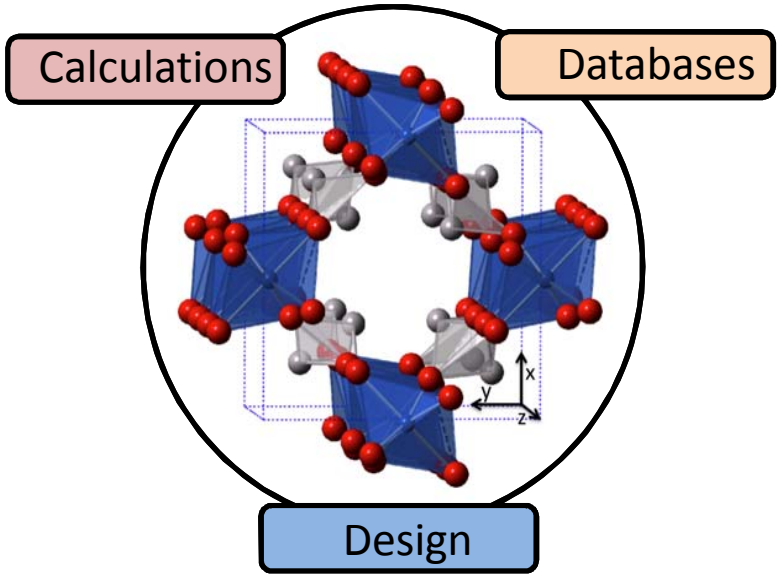
Most of the solutions could arise from an improved understanding of nanoscale phenomena…
specifically atomistic interactions and how they affect the measurable properties of a device.

Critical need to successfully couple theoretical modeling and experimental endeavors.

Our Approach

To design and discover new multifunctional materials we combine:

1) Crystallographic database searching
(Inorganic Crystal Structural Database)
input structural information
and
2) First-principles calculations
(Density Functional Theory: LDA)
output properties



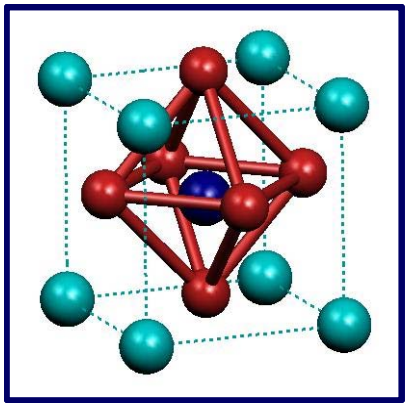
Structure-property relations…
platforms for functionality

We perform high-throughput studies of underdeveloped families of materials to screen for exceptional members of potentially functional families.

Outline

The ABO_3 Perovskites

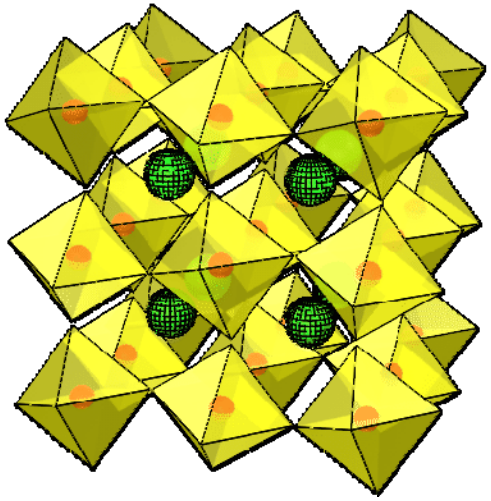
A Canonical Family



Moving Beyond the Perovskites

A New Class of Piezoelectrics

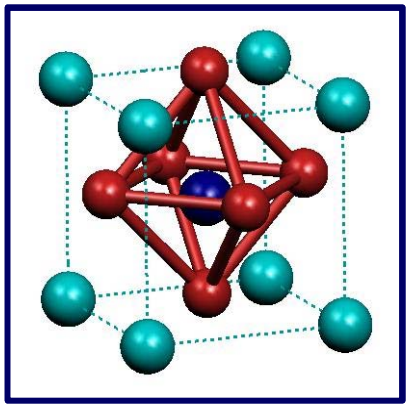
A New Class of Ferroelectrics



A New Class of Antiferroelectrics

Concluding Thoughts

The Perovskites: A Canonical Family

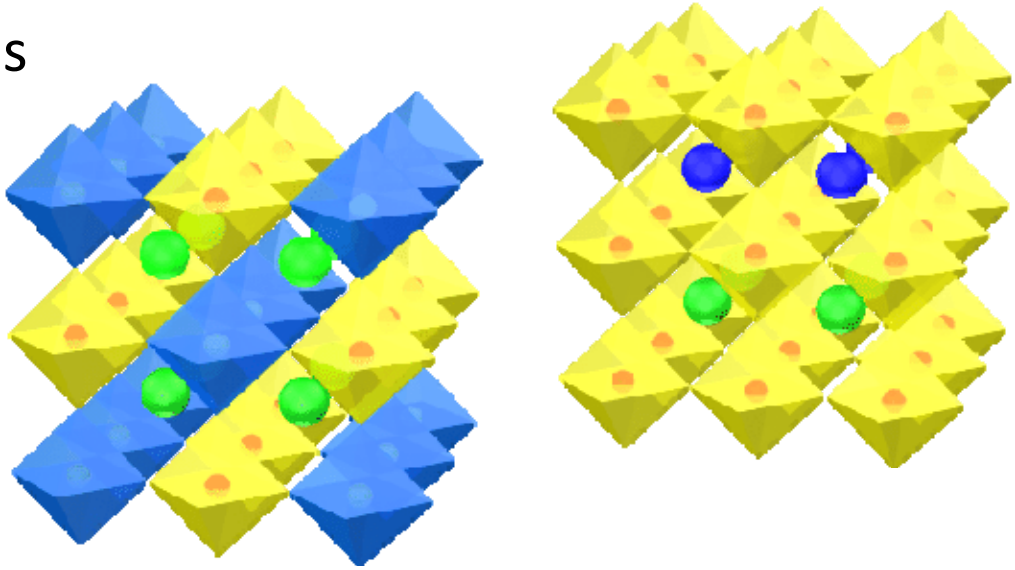


ABO_3 solid oxide **perovskites:**

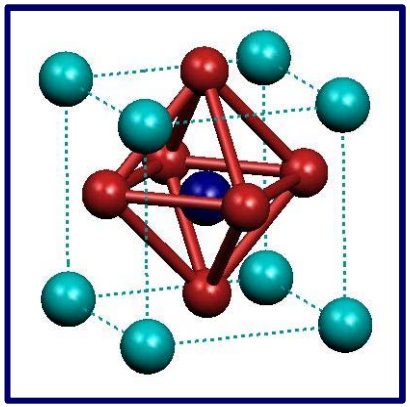
A at corners (12-fold coordinate)
B inside of O octahedron
(6-fold coordinate)
O octahedron are **corner-sharing**

Flexible structure with choice of *A* and *B* sites combinations almost unlimited
$PbTiO_3$, $BaZrO_3$, $LiNbO_3$

Solid solutions as well
AA'BB'O_3
$Pb(Zr,Ti)O_3$



The Perovskites: A Functional Family



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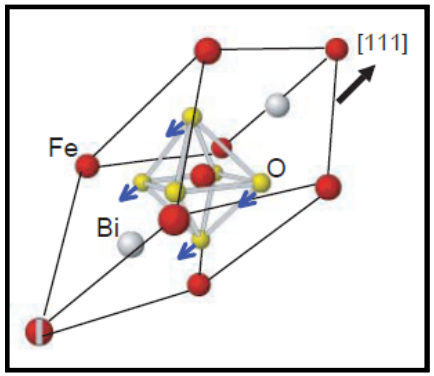
Solid solutions as well
AA'BB'O_3
$Pb(Zr,Ti)O_3$

A **piezoelectric** used in a **variety of applications!**

SONAR
ultrasound
positioning
sensors and actuators

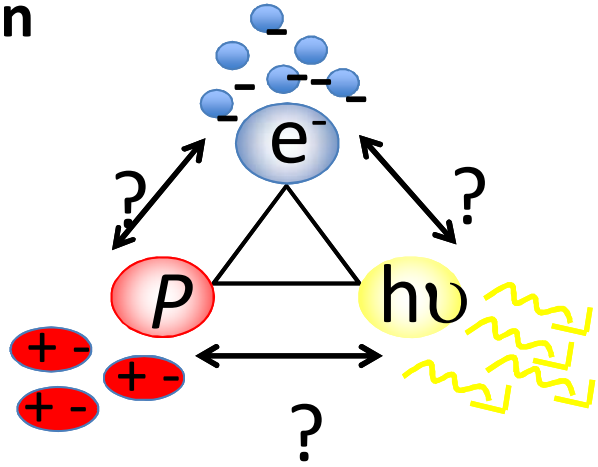
$BiFeO_3$: A Multifunctional Perovskite

Bi distort **along (111) as O_6 tilt** to generate
R_3c symmetry, a **polar** space group.
This polarization is reversible: **ferroelectric**.



AND…Fe^{3+} is **magnetic**
We can **couple polarization and magnetization**
in one material!

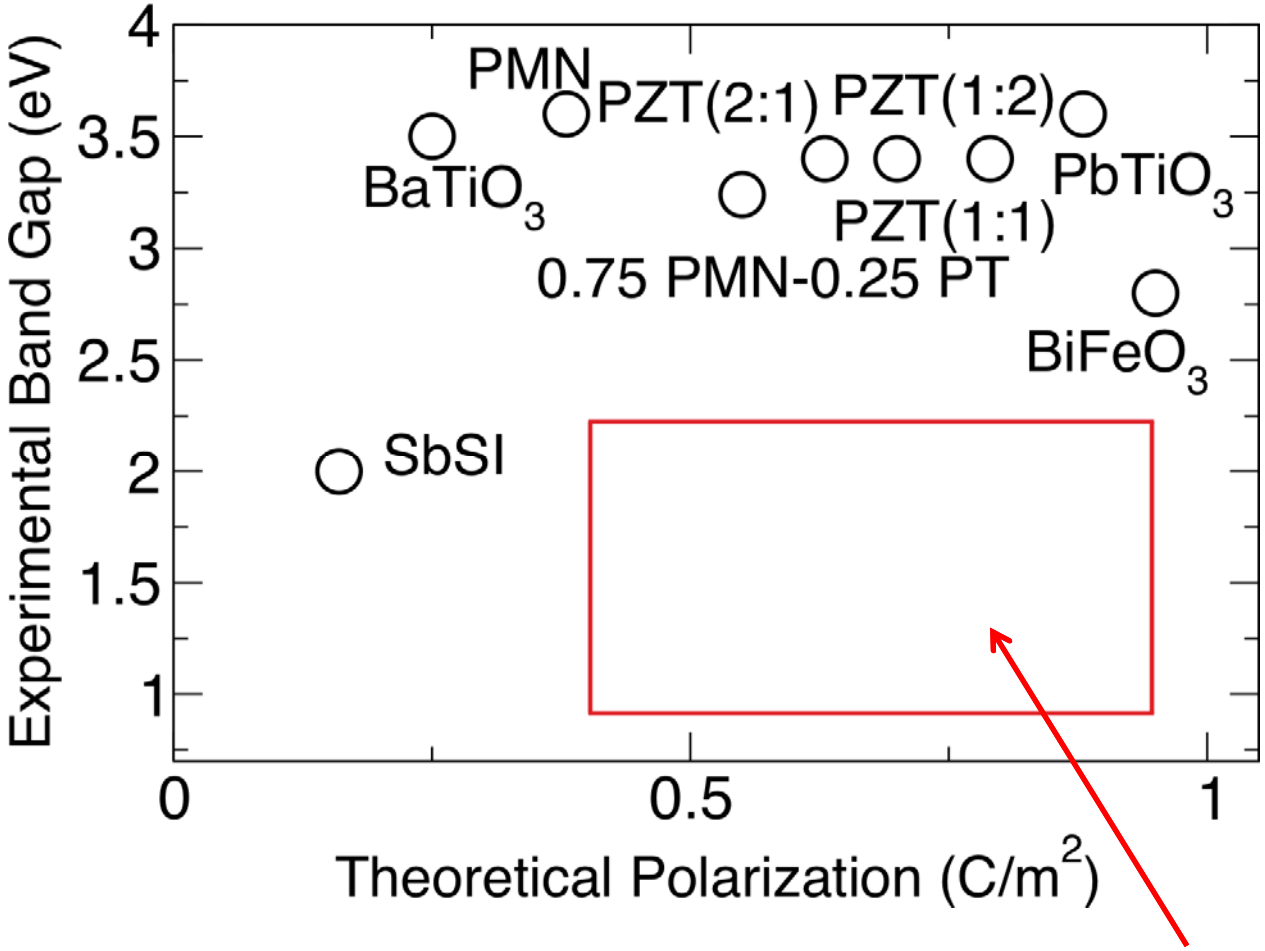
AND…$BiFeO_3$ shows BPVE with **visible light**!
AND…it's been incorporated as a diode!



Wang *et al.*, Science 2003, 1719
Choi *et al.*, Science 2009, 63
Katiyar & Scott, 2011

We want more materials like $BiFeO_3$!

What About the Band Gap?

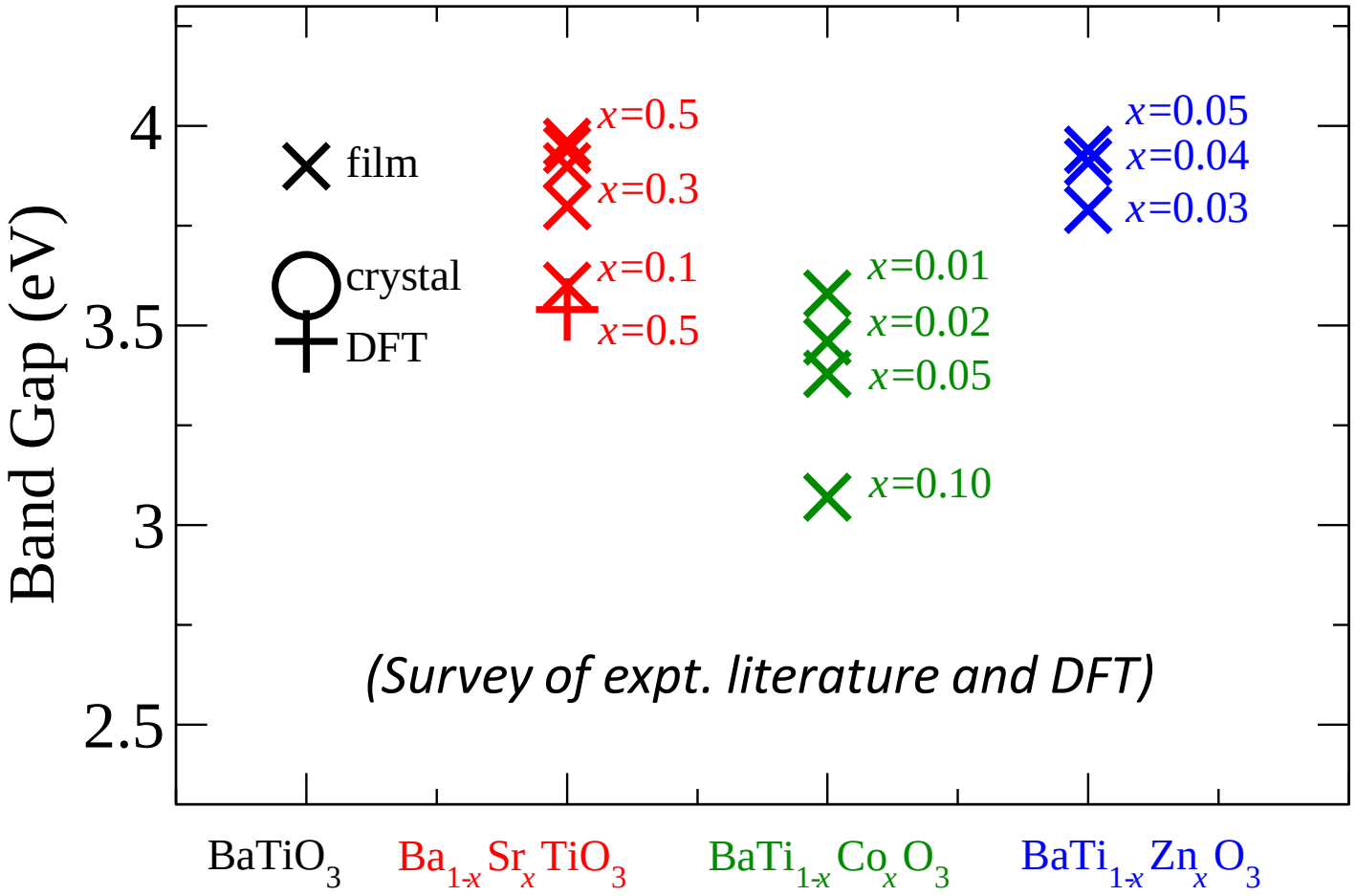


Can we go **beyond $BiFeO_3$**?

How do we do that? Solid solutions?

Bennett *et al.*, JACS 2008, 17409

Band Gaps of Solid Solutions of $BaTiO_3$

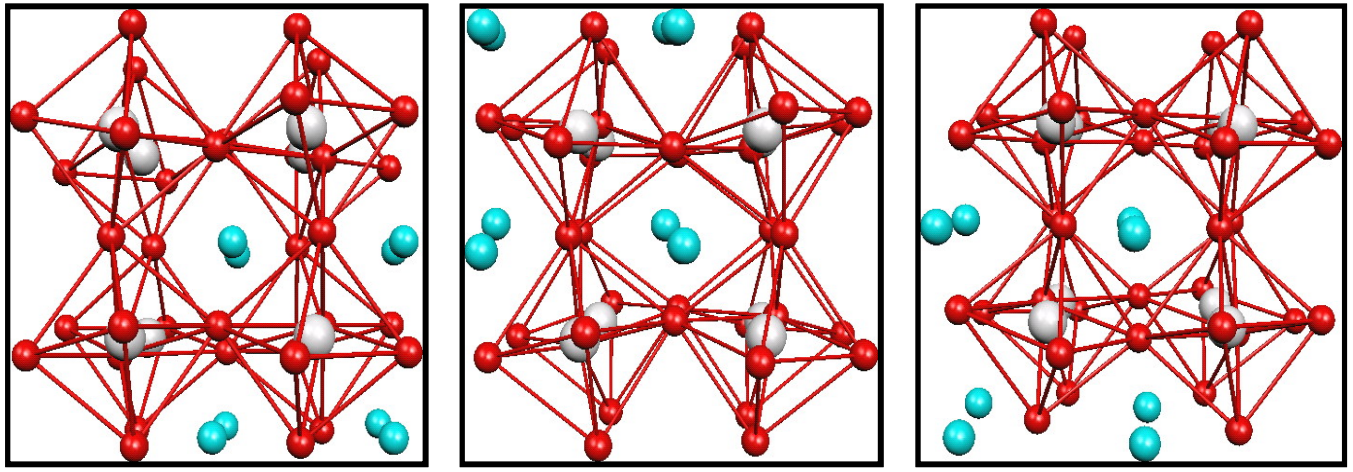


Bennett et al., Phys. Rev. B., 2010, 184106

Sulfide Perovskites?

$BaZrS_3$: DFT **band gap decreases**
from 3.9 to 1.7 eV relative to $BaZrO_3$

Non-polar -- ***Pnma*** symmetry:
rotations hinder concerted displacements…
Most are non-polar orthorhombic or
hexagonal…**no ferroelectric effect**!



(100) (010) (001)

Bennett et al., Phys. Rev. B., 2009, 235115

High-Throughput Search: New Perovskites

So far, we've only discussed studying a few materials at one time…
but what about many at once?

Since 2005, the Ceder group at MIT has published extensively on a combination of adapted machine learning, database mining and first-principles screening to search for new materials.

Morgan et al., *Mat. Sci. Tech*. 296 (2005)
Fischer et al., *Nature Mater.* 641 (2006)
Hautier et al., *Chem. Mater.* 3762 (2010)
Armiento et al., *Phys. Rev. B.* 014103 (2011)
Jain et al., *Comp. Mat. Sci.* 2295 (2011)

They've uncovered about 50 candidate ABO_3 compounds as targets for materials realization…most of which are as yet to be synthesized!

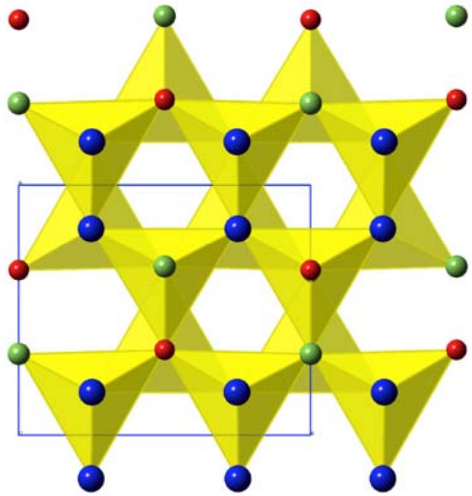
Outline

The ABO_3 Perovskites

Moving Beyond the Perovskites

We need to create a road map!

***J. Solid State Chem.* (2012) 195, 21**

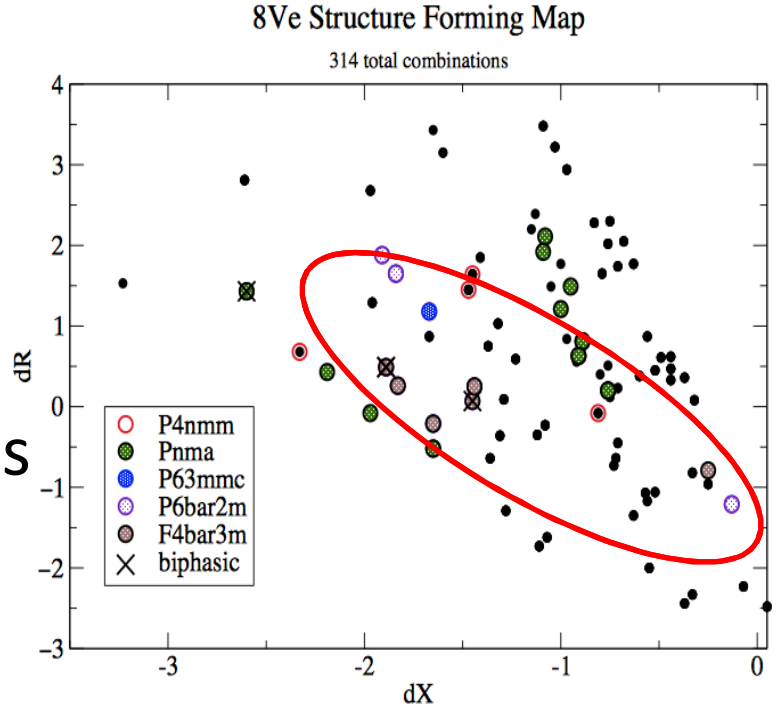


A New Class of Piezoelectrics

A New Class of Ferroelectrics

A New Class of Antiferroelectrics

Concluding Thoughts



Inorganic Crystal Structural Database

Database of completely identified inorganic structures.
150,000 peer-reviewed entries, dating back to 1913.
7,000 added annually, in conjunction with NIST databases

Structural Information:
Each entry is assigned to one of the 230 space groups
Lattice constants, Wyckoff parameters, occupancies

Structure types:
Currently 6,250 structure types
Over 70% of the structures have been assigned a structure type

Other search fields include:
Quality of refinement data, warnings/comments…

http://www.fiz-karlsruhe.de/icsd.html

Related Functions in Materials

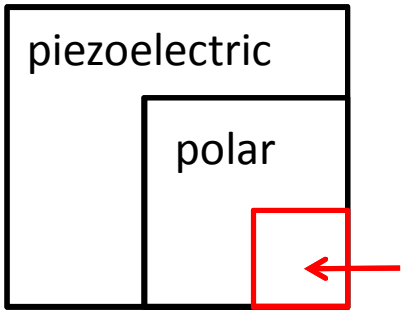
piezoelectric-polar-**ferroelectric**

The **piezoelectric effect** is an electromechanical interaction
(this means that electricity is generated by a mechanical force)

1) The material needs to be **insulating**
2) The material has **no inversion center**

Relative displacement between positive and negative ions

3) Measurable **macroscopic polarization**



4) **Switchable polarization**

But we can't just search ICSD for ferroelectrics.

How Many Polar Materials Are Known?

Of the 230 crystallographic space groups, 68 are polar (**30%**).
As of this year, 12,553 total polar entries (**less than 10% total**)

1) hexagonal (*6mm* and *6*, with 2264 compounds, 18.0%)

2) rhombohedral (*3mm* and *3*, with 2411 compounds at 19.2%)

3) tetragonal (*4mm* and *4* with 851 compounds, 6.8%)

4) orthorhombic (*mm2* with 4033 compounds, 32.1%)

5) monoclinic (*2* and *m* with 2534 compounds, 20.2%)

6) triclinic (*1* with 460 compounds, 3.7%)

Bennett and Rabe: *J. Solid State Chem* (2012) 195, 21

How Many Polar Materials Are Known?

Of the 230 crystallographic space groups, 68 are polar (30%).
As of this year, 12,553 total polar entries (less than 10% total)

This is an interesting result!

Most familiar ferroelectric materials are rhombohedral ($LiNbO_3$ perovskite), hexagonal ($YMnO_3$) or tetragonal ($PbTiO_3$ and $BaTiO_3$ perovskites)….

Could there be exotic new ferroelectrics that we don't know about, simply because we haven't yet looked?

Bennett and Rabe: *J. Solid State Chem* (2012) 195, 21

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rhombohedral ($LiNbO_3$ perovskite), hexagonal ($YMnO_3$)
or tetragonal ($PbTiO_3$ and $BaTiO_3$ perovskites)….

2x as many polar orthorhombic entries as
there are either rhombohedral or hexagonal

3x as many monoclinic entries as 2500
there are tetragonal entries! vs. 800

5x as many polar orthorhombic entries 4000
than there are tetragonal entries! vs. 800

What Are They?

How many unique chemical elements per polar entry?

1 (0.3%), 2 (14.3%), 3 (29.9%), 4 (30.4%) or 5+ (25.1%)

Less than 1% are “polar elements” (*A*)

14.3% are binary compositions (*AB*)

29.9% are tertiary compositions (*ABC*)

30.4% are quaternary compositions (*ABCD*)

This is 3/4 of the polar entries.

5+ elements are mostly solid solutions with fractional occupations (alloys, dopants, etc. based on *AB*, *ABC* or *ABCD*)

Structure Types

Common polar structure types:

In 186: ZnS with 445 entries and LiGaGe with 139 entries
(or 44.0% of the 1327 total entries).

In 99: $PbTiO_3$ (210 entries), $KNbO_3$ (17 entries) and $PbVO_3$ (12 entries)
…all related to the perovskite structure
and account for 79.3% of the 299 entries.

At the other extreme:

there are 12 polar space groups with no familiar structure types!

183, 172, 171, 158, 106, 105, 101, 80, 78, 37, 35 and 3
total number of entries in these groups is only 196, or 1.6%

For Our Initial ICSD Search(es)

Two strategies for the discovery of novel functional materials:
1) identify previously-overlooked systems in a familiar structure type
2) identify unfamiliar structure types

Want to find families of intermetallic semiconductors
with potentially untapped functional behavior

Need a simple chemical formula that involves three atoms: ABC

Most functional materials have three types of atoms
(two types form a rigid crystal structure, the third adds flexibility)

Keeping in mind that:
-we do not want corner-sharing octahedra
-we do not want hundreds of oxides

Outline

The ABO_3 Perovskites

Moving Beyond the Perovskites

A New Class of Piezoelectrics

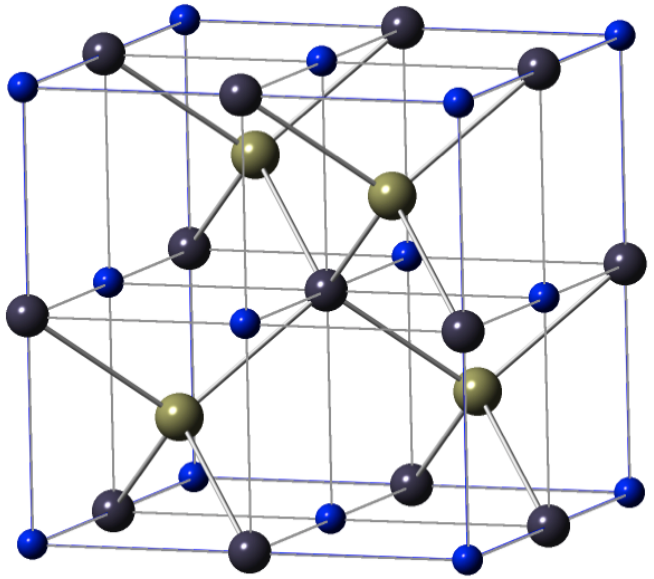
The Cubic LiAlSi Family

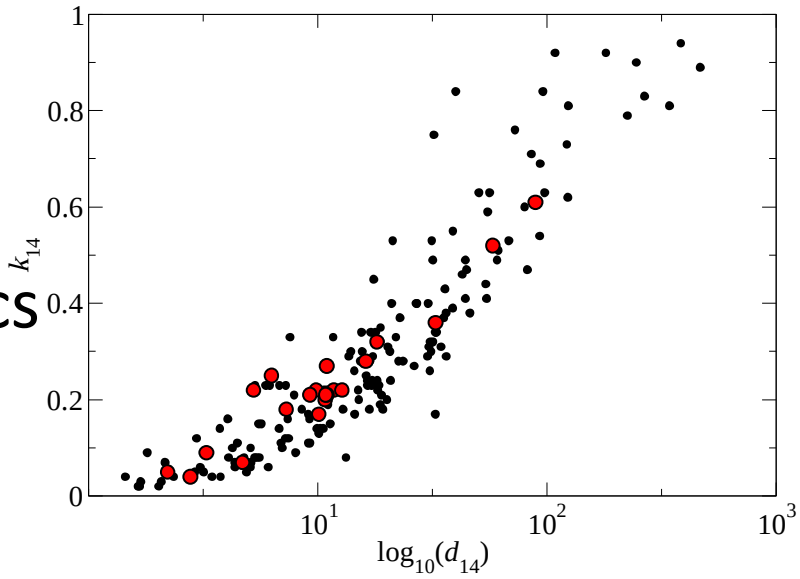
***Phys. Rev. Lett.* (2012) 109, 037602**

A New Class of Ferroelectrics

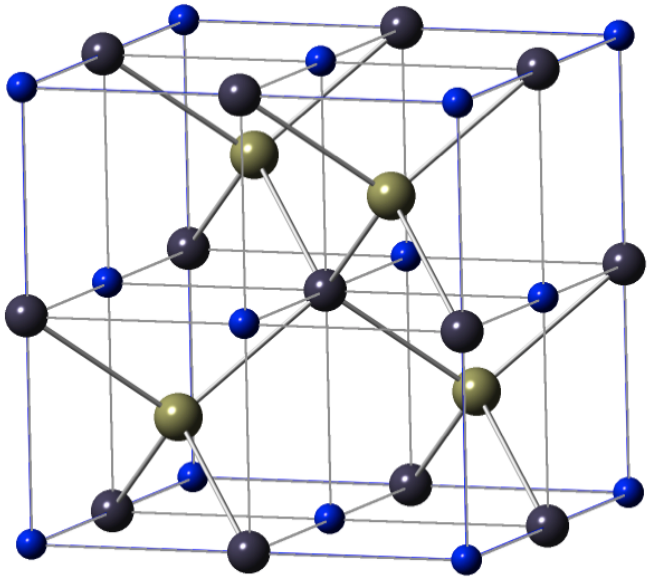
A New Class of Antiferroelectrics

Concluding Thoughts





LiAlSi: Target For a High-Throughput Study



A (black) and B (blue) rocksalt
C (gold) tetrahedrally bound

Half-Heusler: three atoms, *ABC:*

A and B form a rocksalt lattice

C occupies 1/2 of the the tetrahedral sites…
most electronegative element?

Have three different variations

Gaining popularity as multifunctional materials!

F4bar3m space group means piezoelectricity!
But no mention of this in the literature!
How many LiAlSi are known? Go to the ICSD!

With Regards to Database Searching

Warnings and Comments:
These are a must-read.

Some combinations are reported In more than one similar structure:
This is a great use of theoretical modeling!

Some entries could be assigned to more than one structure type:
Another great use of theoretical modeling! Phase transitions?

Some entries could be misassigned:
Check nonpolar structures for polar instabilities with ISOTROPY
A new way to obtain improper ferroelectrics.

Some entries are simply missing information:
Missing 1 of 3 elements: where's the *C* in *ABC*?

Searching the ICSD for *ABC*

F4bar3m (#216), cubic nonpolar: 269 total (260 LiAlSi)

Number of entries **without magnetic cations: 49**

Basic search for platform to support functionality

(We can add these back in later)

Searching the ICSD for *ABC*

F4bar3m (#216), cubic nonpolar: 269 total (260 LiAlSi)

Number of entries **without magnetic cations: 49**

Number of entries with **8 or 18 valence electrons: 38**

Want to promote a band gap

(Insulating intermetallics usually require a filled octet)

Searching the ICSD for *ABC*

F4bar3m (#216), cubic nonpolar: 269 total (260 LiAlSi)

Number of entries **without magnetic cations: 49**

Number of entries with **8 or 18 valence electrons: 38**

Examples, divided into families
I-II-V: LiMgP, LiMgAs
X-III-V: PdYSb, PtYSb
X-IV-IV: NiTiSn, PdHfSn
XI-III-IV: AuScSn
I-XII-V: LiCdP

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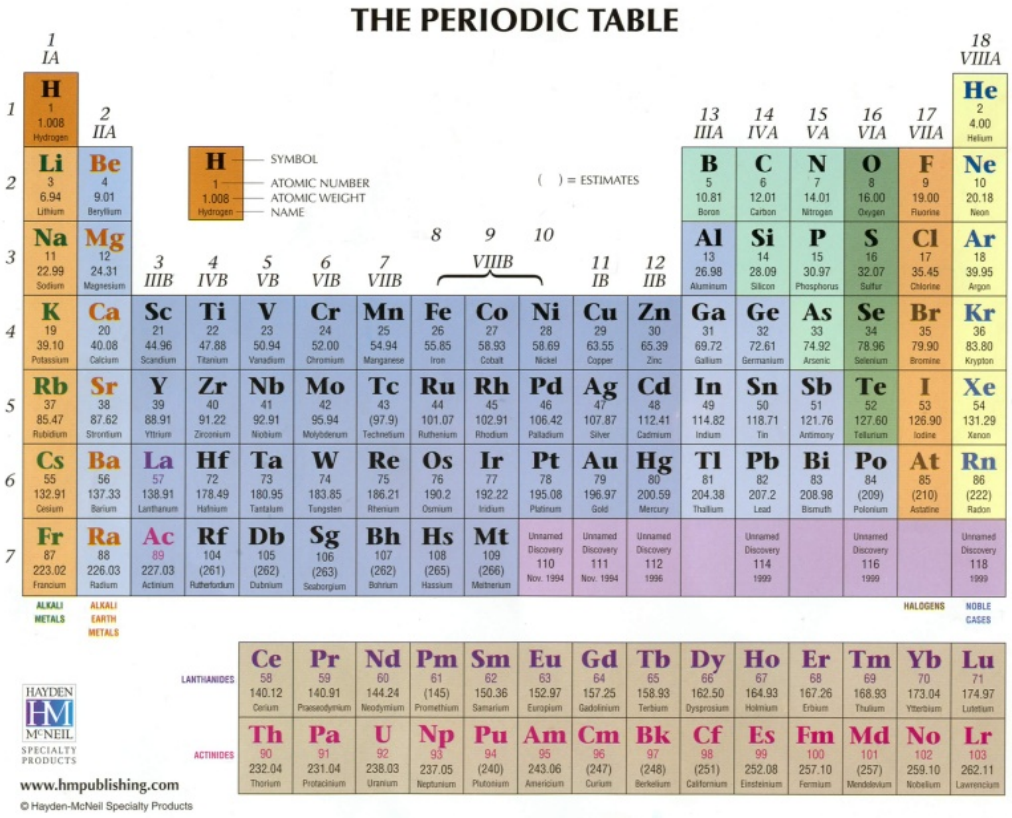
I-II-V: LiMgP, LiMgAs, NaBeAs, KMgSb…
X-III-V: PdYSb, PtYSb, NiAlAs, PtScBi…
X-IV-IV: NiTiSn, PdHfSn, NiZrGe, NiSiSn…
XI-III-IV: AuScSn, CuYPb, AgAlGe…
I-XII-V: LiCdP, NaZnBi, KZnP…

But couldn't there be more? Like hundreds or thousands more?

High-Throughput: Over 900 Combinations!



How do we get over 900? Investigate all of these triplets:

I-II-V, I-III-IV, I-I-VI
II-II-IV, II-III-III
X-III-V, X-IV-IV
XI-II-V, XI-III-IV
XII-II-IV, XII-I-V

Total is 8 or 18 Ve.

I=Li, Na, K; II=Be, Mg, Ca, Sr, Ba; III=Sc, Y, B, Al, Ga;
IV=Ti, Zr, Hf, C-Pb; V=N-Bi; VI=O-Te
X=Ni, Pd, Pt; XI=Cu, Ag, Au; XII=Zn, Cd

A Word of Caution

High throughput studies:

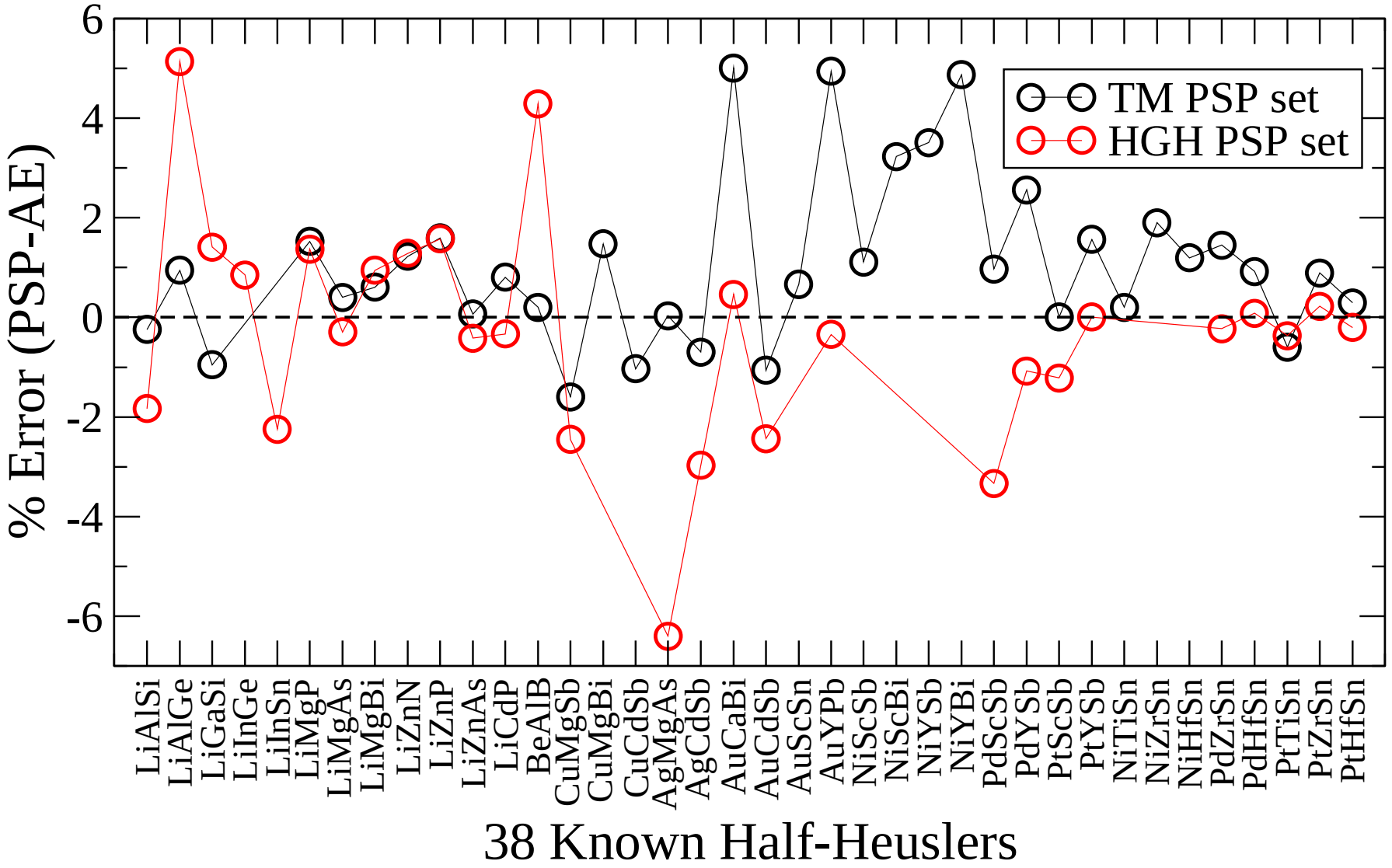
Pseudopotential testing is a must!

Do they match all electron (AE) DFT calculations? **I used Wien2k**.

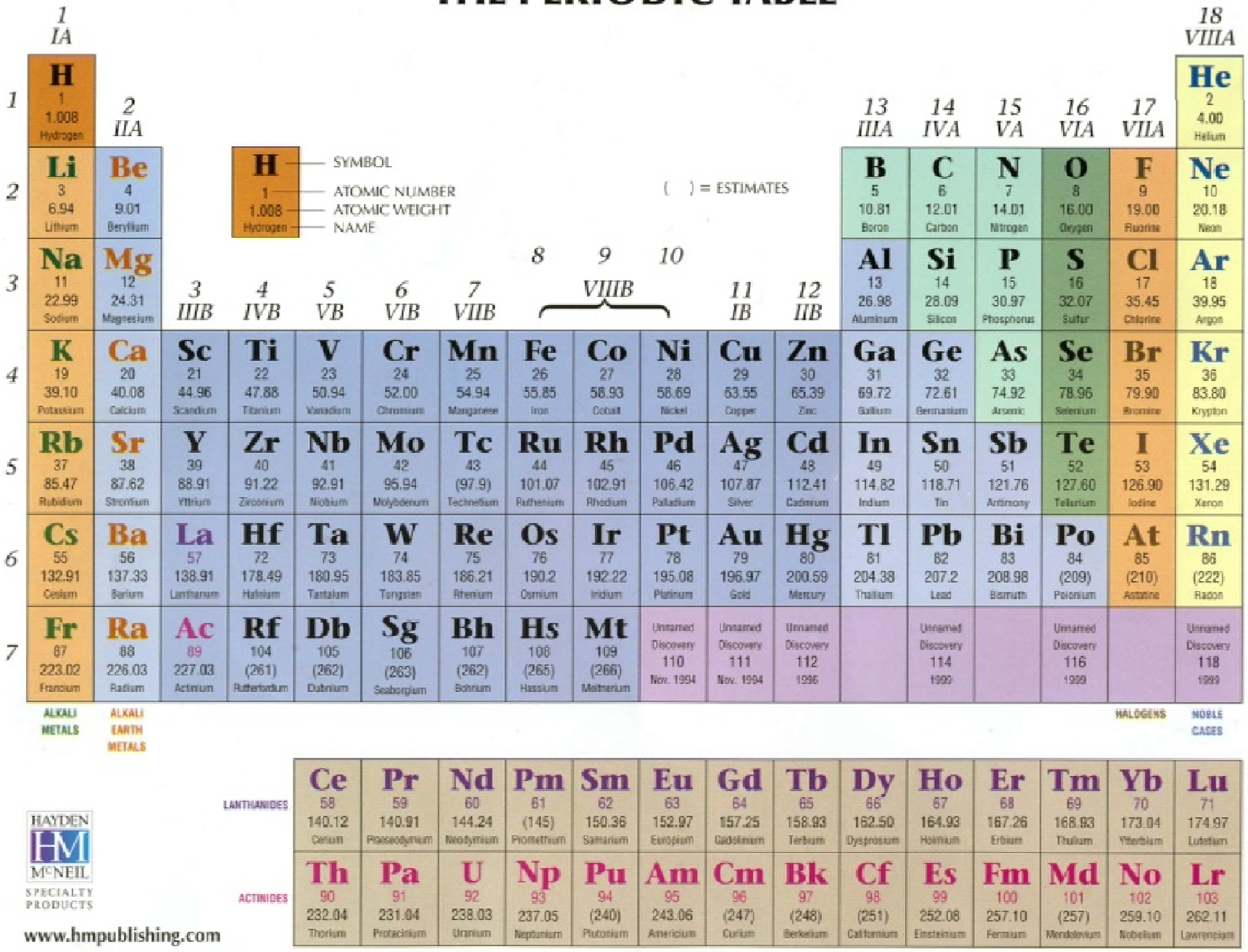
Set up a few test calculations before your high-throughput study!

Obtain (at least) the lattice parameters from AE and PSP to see how well they agree, or disagree...

PSP Test of Known *ABC* Lattice Constants



THE PERIODIC TABLE



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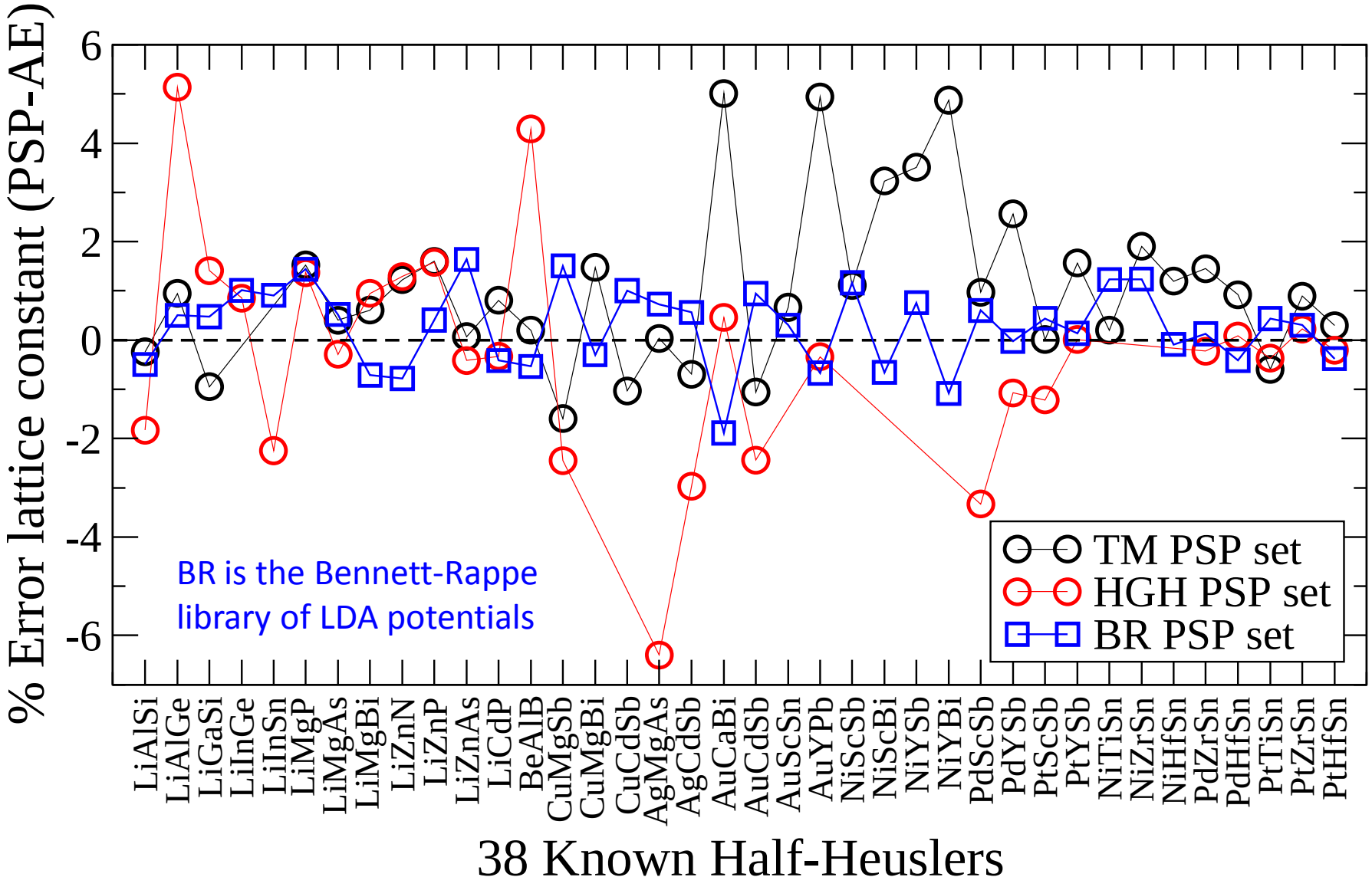
THE PERIODIC TABLE

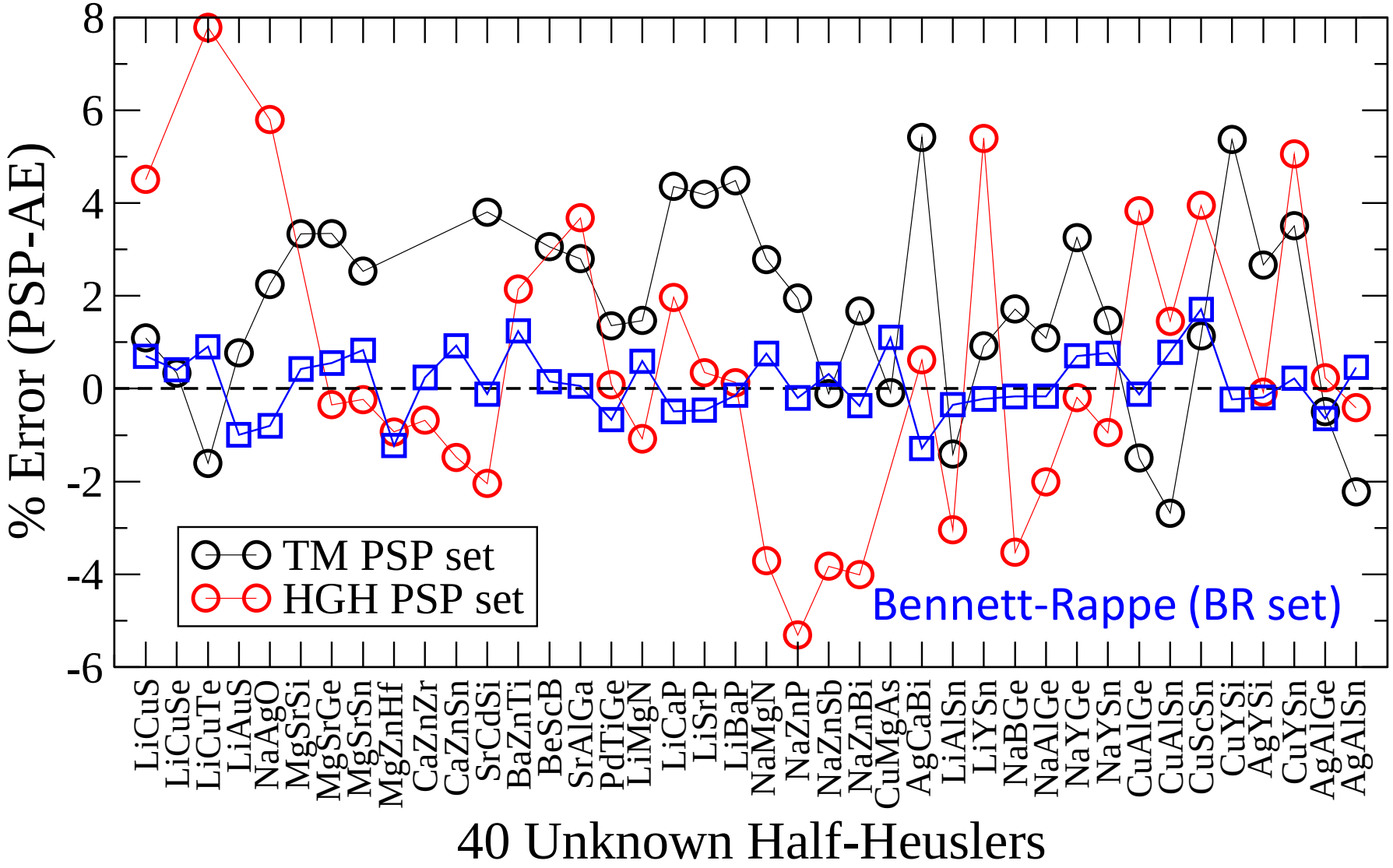
The Bennett-Rappe library of OPIUM constructed designed non-local optimized norm-conserving pseudopotentials

J. W. Bennett
Dept. of Physics and Astronomy,
Rutgers, The State University of New Jersey
http://physics.rutgers.edu/~bennett/PSP_v2.pdf

PSP Test of Known *ABC* Lattice Constants



What About the Hypothetical *ABC*?



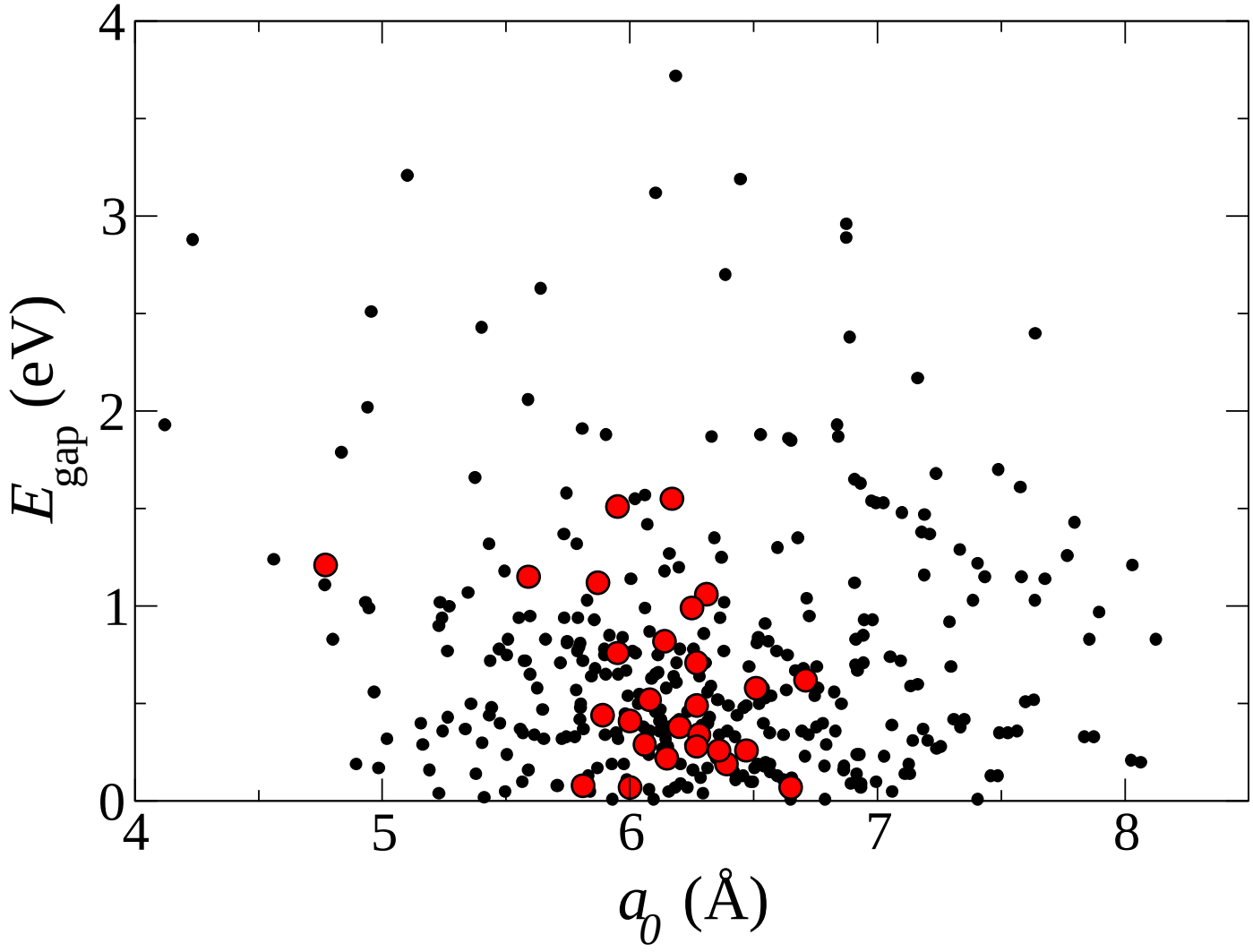
High-Throughput Study of Half-Heuslers

over 900 combinations

1) **Ground state DFT-LDA calculation.**
   3 possible structural variants (2700 calc.!).
   Which atom sits in the tetrahedral site?
   Calculate the differences in total energy

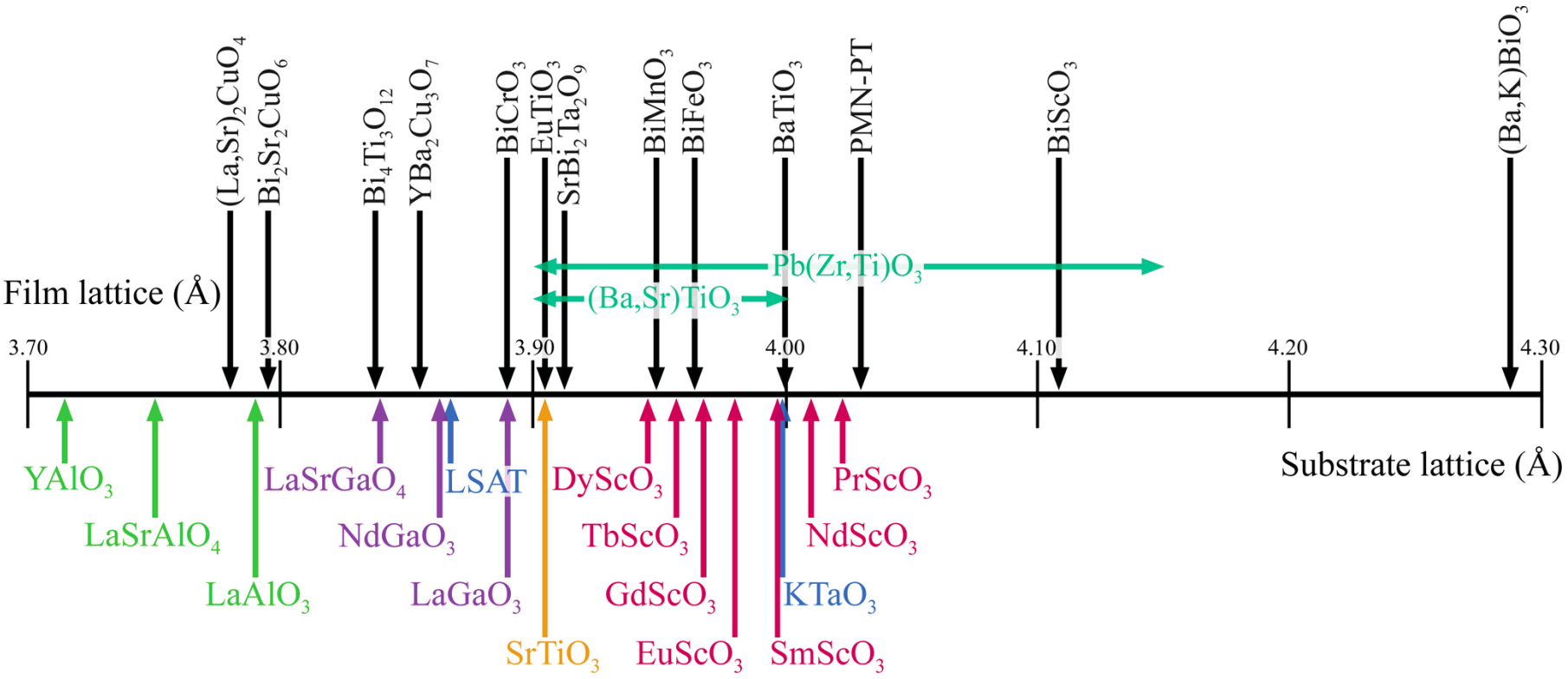
2) **Insulating or metallic?**

What Do We Find?

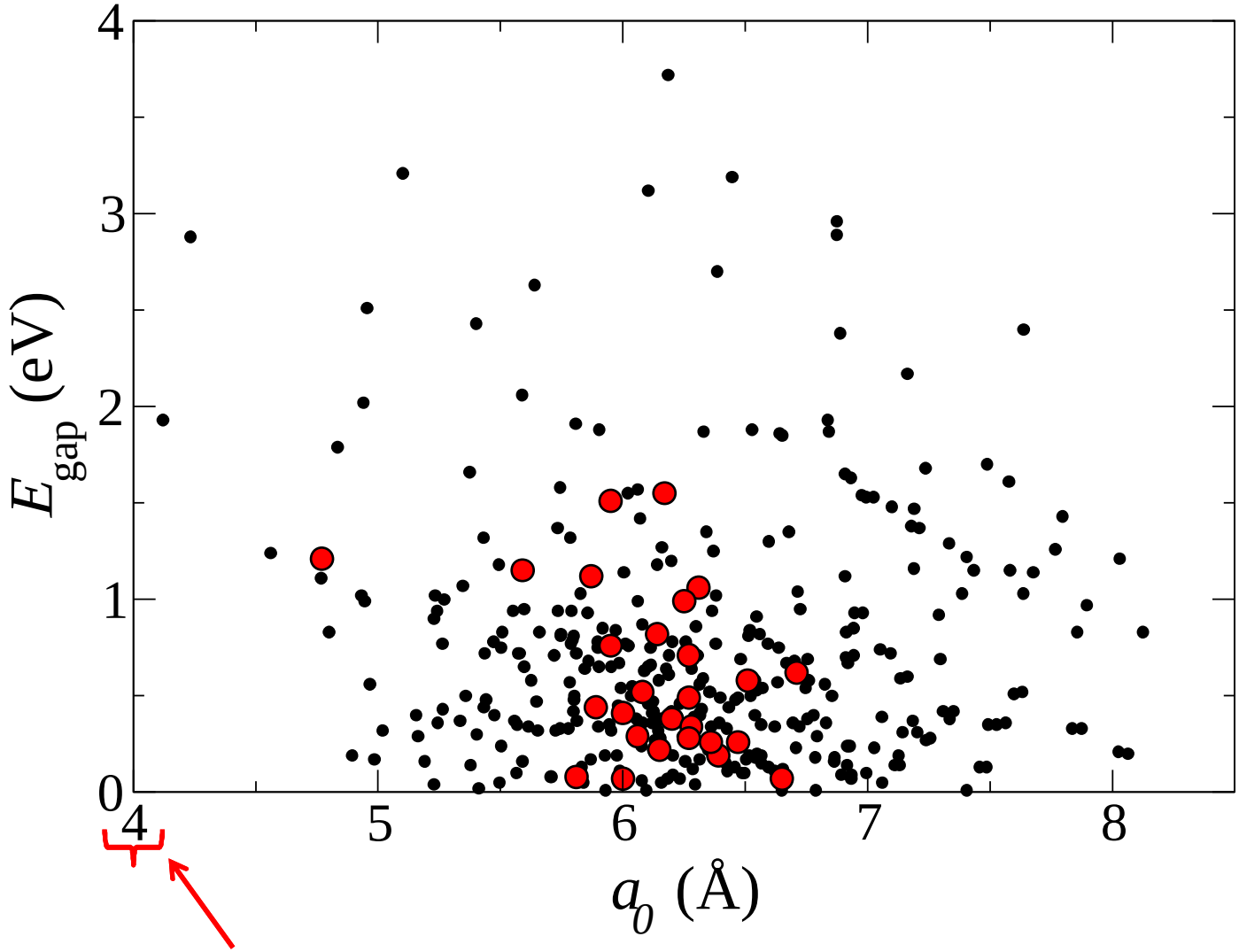


Choice of **band gap and lattice constant** match for **many applications** is very large!

Perovskite Substrates

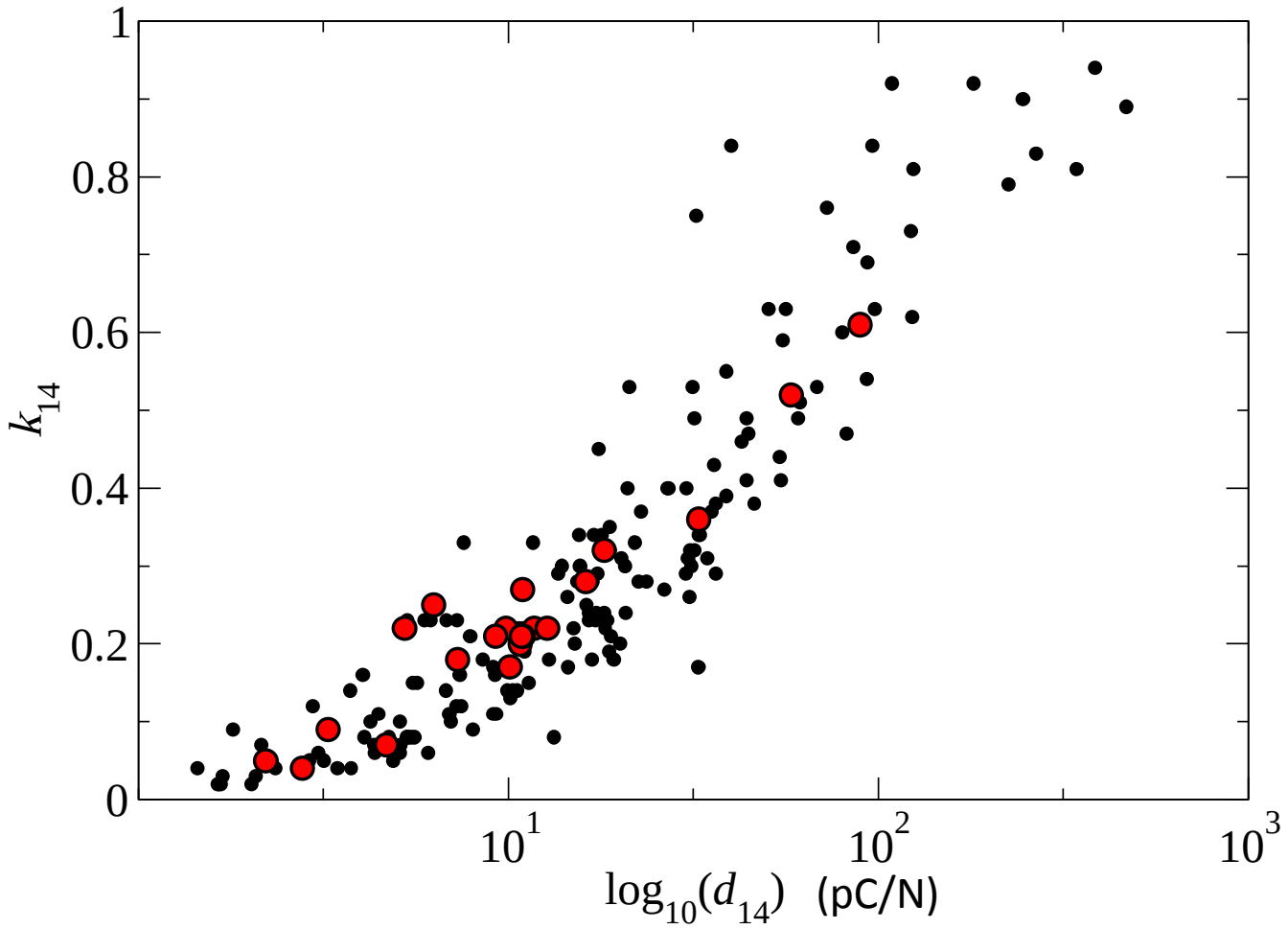


Why Is This Important?



The range of the perovskites!

And The Piezoelectric Coefficients?



Electromechanical coupling (k_{14}) vs. **piezoelectric constant** (d_{14}) is on **a logarithmic scale** ….orders of magnitude to choose from!

Top Half-Heuslers

ABC	a	E_{gap}	e_{14}	d_{14}	C_{44}	k_{14}	ϵ_0
KMgP	6.71	1.04	1.19	346.28	0.03	0.89	13
LiNaS	6.10	3.12	0.92	208.22	0.04	0.86	8
LiSrAs	6.84	1.93	0.79	286.27	0.03	0.85	10
LiNaSe	6.39	2.70	0.75	227.09	0.03	0.84	8
NaMgN	5.43	0.72	1.50	165.23	0.09	0.83	13
NaBeP	5.59	2.06	1.02	192.98	0.05	0.82	11
KMgAs	6.92	0.67	1.06	205.75	0.05	0.81	13
KScPb	7.35	0.42	1.21	330.83	0.04	0.80	25
MgBaSi	7.18	0.37	1.13	290.51	0.04	0.80	21
BeBaSn	6.86	0.16	0.49	1036.54	0.01	0.80	33
KScSn	7.31	0.42	1.19	294.69	0.04	0.79	24

These are all **WAY better piezoelectrics** than those listed for *F4bar3m* in Landolt-Bornstein database!

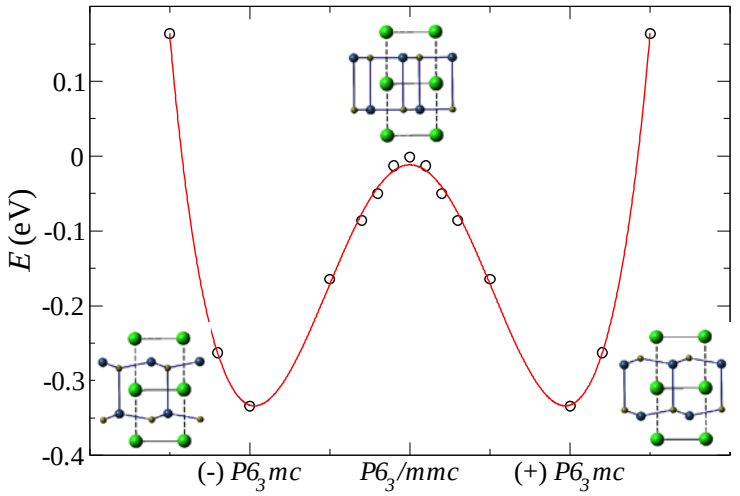
(Best known member in LB database is Tl_3TaS_4 with d_{14}=58 pC/N)

Outline

The ABO_3 Perovskites

Moving Beyond the Perovskites

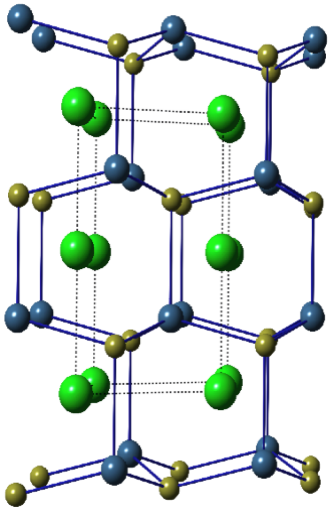
A New Class of Piezoelectrics



A New Class of Ferroelectrics

The Hexagonal LiGaGe family

***Phys. Rev. Lett.* (2012) 109, 167602**



A New Class of Antiferroelectrics

Concluding Thoughts

Revisiting the ICSD: the ABC's

Listed in the database, we find:
51,000 entries with three unique chemical elements!

Of these, **3700 have the chemical formula *ABC***.

F4bar3m (#216), cubic nonpolar: 269 total (260 LiAlSi)

This is less than 10% of the known entries.

Revisiting the ICSD: the ABC's

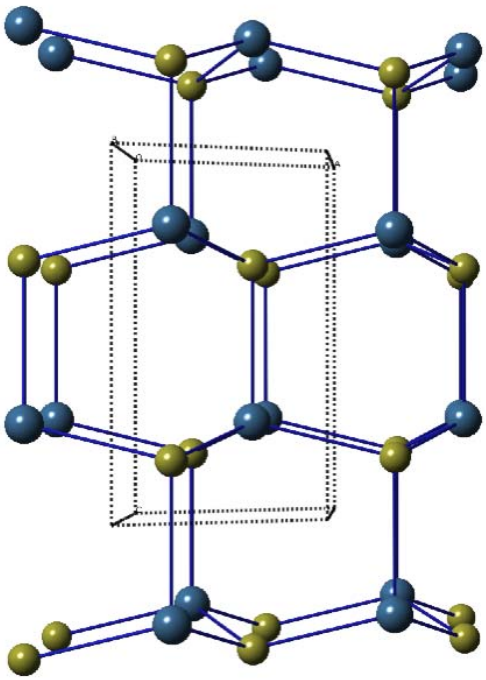
Listed in the database, we find:
51,000 entries with three unique chemical elements!

Of these, **3700 have the chemical formula *ABC***.

F4bar3m (#216), cubic nonpolar: 269 total (260 LiAlSi)
$P6_3/mmc$ (#194), hexagonal nonpolar: 297 total (200 ZrBeSi)
P6bar2m (#189), hexagonal nonpolar: 712 total (680 Fe_2P)
P6barm2 (#187), hexagonal nonpolar: 47 total (40 BaPtSb)
$P6_3mc$ (#186), hexagonal polar: 153 total (120 LiGaGe)
P4/nmm (#129), tetragonal nonpolar: 613 total (450 PbClF)
Pnma (#62), orthorhombic nonpolar: 548 total (450 MgSrSi)

$P6_3mc$ is one of the polar space groups that we identified in our database search as well-known. Common structure types included LiGaGe and wurtzite, which is not ferroelectric.

Wurtzite



Our DFT results
a=3.19 Ang. (3.21 Ang)
c=5.15 Ang. (5.25 Ang)
u=0.379 (0.375)

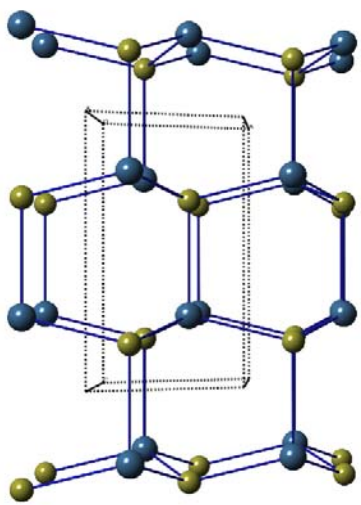
Polar hexagonal $P6_3mc$ structure
Each Zn is tetrahedrally bound to 4 O
Each O is tetrahedrally bound to 4 Zn
Strong sp^3 bond formation is driving force for formation…rigid structure!

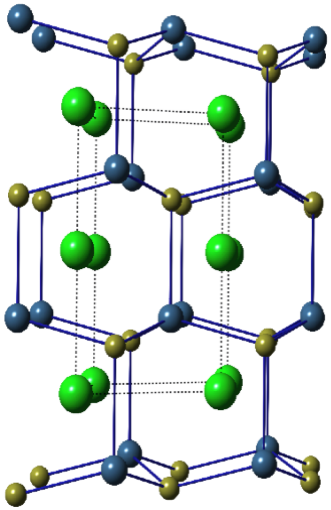
Switching would have to include:

1) breaking sp^3 bonds
2) high-symmetry planar structure ($P6_3/mmc$)
3) re-forming sp^3 bonds

This is more than 0.6 eV by DFT!

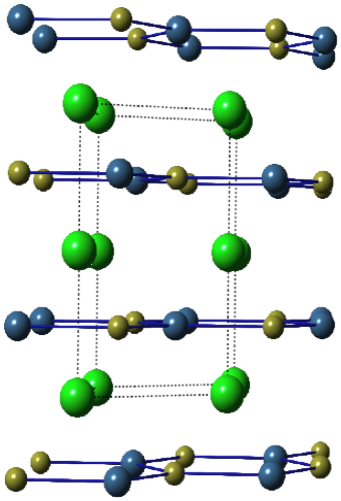
LiGaGe is “Stuffed Wurtzite”





LiGaGe, or “stuffed wurtzite” is the polar $P6_3mc$ phase

ZrBeSi: A Non-Polar Structure

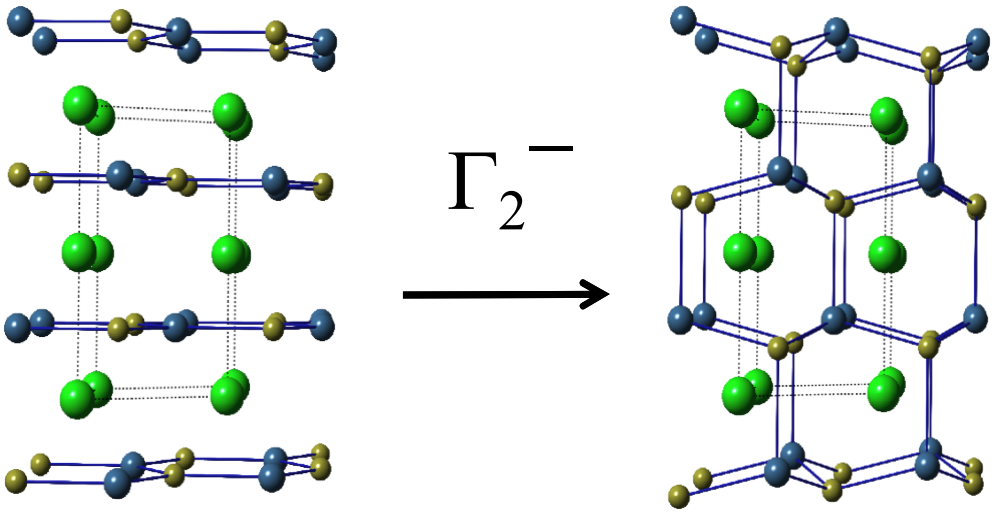


LiGaGe, or “stuffed wurtzite” is the polar $P6_3mc$ phase

ZrBeSi in the layered non-polar $P6_3/mmc$ phase…

There’s at least 6 combinations reported in both space groups.

A Polar Distortion!



LiGaGe, or “stuffed wurtzite” is the polar *P6$_3$mc* phase
ZrBeSi in the layered non-polar *P6$_3$/mmc* phase…
There’s at least 6 combinations reported in both space groups.
ISOTROPY shows that a Gamma mode relates the two phases
Unlike Perovskites: No competing octahedral rotations!
Use first-principles to screen this family (6 atoms/cell).
Can we make wurtzite ferroelectric?

http://stokes.byu.edu/isotropy

Known LiGaGe Compounds

		a		c		z_{2b}		z'_{2b}		E_{gap}	ΔE
I-III-IV	LiGaGe	4.139	(4.175)	6.713	(6.783)	0.314	(0.312)	0.698	(0.700)	0	0.80
	CuScSn	4.351	(4.388)	6.795	(6.830)	0.330	(0.326)	0.729	(0.229)	0	0.45
	CuYSn	4.475	(4.543)	7.148	(7.274)	0.320	(0.316)	0.728	(0.733)	0	0.32
	CuYPb	4.512	(4.559)	7.191	(7.334)	0.321	(0.323)	0.729	(0.729)	0	0.34
	AgYSn	4.634	(4.683)	7.240	(7.372)	0.314	(0.308)	0.702	(0.719)	0	0.39
	AuScGe	4.263	(4.308)	6.679	(6.846)	0.196	(0.200)	0.793	(0.798)	0	0.61
	AuScSn	4.507	(4.593)	7.066	(7.202)	0.348	(0.340)	0.730	(0.731)	0	0.75
	AuYSi	4.247	(4.288)	7.358	(7.546)	0.228	(0.234)	0.780	(0.775)	0	0.05
	AuYGe	4.364	(4.410)	7.084	(7.309)	0.219	(0.216)	0.789	(0.791)	0	0.26
	AuYSn	4.614	(4.636)	7.293	(7.373)	0.173	(0.194)	0.774	(0.821)	0	0.70
I-II-V	LiBeSb	4.091	(4.152)	6.636	(6.738)	0.350	(0.341)	0.733	(0.732)	1.45	0.79
	LiZnSb	4.327	(4.431)	7.024	(7.157)	0.290	(0.304)	0.668	(0.689)	0.99	0.93
	CaAgBi	4.730	(4.811)	7.564	(7.827)	0.318	(0.312)	0.715	(0.721)	0	0.36
II-II-IV	CaZnSn	4.595	(4.655)	7.331	(7.628)	0.218	(0.220)	0.813	(0.805)	0	0.32
	CaHgSn	4.754	(4.800)	7.547	(7.760)	0.289	(0.310)	0.686	(0.720)	0	0.53
	SrHgSn	4.878	(4.893)	7.801	(8.217)	0.305	(0.300)	0.712	(0.720)	0	0.36
	SrHgPb	4.894	(4.995)	8.054	(8.172)	0.311	(0.300)	0.719	(0.720)	0	0.19

We have 17 combinations with reliable structural data

Known LiGaGe Compounds

	a	c	z_{2b}	z'_{2b}	E_{gap}	ΔE
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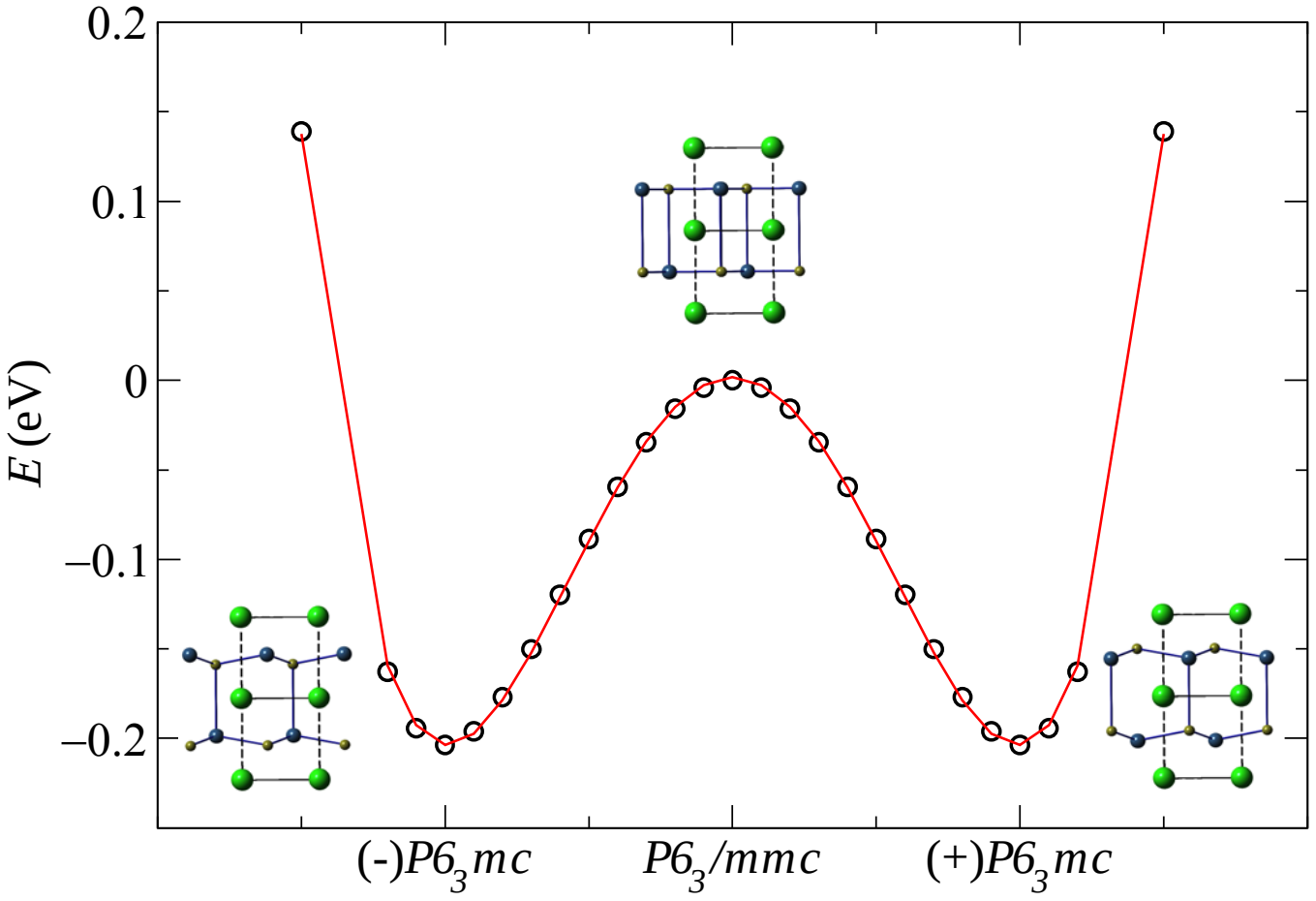
SrHgPb	4.894 (4.995)	8.054 (8.172)	0.311 (0.300)	0.719 (0.720)	0	0.19

Two are insulators of the I-II-V type…we can expand the set to 72!

We choose I=Li, Na, K; II=Be, Mg, Ca, Sr, Ba, Zn; and V=P, As, Sb, Bi.

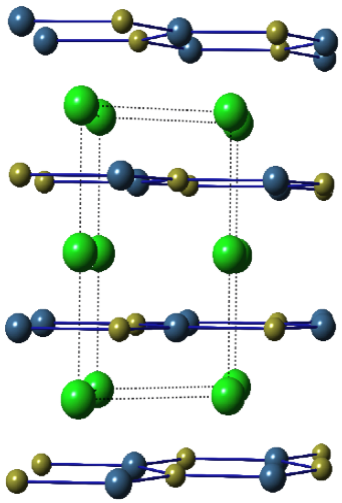
A Double Well!

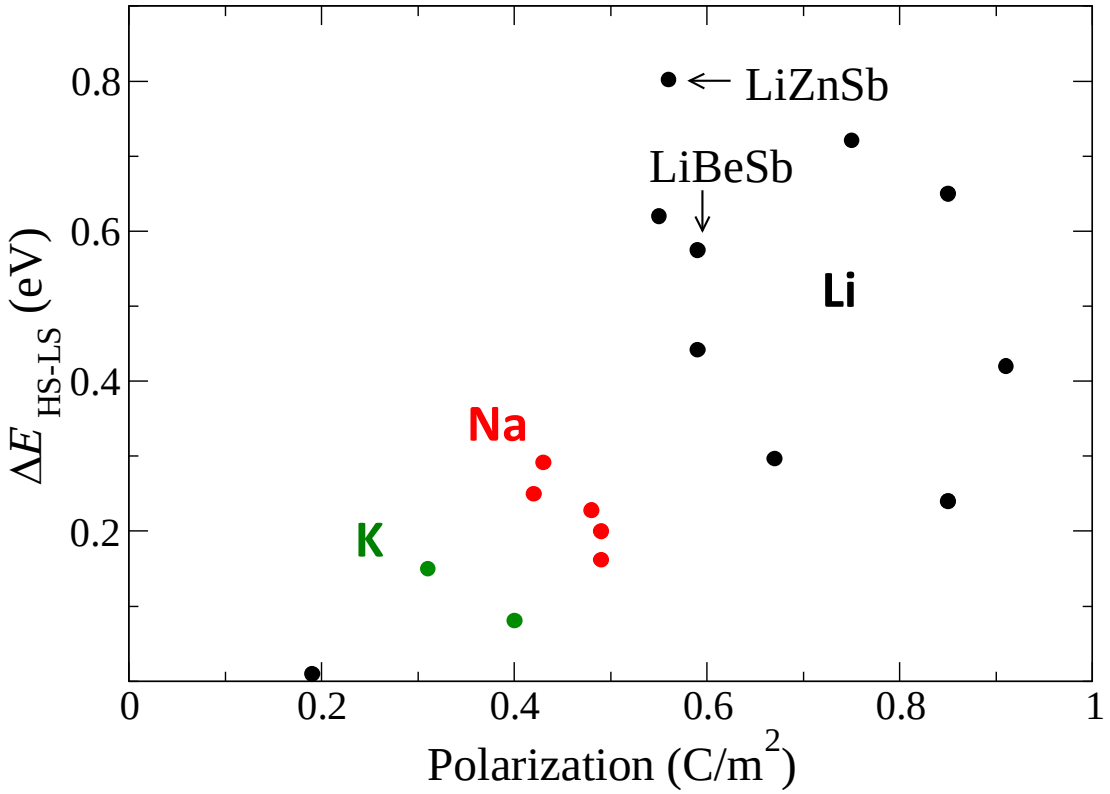


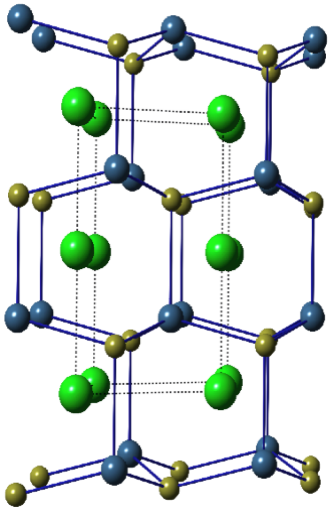
The **difference in energy** between *P6$_3$/mmc* and either polar phase for **NaMgP is 0.21 eV… barrier for PbTiO$_3$ is 0.2 eV.**

This is reminiscent of switchability observed in the perovskites!

A New Class of Ferroelectrics Based on Wurtzite!







Difference in energy between paraelectric and ferroelectric structures for all **17 polar combinations.**

10 are below 0.3 eV and potentially switchable.

The larger the stuffing cation, the smaller the barrier to switch polarization…**This is a new class of ferroelectrics!**

Outline

The ABO_3 Perovskites

Moving Beyond the Perovskites

A New Class of Piezoelectrics

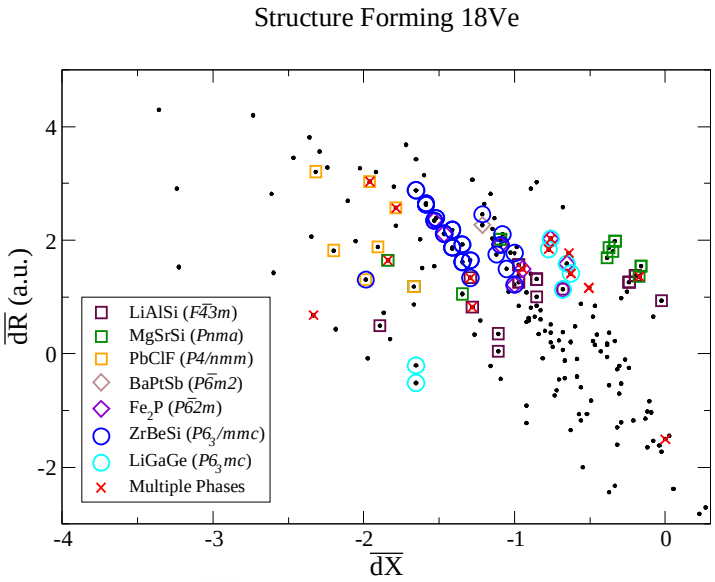
A New Class of Ferroelectrics

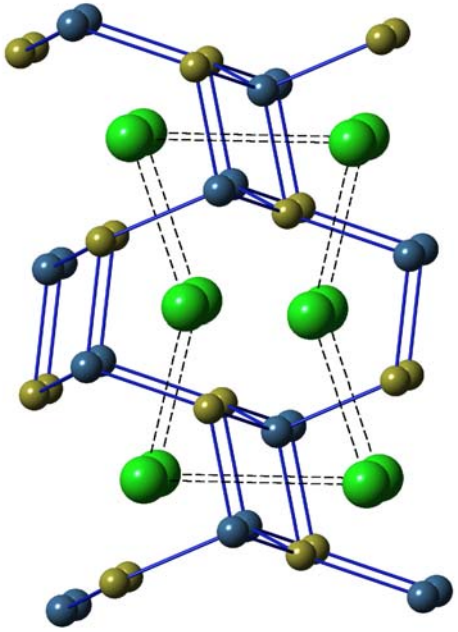
A New Class of Antiferroelectrics

The Orthorhombic MgSrSi Family

***Phys. Rev. Lett.* (2013) 110, 017603**

Concluding Thoughts





What is an antiferroelectric?

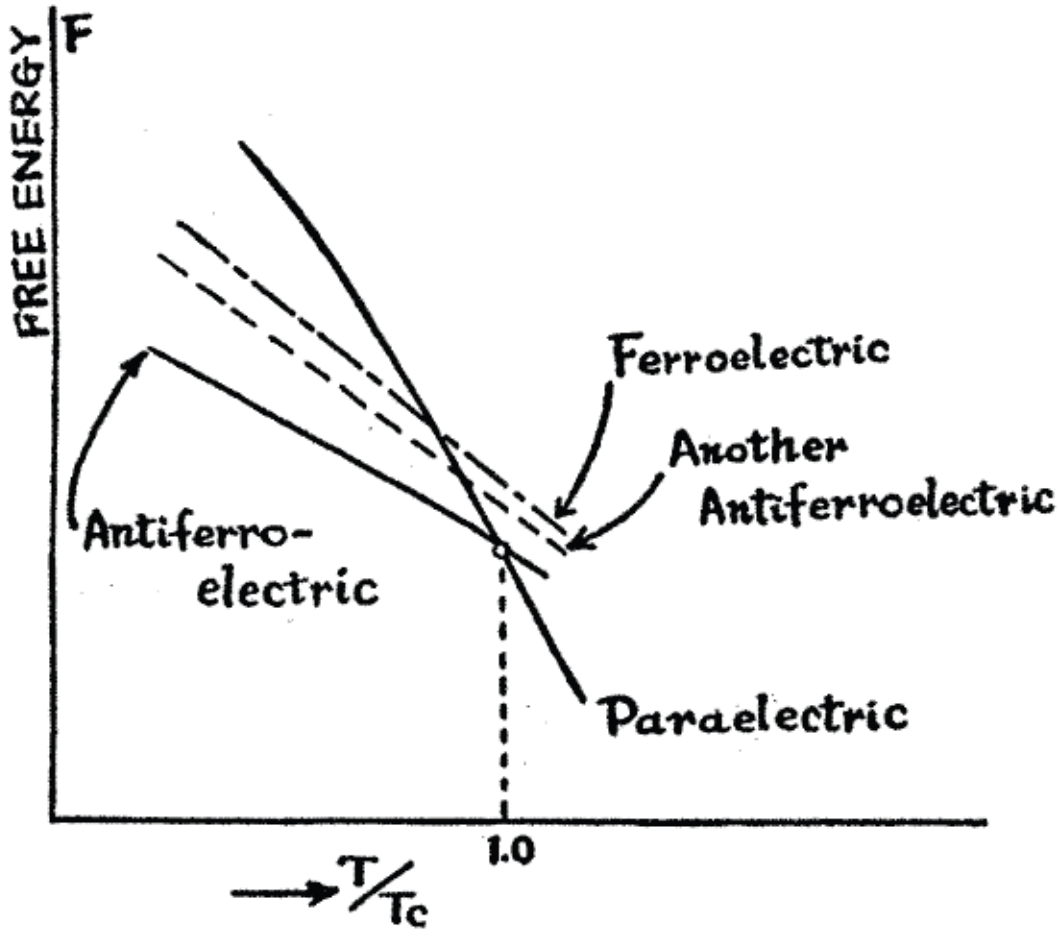
Two important criteria:

1) Structure

Antipolar ground state crystal structure (Kittel, 1951)

2) Energy

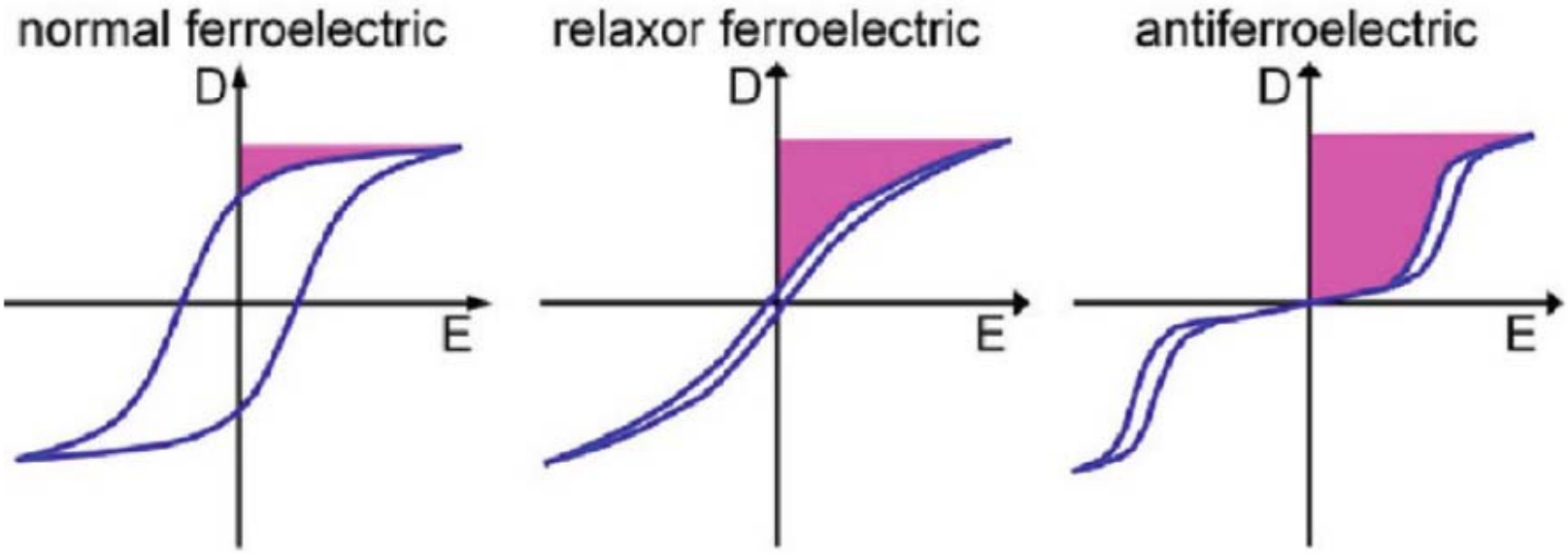
Competition with a polar ferroelectric phase (Shirane, 1952)
electric-field induced first-order phase transition



K. M. Rabe: Antiferroelectricity in oxides: A reexamination
Functional Metal Oxides: New Science and Novel Applications (2012)

So, why are antiferroelectrics important?

Increased Capacitance: Energy Storage!

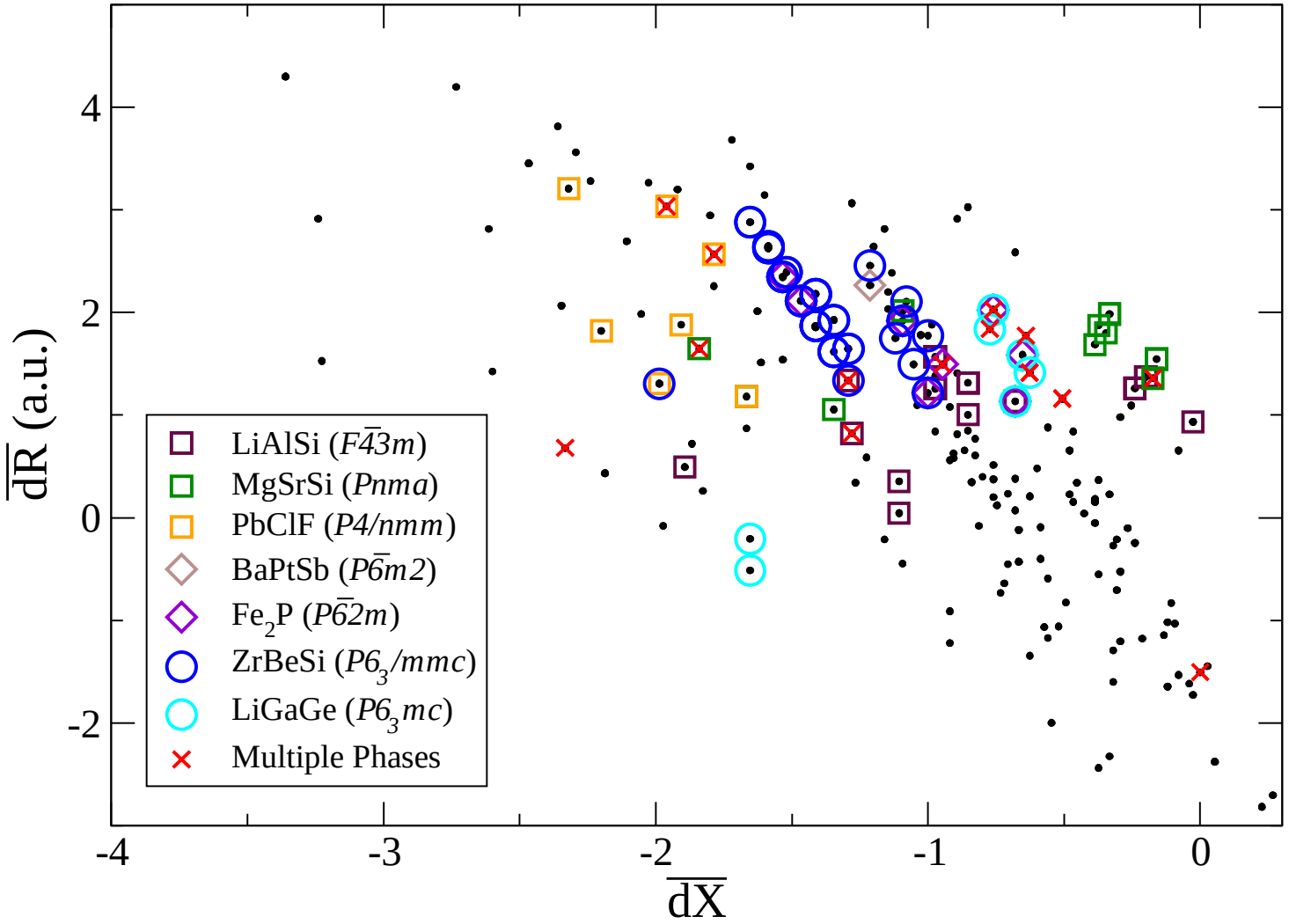


The double hysteresis loop of the antiferroelectric has a much greater capacity to store and release energy. Can we find any with the chemical formula *ABC*?

Zhu and Wang, *Macromolecules* (2012), 2937

My secret weapon…Villars maps

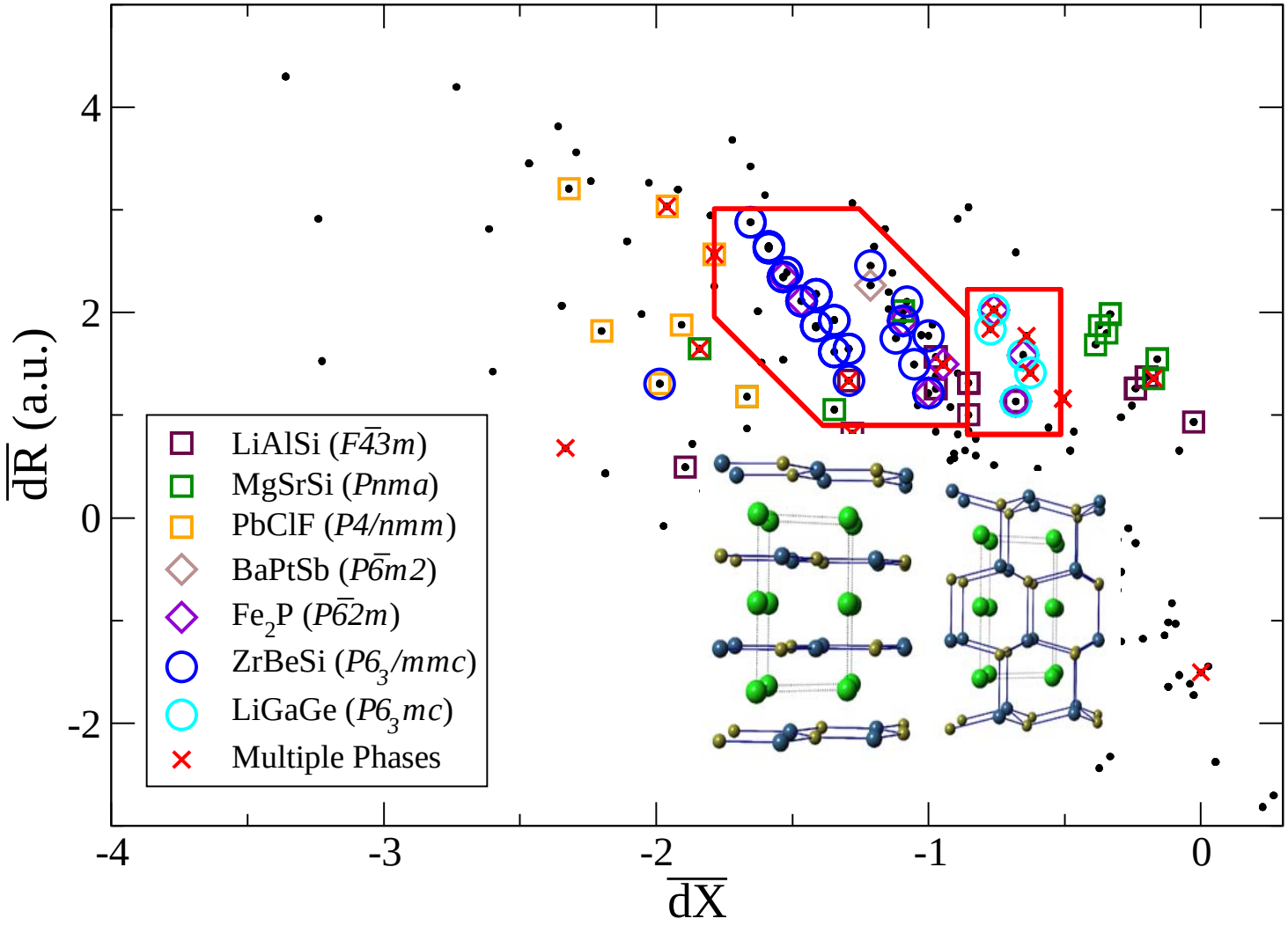
Structure Forming 18Ve



Villars *et al.*, *J. Less Common Metals* (1986) 175, (1987) 289

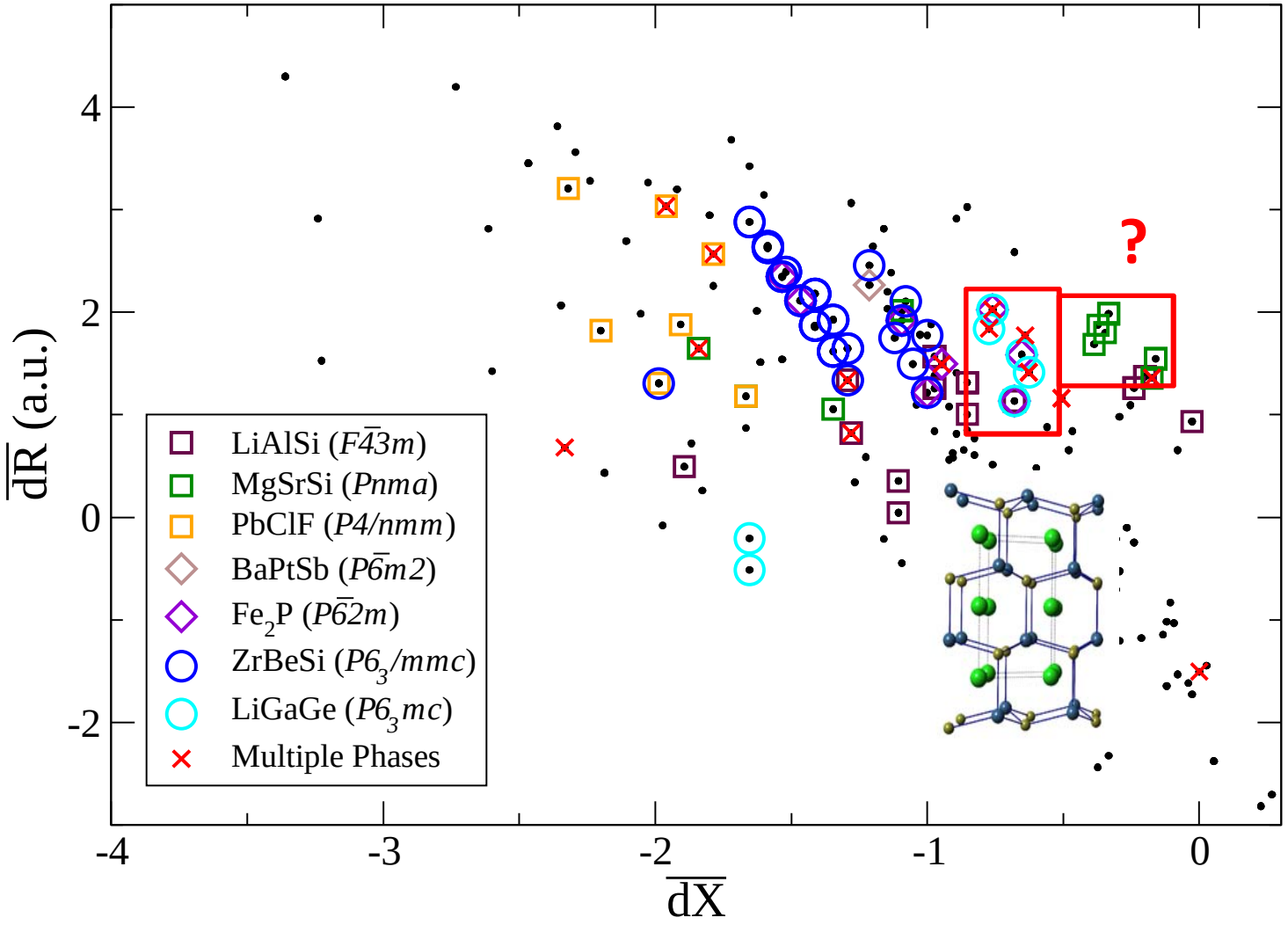
We know about this transition…

Structure Forming 18Ve



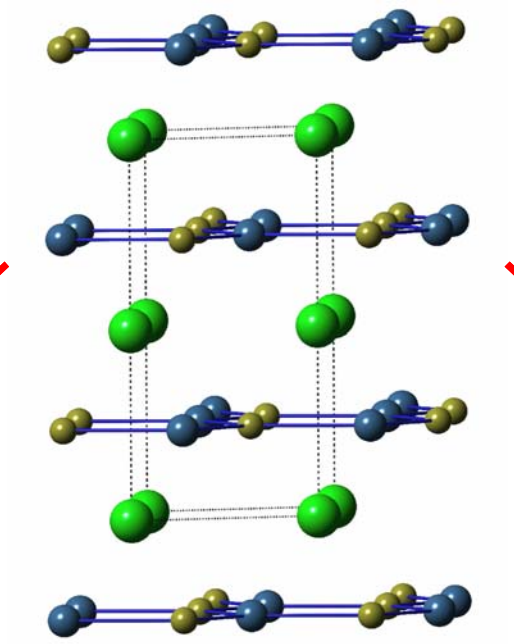
… are other transitions possible?

Structure Forming 18Ve



Orthorhombic *ABC* as antiferroelectrics

Nonpolar

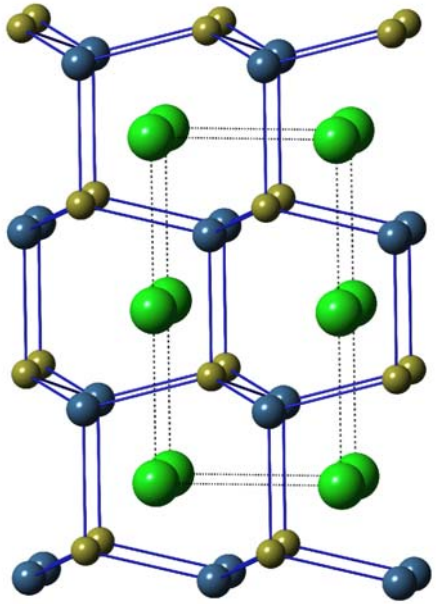


$P6_3/mmc$ ZrBeSi

Γ_2^-

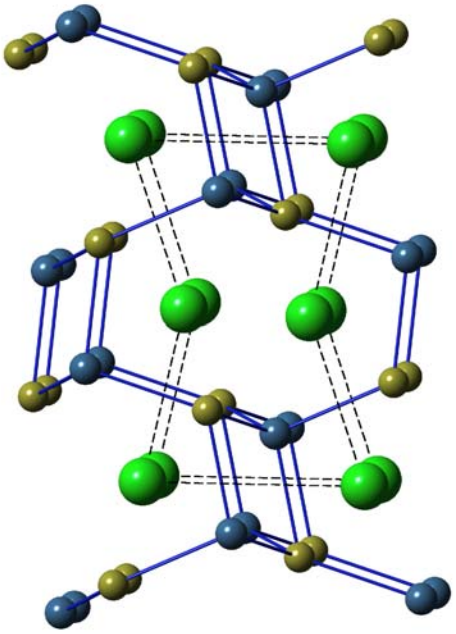
Γ_5^+, M_2^-

Polar



$P6_3mc$ LiGaGe

Antipolar



Pnma MgSrSi

1st order phase transition

Orthorhombic *ABC* as antiferroelectrics

Our search set is composed of three subsets:

1) The compounds in ICSD in the MgSrSi structure type

2) The compounds we previously identified as polar $P6_3mc$.

3) The compounds predicted to be *Pnma* in a high-throughput study by Zhang et al., *Adv. Funct. Mater.* (2012)

This gives us 70 total combinations, for which we need to calculate $P6_3/mmc$, $P6_3mc$ and *Pnma* (12 atom/cell) symmetries.

We also need to calculate the three possible structural variants.
70 x 3 x 3=630 calculations

Orthorhombic *ABC* as antiferroelectrics

ABC	ΔE_{SW} (meV)	P (C/m^2)	Γ_5^+	M_2^-	ΔE (meV)	ΔV (Å^3)	$\Delta V/V$ (%)
LiBeP	119	0.85	0.26	1.26	18	1.23	3.7
MgLiP	20	0.38	0.41	1.28	230	0.49	1.1
MgLiAs	30	0.39	0.42	1.35	207	0.12	0.2
CaLiSb	7	0.18	0.19	1.17	79	0.09	0.1
CaLiBi	7	0.19	0.20	1.16	80	−0.10	−0.1
NaMgP	102	0.49	0.31	1.43	275	1.88	3.2
NaMgAs	114	0.48	0.34	1.44	232	1.65	2.5
NaMgSb	146	0.43	0.40	1.51	154	0.93	1.2
NaMgBi	127	0.42	0.44	1.51	143	1.14	1.4
KMgSb	41	0.40	0.33	1.77	254	2.17	2.6
KMgBi	73	0.31	0.34	1.78	227	1.65	1.8
NaZnSb	81	0.49	0.18	1.48	42	2.68	4.1
NaLiTe	23	0.20	0.30	1.41	114	0.96	1.4
KNaS	12	0.17	0.32	1.36	149	1.60	2.3
KNaSe	13	0.15	0.33	1.38	131	2.09	2.7
KNaTe	14	0.13	0.38	1.42	96	2.81	2.9
NaAgSe	51	0.65	0.62	1.63	134	0.11	0.2
BaCaSi	11	0.34	0.35	1.62	310	0.37	0.4

Outline

The ABO_3 Perovskites

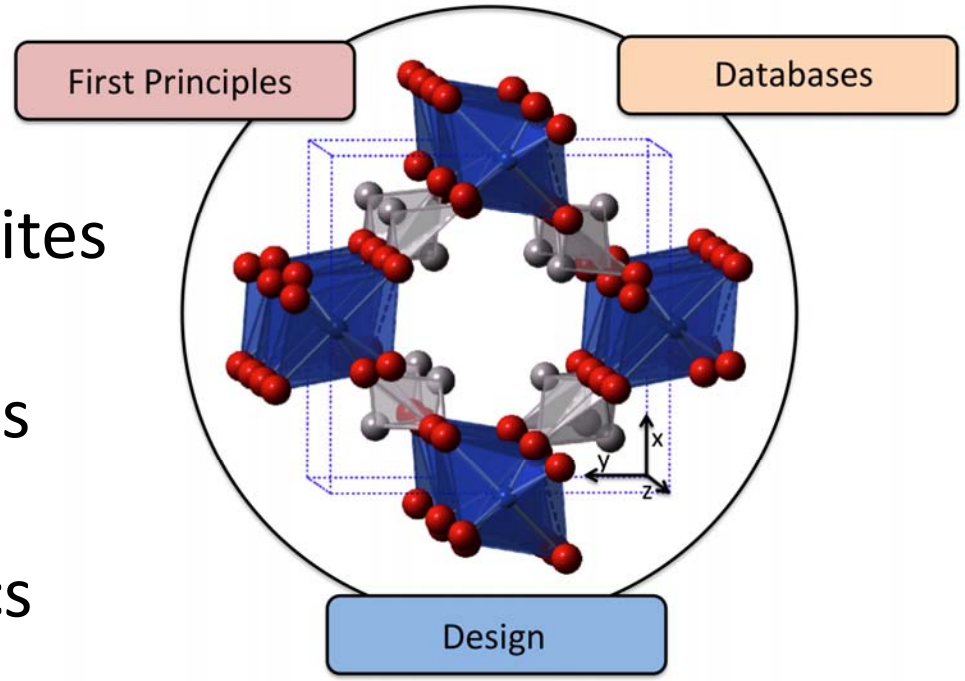
Moving Beyond the Perovskites

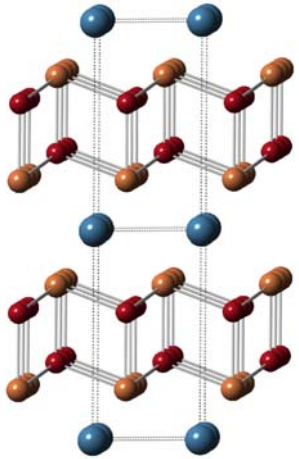
A New Class of Piezoelectrics

A New Class of Ferroelectrics

A New Class of Antiferroelectrics

Concluding Thoughts





New Platforms for Functionality

The half-Heuslers have piezoelectric properties comparable to the perovskites and a range of lattice constants and band gaps

The hexagonal ferroelectrics have a different shape… wurtzite, which is used in many commercial technologies

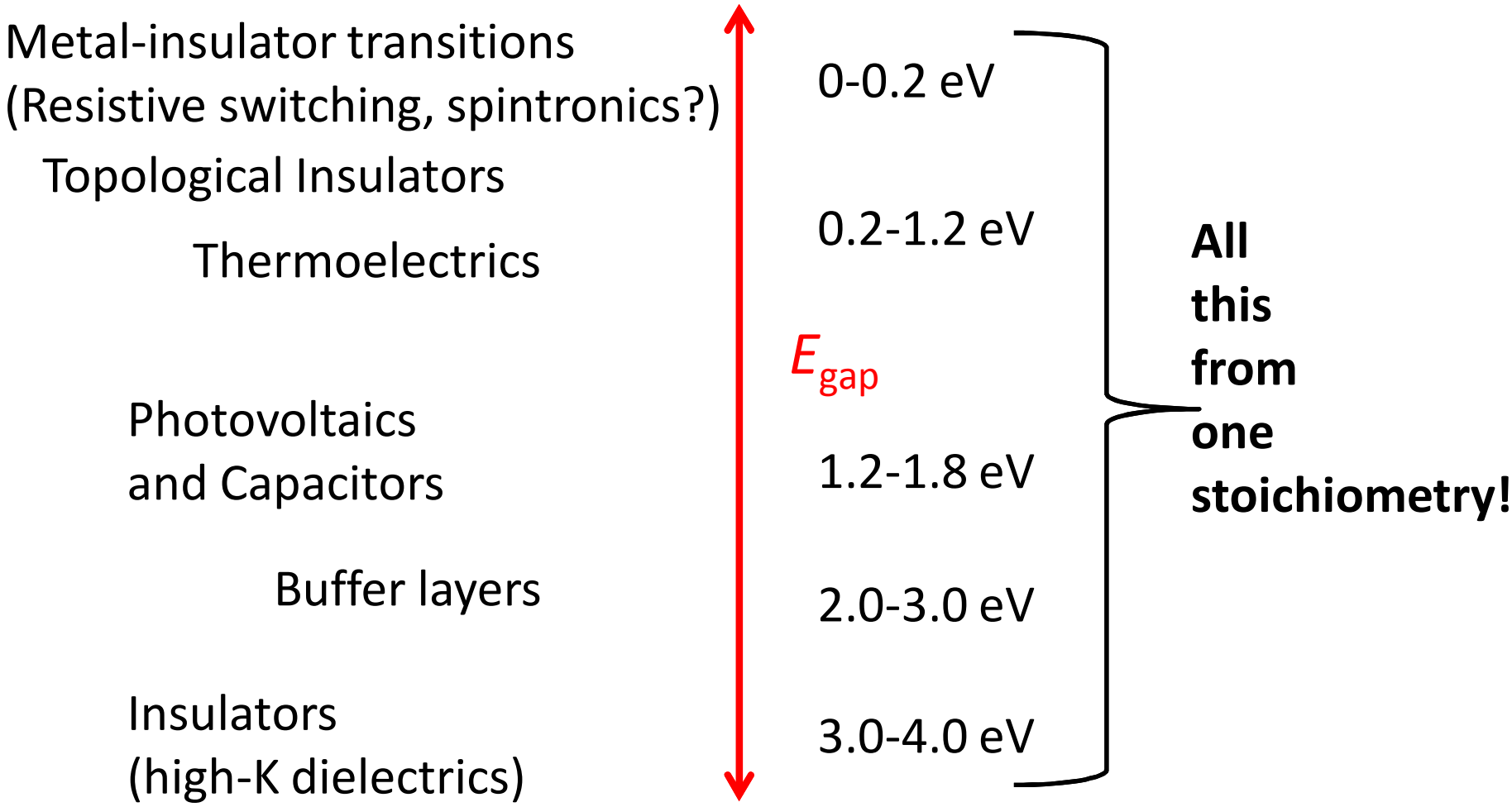
Some of the *ABC* orthorhombic variants are antiferroelectrics. (energy storage! metal-insulator transitions? optics?)

Additional database searching shows that there's more than one way to stuff wurtzite and make it functional!

Could we think of ways to replace the materials in current devices?

What do I mean?

We now have intermetallic semiconductors in which a variety of functional properties that can potentially be coupled to:



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Dr. Eric J. Walter (William and Mary)
Dr. David Stein, Dr. Ilya Grinberg,
Prof. Peter Davies
Prof. Andrew M. Rappe

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At Cornell Univ.:
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Dr. Derek Stewart

At UGA:
Prof. Steve Lewis

At Univ. Houston:
Prof. P Shiv Halasyamani

With Regards to the Calculations

High throughput studies:
Pseudopotential testing is a must!
Set up a few test calculations before your high-throughput study!

Converged data for functional property of interest:
d_{14} vs. e_{14} and k_{14}, need to increase k-point sampling, E_{cut}, etc.

Post-DFT methods may be necessary:
Looking for semiconductive materials, want an accurate band gap
LDA+*U*, PBE0, or GW for the exceptional candidates
See both G. Gou *et al.*, PRB (2011) 205115, and *our JSSC paper*

Some Calculations Simply Fail:
This is most times a hardware issue, sometimes software (dilatmx)

No One Wants HgPbAs In Their Cell Phone

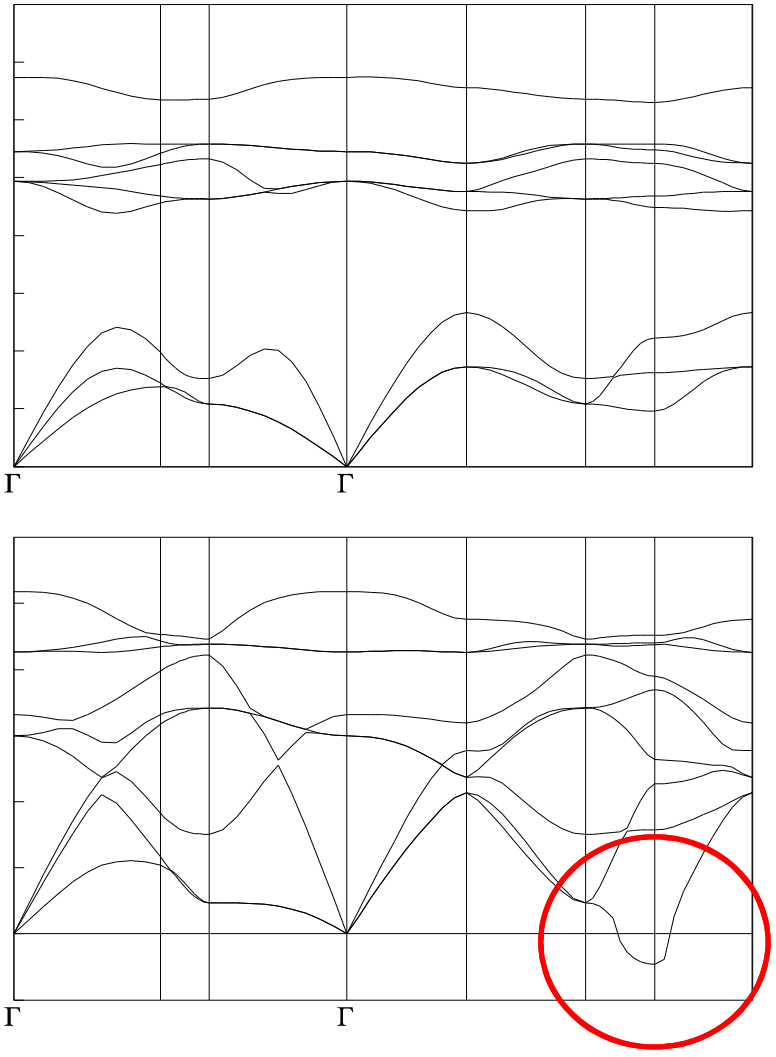
Apply these criteria:

1) Must not contain toxic or expensive elements

2) DFT band gap > 0.4 eV
(experimental leakage)

3) dE > 0.15 eV
(difference between 2 lowest configurations)

4) Instabilities at some point in the BZ?



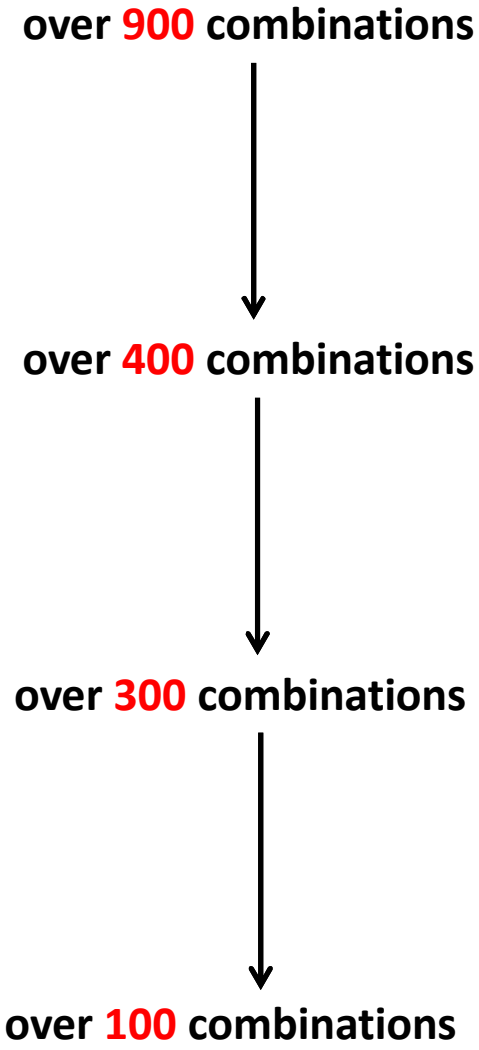
High-Throughput Study of Half-Heuslers

1) **Ground state DFT-LDA calculation.**
   3 possible structural variants (2700 calc.!).
   Which atom sits in the tetrahedral site?
   Calculate the differences in total energy

2) **Insulating or metallic?**

3) **Phonon response calculation.**
   Unstable at Gamma?
   (won't form half-Heusler…
   not dynamically stable)

4) **Toxic or expensive elements, dE, etc.**



High-Throughput Study of Half-Heuslers

Sorting Stable vs. Unstable Hypothetical Compounds:
The case of multifunctional *ABX* half-Heusler
filled tetrahedral structures
by Zhang, Yu, Zakuthayev and Zunger (2012)

Considered stability with regards to binary compositions
(thermodynamic stability wrt decomposition)
and alternative structures. Used GW to predict band gap.

Of the 488 *ABC* not yet reported, predicted 235 to be stable.

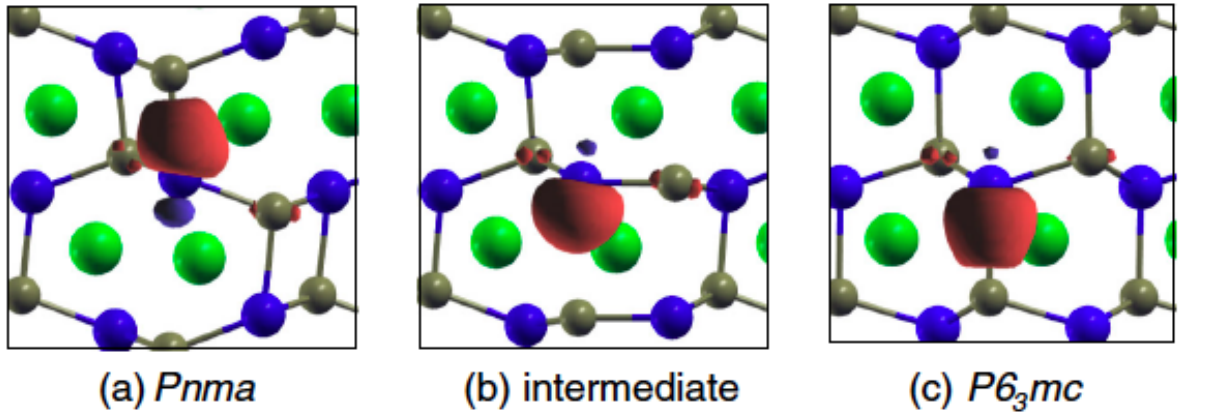
Our approach assumes that if we could potentially stabilize
an *ABC* combination in an insulating half-Heusler structure,
then we could measure their piezoelectric properties

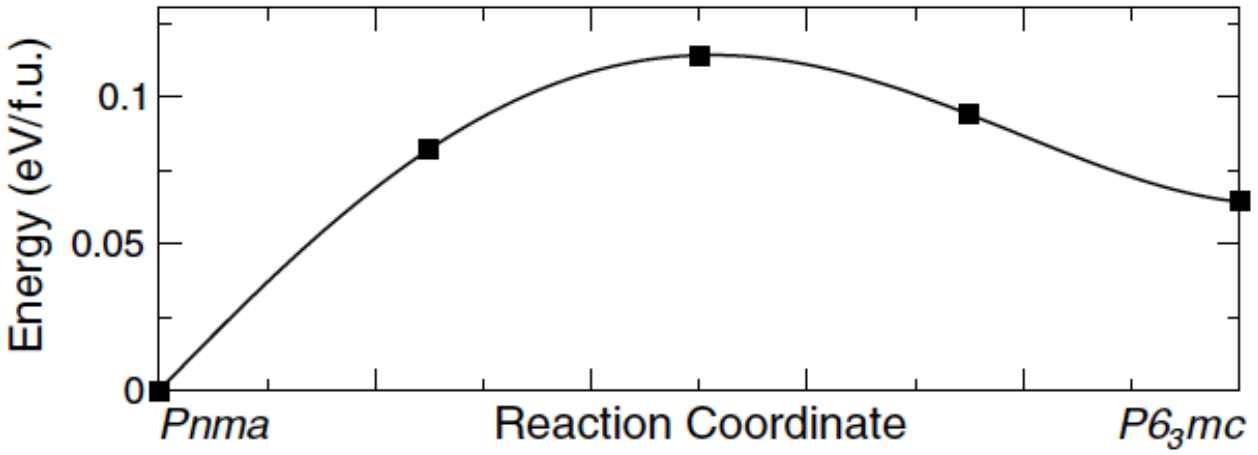
AFEs metal/insulator

TABLE II. Same as Table I, but for compounds in the search set for which either the *Pnma* state or the $P6_3mc$ state is metallic in our discrete Fourier transform (DFT) calculation. A dash in the polarization (P) column indicates that the $P6_3mc$ state is metallic.

ABC	ΔE_{SW} (meV)	P (C/m^2)	Γ_5^+	M_2^-	ΔE (meV)	ΔV (Å^3)	$\Delta V/V$ (%)
MgLiSb	50	...	0.48	1.42	142	1.32	2.2
MgLiBi	41	...	0.52	1.45	126	1.52	2.4
MgCuP	1	0.36	0.42	1.43	174	−0.58	−1.3
NaZnBi	328	...	0.18	1.28	18	2.50	3.6
NaCdAs	199	0.40	0.31	1.44	50	1.54	2.4
SrCaGe	2	0.04	0.27	1.36	186	3.72	4.6
BaCaGe	11	0.26	0.37	1.59	289	1.04	1.1

AFE Wannier Functions: NaCdAs NEB path





Solid State Testing

What is your project?

Simple binary oxide (MO, MO_2, M_2O_3, etc.)
tertiary oxide (ABO_3)
III-V semiconductor (GaAs, InN, etc.)

Use ICSD for structural parameters
Find other DFT references
(Run AE calculations?)

AlP *F4bar3m* a=5.398 Ang. (-0.59 %)
YN *F4bar3m* a=5.192 Ang. (-0.09 %)
BaO *Fm3barm* a=5.539 Ang. (-1.51 %)
PbS *Fm3barm* a=5.842 Ang. (-1.54 %)
TiO_2 *hex.* a=4.549 Ang. (-0.98 %); c=2.958 Ang. (-1.05 %)

Calculation of Properties

Use Landolt Bornstein (LB) for properties like piezoelectric response.
Find other DFT references. What do they report?

Set up a phonon response calculation.
In ABINIT, there are tutorials that will guide you through this.

For example, results of my potentials using telast tutorials:

InSb

d_{14} = -2.29 pC/N (-2.35 pC/N LB)
e_{14} = -0.066 C/m^2 (-0.07 C/m^2 LB)

GaAs

d_{14} = -2.89 pC/N (-2.60 pC/N LB)
e_{14} = -0.15 C/m^2 (-0.16-0.21 C/m^2 LB)

While this is in good agreement,
it is not an indication
that the potential is perfect…
but it is promising.

Hexagonal and Trigonal Polar Groups

Crystal Class	Space Group	Total	1	2	3	4	5+	Most Common Structure Types	No Type
$6mm$	186	1327	6	374	551	248	148	GaGeLi (139), ZnS (445)	118 (8.9%)
	185	169	0	32	67	52	18	$LuMnO_3$ (54), LaF_3 (25)	46 (27.2%)
	184	15	0	0	5	2	8	zeolite (9)	5 (33.3%)
	183	19	0	1	7	9	2	none	19 (100%)
6	173	681	0	29	125	304	223	Apatite (39), La_3CuSiS_7 (177)	145 (21.3%)
	172	1	0	0	0	1	0	none	1 (100%)
	171	5	0	3	0	1	1	none	5 (100%)
	170	13	0	1	0	7	5	$Ba(NO_2)_2$*$2H_2O$ (5)	7 (53.9%)
	169	33	0	6	9	6	12	Al_2S_3 (11)	16 (48.5%)
	168	1	0	0	0	1	0	none	0 (0.0%)
$3mm$	161	587	0	22	212	221	132	$LiNbO_3$ (287), whitlockite (61)	118 (20.1%)
	160	798	0	276	215	102	205	ZnS (123), $FeBiO_3$ (79)	216 (27.1%)
	159	168	2	27	22	57	60	Si_3N_4 (18)	80 (47.6%)
	158	22	0	5	3	7	7	none	22 (100%)
	157	72	0	3	28	26	15	$Mg_3Si_2O_5(OH)$ (19)	30 (41.7%)
	156	347	0	259	29	53	6	CdI_2 (137)	116 (33.4%)
3	146	214	1	12	76	76	49	Ni_3TeO_6 (12)	131 (61.2%)
	145	22	0	1	7	6	8	$RbNO_3$ (2)	19 (86.4%)
	144	82	0	16	23	32	11	$RbNO_3$ (16)	42 (51.2%)
	143	99	1	13	33	21	31	NiTi (6)	86 (86.9%)

J. W. Bennett and K. M. Rabe: http://arxiv.org/abs/1201.2743

Tetragonal Polar Groups

$4mm$	110	51	0 4	28	10	9	$Li_2B_4O_7$ (22)	11 (21.6%)
	109	50	0 11	30	6	3	LaPtSi (16)	19 (38.0%)
	108	29	0 1	21	5	2	$Pb_5Cr_3F_{19}$ (4)	25 (86.2%)
	107	121	0 13	69	17	22	$BaNiSn_3$ (43)	44 (36.4%)
	106	5	0 0	2	3	0	none	5 (100%)
	105	5	0 0	4	1	0	none	5 (100%)
	104	9	0 0	5	0	4	Tl_4HgI_6 (4)	5 (55.6%)
	103	8	0 6	2	0	0	$NbTe_4$ (7)	1 (12.5%)
	102	23	4 6	5	4	4	Al_2Gd_3 (4)	12 (52.2%)
	101	3	0 0	3	0	0	none	3 (100%)
	100	97	0 1	16	57	23	BSN (21), $Ba_2TiOSi_2O_7$ (23)	20 (20.6%)
	99	299	0 6	104	82	107	$PbTiO_3$ (210), $PbVO_3$ (12)	32 (10.7%)
4	80	16	0 3	6	5	2	none	16 (100%)
	79	42	0 5	20	7	10	$U_3Al_2Si_3$ (6)	29 (69.1%)
	78	12	1 0	6	1	4	none	12 (100%)
	77	10	0 4	4	2	0	H_2S (3)	7 (70.0%)
	76	48	2 5	22	4	15	$Ca_2P_2O_7$ (16)	23 (47.9%)
	75	23	0 7	4	6	6	$K_4CuV_5O_{15}Cl$ (4)	19 (82.6%)

J. W. Bennett and K. M. Rabe: http://arxiv.org/abs/1201.2743

Orthorhombic Polar Groups

Crystal Class	Space Group	Total	1	2	3	4	5+	Most Common Structure Types	No Type
$mm2$	46	179	0	4	52	52	71	Ca_2AlFeO_5 (79), $ErSr_2GaCu_2O_7$ (27)	53 (29.6%)
	45	33	0	0	15	8	10	$Ca_{11}InSb_9$ (5), $Sr_4Fe_6O_{13}$ (15)	17 (51.5%)
	44	153	0	25	78	31	19	$NaNO_2$ (13)	74 (48.4%)
	43	287	0	43	44	87	113	Natrolite (61)	111 (38.7%)
	42	69	1	23	21	16	8	NbS_2 (10)	47 (68.1%)
	41	117	0	18	24	54	21	$Bi_4Ti_3O_{12}$ (15)	71 (60.7%)
	40	107	0	15	16	58	18	$NaCu_2NbS_4$ (14)	55 (51.4%)
	39	42	0	14	15	7	6	LaS (5)	31 (73.8%)
	38	186	2	51	86	37	10	$CeNiC_2$ (29)	108 (58.1%)
	37	22	0	0	6	4	12	none	22 (100%)
	36	691	1	65	268	214	143	Bi_3TiNbO_9 (87)	249 (36.0%)
	35	41	0	1	6	16	18	none	41 (100%)
	34	55	0	5	8	25	17	$Ca_2B_5O_9Br$ (12)	35 (63.6%)
	33	1087	2	68	300	377	340	$Cu_2Sc_2O_5$ (18), $NaFeO_2$ (56)	258 (23.7%)
	32	48	0	5	15	10	18	$K_{1-x}FeF_3$ (4)	33 (68.8%)
	31	376	0	16	136	114	110	Cu_3AsS_4 (56)	157 (41.8%)
	30	20	0	2	3	5	9	$Fe_3(PO_4)_2{*}H_2O$	19 (95.0%)
	29	305	1	11	83	124	86	boracite (16)	184 (60.3%)
	28	30	0	6	12	2	10	$AuTe_2$ (5)	20 (66.7%)
	27	5	0	1	3	1	0	V_4H_3 (1)	4 (80.0%)
	26	133	0	9	37	59	28	$NaNbO_3$ (5)	88 (66.2%)
	25	47	0	17	12	12	6	GaAs (7)	29 (61.7%)

J. W. Bennett and K. M. Rabe: http://arxiv.org/abs/1201.2743

Mono and Triclinic Polar Groups

m	9	621	0	40	159	215	207	$Pb(Ti,Zr)O_3$ (14)	339 (54.6%)
	8	350	0	30	103	116	101	$Ca_5(BO_3)_3F$ (17), Pb_2FeNbO_6 (48)	199 (56.9%)
	7	307	0	51	68	108	80	WO_3 (32)	189 (61.6%)
	6	59	0	7	13	22	17	PMN-PT and $(Na,K)NbO_3$ (17)	42 (71.2%)
2	5	430	1	30	123	152	124	many	292 (67.9%)
	4	722	10	35	151	282	244	many	415 (57.5%)
	3	45	2	4	11	13	15	none	45 (100%)
1	1	460	6	52	118	150	134	many	324 (70.4%)

J. W. Bennett and K. M. Rabe: http://arxiv.org/abs/1201.2743

Landolt-Bornstein database

Some materials are very well characterized! And decent!

Class 3m (*C3v*)	k_{31}	k_{33}	k_{15}	d_{31}	d_{33}	d_{15}	e_{31}	e_{33}	e_{15}
Ag_3SbS_3	0.17	0.4	0.3	23	35	32	0.2	1.1	0.4
$LiNbO_3$	0.02	0.2	0.6	1	18	75	0.7	1.8	3.8

But most really aren't

Class 622 (*D6*)	k_{14}	d_{14}	e_{14}
$CsCuCl_3$	0.12	7.2	0.04
SiO_2	?	2	?

Class 3 (*C3*)	k_{31}	k_{33}	e_{31}	e_{33}
$Pb_5Ge_3O_{11}$	0.08	0.13	0.61	0.77

where's the d_{ij} values?

Class 4bar3m	k_{14}	d_{14}	e_{14}
AlSb	0.10	1.6	0.07
CdTe	0.03	1.7	0.04
GaAs	0.09	2.6	0.16
Tl_3TaS_4	**0.55**	**58**	**0.32**
ZnS	0.09	3.2	0.15
ZnSe	0.03	1.1	0.05
ZnTe	0.02	0.9	0.03

What is a piezoelectric?

1) A material that needs to be **insulating**
2) A material that has **no inversion center**

The **piezoelectric effect** is an electromechanical interaction
(this means that electricity is generated by a mechanical force)

We **measure** how great this effect is
(via response to a deformation)
with **tensors** e_{ij} and d_{ij}

$$e_{i\alpha} = \frac{\partial P'_i}{\partial \eta_\alpha} \qquad d_{i\alpha} = S_{\alpha\beta} e_{i\beta}$$

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(this means that electricity is generated by a mechanical force)

We **measure** how great this effect is
(via response to a deformation)
with **tensors** e_{ij} and d_{ij}

$$k_{i\alpha} = \frac{|d_{i\alpha}|}{\sqrt{\varepsilon_{ii}^{\sigma} S_{\alpha\alpha}}}$$

However, the **figure of merit is k_{14}**!