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 $\textit{ABO}_3$ Perovskites
$A \textit{Canonical Family}$

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

$\text{ABO}_3$ 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

$\text{AA'}\text{BB'}\text{O}_3$

Pb(Zr,Ti)O$_3$
The Perovskites: A Functional 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$_3$

**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!

We want more materials like BiFeO$_3$!

Wang et al., Science 2003, 1719
Choi et al., Science 2009, 63
Katiyar & Scott, 2011
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$_3$

(Survey of expt. literature and DFT)

Sulfide Perovskites?

\( \text{BaZrS}_3 \): DFT band gap decreases from 3.9 to 1.7 eV relative to \( \text{BaZrO}_3 \)

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

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.

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!*


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**

**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%)

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?

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 )....

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)

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*


A New Class of Ferroelectrics

A New Class of Antiferroelectrics

Concluding Thoughts
LiAlSi: Target For a High-Throughput Study

Half-Heusler: three atoms, $ABC$:

A and B form a rocksalt lattice

C occupies 1/2 of the tetrahedral sites...

most electronegative element?

Have three different variations

Gaining popularity as multifunctional materials!

$F4\text{bar}3m$ 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 $ABC$

$F4\bar{b}ar3m$ (#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
Searching the ICSD for ABC

\textit{F4bar3m} (#216), cubic nonpolar: 269 total (260 LiAlSi)

Number of entries \textbf{without magnetic cations}: 49

Number of entries with \textbf{8 or 18 valence electrons}: 38

\textbf{Examples, divided into families}

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

38 Known Half-Heuslers

% Error (PSP-AE)
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

38 Known Half-Heuslers

BR is the Bennett-Rappe library of LDA potentials

- TM PSP set
- HGH PSP set
- BR PSP set
What About the Hypothetical $ABC$?

![Graph showing error percentages for 40 unknown Half-Heuslers. The graph compares TM PSP set and HGH PSP set.](image)
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?**
What Do We Find?

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

Film lattice (Å)

3.70

YAlO$_3$

LaSrAlO$_4$

LaAlO$_3$

NdGaO$_3$

LaGaO$_3$

SrTiO$_3$

[110] DyScO$_3$, d=32mm

3.90

LaSrGaO$_4$

LSAT

TbScO$_3$

GdScO$_3$

EuScO$_3$

SmScO$_3$

[110] GdScO$_3$, d=32mm

4.00

Pb(Zr,Ti)O$_3$

[Ba,Sr]TiO$_3$

[4.10] BiScO$_3$

4.20

PMN-PT

4.30

Bi$_2$Ti$_2$O$_7$

BiFeO$_3$

BiMnO$_3$

Bi$_2$O$_3$

Bi$_4$Ti$_3$O$_12$

Bi$_4$Ti$_2$O$_7$

YBa$_2$Cu$_3$O$_7$

Bi$_2$Sr$_2$CuO$_6$

(Ba,K)Bi$_2$O$_3$

Substrate lattice (Å)
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

<table>
<thead>
<tr>
<th>ABC</th>
<th>a</th>
<th>$E_{\text{gap}}$</th>
<th>$e_{14}$</th>
<th>$d_{14}$</th>
<th>$C_{44}$</th>
<th>$k_{14}$</th>
<th>$\epsilon_0$</th>
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<tbody>
<tr>
<td>KMgP</td>
<td>6.71</td>
<td>1.04</td>
<td>1.19</td>
<td>346.28</td>
<td>0.03</td>
<td>0.89</td>
<td>13</td>
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<tr>
<td>LiNaS</td>
<td>6.10</td>
<td>3.12</td>
<td>0.92</td>
<td>208.22</td>
<td>0.04</td>
<td>0.86</td>
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<tr>
<td>LiSrAs</td>
<td>6.84</td>
<td>1.93</td>
<td>0.79</td>
<td>286.27</td>
<td>0.03</td>
<td>0.85</td>
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<tr>
<td>LiNaSe</td>
<td>6.39</td>
<td>2.70</td>
<td>0.75</td>
<td>227.09</td>
<td>0.03</td>
<td>0.84</td>
<td>8</td>
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<tr>
<td>NaMgN</td>
<td>5.43</td>
<td>0.72</td>
<td>1.50</td>
<td>165.23</td>
<td>0.09</td>
<td>0.83</td>
<td>13</td>
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<tr>
<td>NaBeP</td>
<td>5.59</td>
<td>2.06</td>
<td>1.02</td>
<td>192.98</td>
<td>0.05</td>
<td>0.82</td>
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<tr>
<td>KMgAs</td>
<td>6.92</td>
<td>0.67</td>
<td>1.06</td>
<td>205.75</td>
<td>0.05</td>
<td>0.81</td>
<td>13</td>
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<tr>
<td>KScPb</td>
<td>7.35</td>
<td>0.42</td>
<td>1.21</td>
<td>330.83</td>
<td>0.04</td>
<td>0.80</td>
<td>25</td>
</tr>
<tr>
<td>MgBaSi</td>
<td>7.18</td>
<td>0.37</td>
<td>1.13</td>
<td>290.51</td>
<td>0.04</td>
<td>0.80</td>
<td>21</td>
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<tr>
<td>BeBaSn</td>
<td>6.86</td>
<td>0.16</td>
<td>0.49</td>
<td>1036.54</td>
<td>0.01</td>
<td>0.80</td>
<td>33</td>
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<tr>
<td>KScSn</td>
<td>7.31</td>
<td>0.42</td>
<td>1.19</td>
<td>294.69</td>
<td>0.04</td>
<td>0.79</td>
<td>24</td>
</tr>
</tbody>
</table>

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

(Best known member in LB database is $\text{Tl}_3\text{TaS}_4$ with $d_{14}=58 \text{ pC/N}$)
Outline

The $\textit{ABO}_3$ Perovskites

Moving Beyond the Perovskites

A New Class of Piezoelectrics

A New Class of Ferroelectrics

\textit{The Hexagonal LiGaGe family}


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)
**P6₃/mmc** (#194), hexagonal nonpolar: 297 total (200 ZrBeSi)
**P6bar2m** (#189), hexagonal nonpolar: 712 total (680 Fe₂P)
**P6barm2** (#187), hexagonal nonpolar: 47 total (40 BaPtSb)
**P6₃mc** (#186), hexagonal polar: 153 total (120 LiGaGe)
**P4/nmm** (#129), tetragonal nonpolar: 613 total (450 PbClF)
**Pnma** (#62), orthorhombic nonpolar: 548 total (450 MgSrSi)

**P6₃mc** 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

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

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

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.
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.
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**

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>c</th>
<th>$z_{2b}$</th>
<th>$z'_{2b}$</th>
<th>$E_{\text{gap}}$</th>
<th>$\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiGaGe</td>
<td>4.139</td>
<td>6.713</td>
<td>0.314</td>
<td>0.698</td>
<td>0.700</td>
<td>0.80</td>
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<tr>
<td>CuScSn</td>
<td>4.351</td>
<td>6.795</td>
<td>0.330</td>
<td>0.729</td>
<td>0.229</td>
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<td>CuYSn</td>
<td>4.475</td>
<td>7.148</td>
<td>0.320</td>
<td>0.728</td>
<td>0.733</td>
<td>0.32</td>
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<tr>
<td>CuYPb</td>
<td>4.512</td>
<td>7.191</td>
<td>0.321</td>
<td>0.729</td>
<td>0.729</td>
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<td>AgYSn</td>
<td>4.634</td>
<td>7.240</td>
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<td>0.702</td>
<td>0.719</td>
<td>0.39</td>
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<tr>
<td>AuScGe</td>
<td>4.263</td>
<td>6.679</td>
<td>0.196</td>
<td>0.793</td>
<td>0.798</td>
<td>0.61</td>
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<tr>
<td>AuScSn</td>
<td>4.507</td>
<td>7.066</td>
<td>0.348</td>
<td>0.730</td>
<td>0.731</td>
<td>0.75</td>
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<tr>
<td>AuYSi</td>
<td>4.247</td>
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<td>0.228</td>
<td>0.780</td>
<td>0.775</td>
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<tr>
<td>AuYGe</td>
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<td>0.219</td>
<td>0.789</td>
<td>0.791</td>
<td>0.26</td>
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<tr>
<td>AuYSn</td>
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<td>7.293</td>
<td>0.173</td>
<td>0.774</td>
<td>0.821</td>
<td>0.70</td>
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<tr>
<td>LiBeSb</td>
<td>4.091</td>
<td>6.636</td>
<td>0.350</td>
<td>0.733</td>
<td>0.732</td>
<td>1.45</td>
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<tr>
<td>LiZnSb</td>
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<tr>
<td>CaAgBi</td>
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<td>0.715</td>
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<tr>
<td>CaZnSn</td>
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<td>CaHgSn</td>
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<td>7.547</td>
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<td>SrHgSn</td>
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<td>0.712</td>
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<tr>
<td>SrHgPb</td>
<td>4.894</td>
<td>8.054</td>
<td>0.311</td>
<td>0.719</td>
<td>0.720</td>
<td>0.19</td>
</tr>
</tbody>
</table>

We have 17 combinations with reliable structural data
**Known LiGaGe Compounds**

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<td>0.698</td>
<td>0</td>
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<td>0.310</td>
<td>0.729</td>
<td>0</td>
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<tr>
<td>CuYSn</td>
<td>4.475</td>
<td>7.148</td>
<td>0.320</td>
<td>0.728</td>
<td>0</td>
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<tr>
<td>CuYPb</td>
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<td>7.191</td>
<td>0.321</td>
<td>0.729</td>
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<td>AgYSn</td>
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<td>7.240</td>
<td>0.314</td>
<td>0.702</td>
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<td>0.39</td>
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<tr>
<td>AuScGe</td>
<td>4.263</td>
<td>6.679</td>
<td>0.196</td>
<td>0.793</td>
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<td>0.668</td>
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<td>0.311</td>
<td>0.719</td>
<td>0</td>
<td>0.19</td>
</tr>
</tbody>
</table>

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.
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!
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
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 \(ABC\)?

My secret weapon...Villars maps

Structure Forming 18Ve

We know about this transition...

Structure Forming 18Ve
... are other transitions possible?

Structure Forming 18Ve
Orthorhombic $ABC$ as antiferroelectrics

Nonpolar

$\Gamma_2^-$

Polar

$\Gamma_5^+, M_2^-$

Antipolar

$P6_3/mmc$ ZrBeSi

$P6_3mc$ LiGaGe

1$^{\text{st}}$ order phase transition

$Pnma$ MgSrSi
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 $P6_3mc$.


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. $70 \times 3 \times 3 = 630$ calculations
Orthorhombic $ABC$ as antiferroelectrics

<table>
<thead>
<tr>
<th>$ABC$</th>
<th>$\Delta E_{sw}$ (meV)</th>
<th>$P$ (C/m²)</th>
<th>$\Gamma_{5}^+$</th>
<th>$M_2^-$</th>
<th>$\Delta E$ (meV)</th>
<th>$\Delta V$ (Å$^3$)</th>
<th>$\Delta V/V$ (%)</th>
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<td>LiBeP</td>
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<td>0.85</td>
<td>0.26</td>
<td>1.26</td>
<td>18</td>
<td>1.23</td>
<td>3.7</td>
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<tr>
<td>MgLiP</td>
<td>20</td>
<td>0.38</td>
<td>0.41</td>
<td>1.28</td>
<td>230</td>
<td>0.49</td>
<td>1.1</td>
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<td>MgLiAs</td>
<td>30</td>
<td>0.39</td>
<td>0.42</td>
<td>1.35</td>
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<td>0.2</td>
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<td>CaLiSb</td>
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<td>0.18</td>
<td>0.19</td>
<td>1.17</td>
<td>79</td>
<td>0.09</td>
<td>0.1</td>
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<td>CaLiBi</td>
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<td>0.19</td>
<td>0.20</td>
<td>1.16</td>
<td>80</td>
<td>$-0.10$</td>
<td>$-0.1$</td>
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<tr>
<td>NaMgP</td>
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<td>1.43</td>
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<td>0.34</td>
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<td>227</td>
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<td>1.8</td>
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<td>1.48</td>
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<tr>
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<td>0.30</td>
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<td>96</td>
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<td>1.63</td>
<td>134</td>
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<td>0.2</td>
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<tr>
<td>BaCaSi</td>
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<td>0.34</td>
<td>0.35</td>
<td>1.62</td>
<td>310</td>
<td>0.37</td>
<td>0.4</td>
</tr>
</tbody>
</table>
Outline

The $\textit{ABO}_3$ 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:

- Metal-insulator transitions (Resistive switching, spintronics?)
- Topological Insulators
- Thermoelectrics
- Photovoltaics and Capacitors
- Buffer layers
- Insulators (high-K dielectrics)

All this from one stoichiometry!
Acknowledgements

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Prof. Karin Rabe

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Dr. Valentino Cooper (ORNL)
Dr. Eric J. Walter (William and Mary)
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Prof. Andrew M. Rappe

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At UCSB:
Prof. Ram Seshadri

At Cornell Univ.:
Prof. Craig Fennie
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

   - over 900 combinations

2) **Insulating or metallic?**

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

   - over 400 combinations

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

   - over 300 combinations

   - over 100 combinations
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.
TABLE II. Same as Table I, but for compounds in the search set for which either the \textit{Pnma} state or the \textit{P6}_3\textit{mc} state is metallic in our discrete Fourier transform (DFT) calculation. A dash in the polarization (\textit{P}) column indicates that the \textit{P6}_3\textit{mc} state is metallic.

<table>
<thead>
<tr>
<th>\textit{ABC}</th>
<th>(\Delta E_{\text{SW}}) (meV)</th>
<th>(P) (C/m\textsuperscript{2})</th>
<th>(\Gamma^+)</th>
<th>(M^-)</th>
<th>(\Delta E) (meV)</th>
<th>(\Delta V) (\text{Å}^3)</th>
<th>(\Delta V/V) (%)</th>
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<tbody>
<tr>
<td>\textit{MgLiSb}</td>
<td>50</td>
<td>...</td>
<td>0.48</td>
<td>1.42</td>
<td>142</td>
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<td>41</td>
<td>...</td>
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<td>1.45</td>
<td>126</td>
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<td>\textit{MgCuP}</td>
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<td>0.42</td>
<td>1.43</td>
<td>174</td>
<td>-0.58</td>
<td>-1.3</td>
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<tr>
<td>\textit{NaZnBi}</td>
<td>328</td>
<td>...</td>
<td>0.18</td>
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<td>18</td>
<td>2.50</td>
<td>3.6</td>
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<tr>
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<td>1.44</td>
<td>50</td>
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<td>2.4</td>
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<td>\textit{SrCaGe}</td>
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<td>186</td>
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<td>\textit{BaCaGe}</td>
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<td>0.37</td>
<td>1.59</td>
<td>289</td>
<td>1.04</td>
<td>1.1</td>
</tr>
</tbody>
</table>
AFE Wannier Functions: NaCdAs NEB path

(a) Pnma  
(b) intermediate  
(c) P6_3mc

![Graph showing energy vs reaction coordinate](image-url)
Solid State Testing

What is your project?

Simple binary oxide (MO, MO₂, M₂O₃, etc.)
tertiary oxide (ABO₃)
III-V semiconductor (GaAs, InN, etc.)

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

AIP $F4_{bar}3m$ $a=5.398$ Ang. (-0.59 %)
YN $F4_{bar}3m$ $a=5.192$ Ang. (-0.09 %)
BaO $Fm3barm$ $a=5.539$ Ang. (-1.51 %)
PbS $Fm3barm$ $a=5.842$ Ang. (-1.54 %)
TiO₂ $hex.$ $a=4.549$ 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**

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

**GaAs**

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

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

<table>
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<tr>
<th>Crystal Space</th>
<th>Total</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5+</th>
<th>Most Common Structure Types</th>
<th>No Type</th>
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<td><strong>6mm</strong></td>
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<td>1327</td>
<td>6</td>
<td>374</td>
<td>551</td>
<td>248</td>
<td>148</td>
<td>GaGeLi (139), ZnS (445)</td>
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<td>67</td>
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<td>18</td>
<td>LuMnO$_3$ (54), LaF$_3$ (25)</td>
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<td>8</td>
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<td>CdI$_2$ (137)</td>
</tr>
<tr>
<td><strong>3</strong></td>
<td>146</td>
<td>214</td>
<td>1</td>
<td>12</td>
<td>76</td>
<td>76</td>
<td>49</td>
<td>Ni$_3$TeO$_6$ (12)</td>
</tr>
<tr>
<td></td>
<td>145</td>
<td>22</td>
<td>0</td>
<td>1</td>
<td>7</td>
<td>6</td>
<td>8</td>
<td>RbNO$_3$ (2)</td>
</tr>
<tr>
<td></td>
<td>144</td>
<td>82</td>
<td>0</td>
<td>16</td>
<td>23</td>
<td>32</td>
<td>11</td>
<td>RbNO$_3$ (16)</td>
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<tr>
<td></td>
<td>143</td>
<td>99</td>
<td>1</td>
<td>13</td>
<td>33</td>
<td>21</td>
<td>31</td>
<td>NiTi (6)</td>
</tr>
</tbody>
</table>

## Tetragonal Polar Groups

<table>
<thead>
<tr>
<th>Group</th>
<th>Symbol</th>
<th>Formula</th>
<th>Number</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>4mm</td>
<td>Li$_2$B$_4$O$_7$</td>
<td>22</td>
<td>11 (21.6%)</td>
</tr>
<tr>
<td>109</td>
<td></td>
<td>LaPtSi</td>
<td>16</td>
<td>19 (38.0%)</td>
</tr>
<tr>
<td>108</td>
<td></td>
<td>Pb$_5$Cr$<em>3$F$</em>{19}$</td>
<td>4</td>
<td>25 (86.2%)</td>
</tr>
<tr>
<td>107</td>
<td></td>
<td>BaNiSn$_3$</td>
<td>43</td>
<td>44 (36.4%)</td>
</tr>
<tr>
<td>106</td>
<td>4mm</td>
<td>none</td>
<td>0</td>
<td>5 (100%)</td>
</tr>
<tr>
<td>105</td>
<td></td>
<td>none</td>
<td>0</td>
<td>5 (100%)</td>
</tr>
<tr>
<td>104</td>
<td></td>
<td>Tl$_4$Hgl$_6$</td>
<td>4</td>
<td>5 (55.6%)</td>
</tr>
<tr>
<td>103</td>
<td>4mm</td>
<td>NbTe$_4$</td>
<td>7</td>
<td>1 (12.5%)</td>
</tr>
<tr>
<td>102</td>
<td></td>
<td>Al$_2$Gd$_3$</td>
<td>4</td>
<td>12 (52.2%)</td>
</tr>
<tr>
<td>101</td>
<td>4mm</td>
<td>none</td>
<td>0</td>
<td>3 (100%)</td>
</tr>
<tr>
<td>100</td>
<td></td>
<td>BSN</td>
<td>(21)</td>
<td>20 (20.6%)</td>
</tr>
<tr>
<td>99</td>
<td></td>
<td>Ba$_2$TiOSi$_2$O$_7$</td>
<td>(23)</td>
<td>32 (10.7%)</td>
</tr>
</tbody>
</table>
| 98    |        | PbTiO$_3$ | (210) | (

Orthorhombic Polar Groups

<table>
<thead>
<tr>
<th>Crystal Class</th>
<th>Space Group</th>
<th>Total</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5+</th>
<th>Most Common Structure Types</th>
<th>No Type</th>
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<td>mm2</td>
<td>46</td>
<td>179</td>
<td>0</td>
<td>4</td>
<td>52</td>
<td>52</td>
<td>71</td>
<td>Ca$_2$AlFeO$_5$ (79), ErSr$_2$GaCu$_2$O$_7$ (27)</td>
<td>53 (29.6%)</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>33</td>
<td>0</td>
<td>0</td>
<td>15</td>
<td>8</td>
<td>10</td>
<td>Ca$_{11}$InSb$_9$ (5)</td>
<td>17 (51.5%)</td>
</tr>
<tr>
<td></td>
<td>44</td>
<td>153</td>
<td>0</td>
<td>25</td>
<td>78</td>
<td>31</td>
<td>19</td>
<td>NaNO$_2$ (13)</td>
<td>74 (48.4%)</td>
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<td>43</td>
<td>287</td>
<td>0</td>
<td>43</td>
<td>44</td>
<td>87</td>
<td>113</td>
<td>Natrolite (61)</td>
<td>111 (38.7%)</td>
</tr>
<tr>
<td></td>
<td>42</td>
<td>69</td>
<td>1</td>
<td>23</td>
<td>21</td>
<td>16</td>
<td>8</td>
<td>NbS$_2$ (10)</td>
<td>47 (68.1%)</td>
</tr>
<tr>
<td></td>
<td>41</td>
<td>117</td>
<td>0</td>
<td>18</td>
<td>24</td>
<td>54</td>
<td>21</td>
<td>Bi$_4$Ti$<em>3$O$</em>{12}$ (15)</td>
<td>71 (60.7%)</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>107</td>
<td>0</td>
<td>15</td>
<td>16</td>
<td>58</td>
<td>18</td>
<td>NaCu$_2$Nb$_5$S$_4$ (14)</td>
<td>55 (51.4%)</td>
</tr>
<tr>
<td></td>
<td>39</td>
<td>42</td>
<td>0</td>
<td>14</td>
<td>15</td>
<td>7</td>
<td>6</td>
<td>LaS (5)</td>
<td>31 (73.8%)</td>
</tr>
<tr>
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<td>38</td>
<td>186</td>
<td>2</td>
<td>51</td>
<td>86</td>
<td>37</td>
<td>10</td>
<td>CeNiC$_2$ (29)</td>
<td>108 (58.1%)</td>
</tr>
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<td>37</td>
<td>22</td>
<td>0</td>
<td>0</td>
<td>6</td>
<td>4</td>
<td>4</td>
<td>none</td>
<td>22 (100%)</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>691</td>
<td>1</td>
<td>65</td>
<td>268</td>
<td>214</td>
<td>143</td>
<td>Bi$_3$TiNbO$_9$ (87)</td>
<td>249 (36.0%)</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>41</td>
<td>0</td>
<td>1</td>
<td>6</td>
<td>16</td>
<td>18</td>
<td>none</td>
<td>41 (100%)</td>
</tr>
<tr>
<td></td>
<td>34</td>
<td>55</td>
<td>0</td>
<td>5</td>
<td>8</td>
<td>25</td>
<td>17</td>
<td>Ca$_2$B$_5$O$_9$Br (12)</td>
<td>35 (63.6%)</td>
</tr>
<tr>
<td></td>
<td>33</td>
<td>1087</td>
<td>2</td>
<td>68</td>
<td>300</td>
<td>377</td>
<td>340</td>
<td>Cu$_2$Sc$_2$O$_5$ (18), NaFeO$_2$ (56)</td>
<td>258 (23.7%)</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>48</td>
<td>0</td>
<td>5</td>
<td>15</td>
<td>10</td>
<td>18</td>
<td>K$_{1-x}$FeF$_3$ (4)</td>
<td>33 (68.8%)</td>
</tr>
<tr>
<td></td>
<td>31</td>
<td>376</td>
<td>0</td>
<td>16</td>
<td>136</td>
<td>114</td>
<td>110</td>
<td>Cu$_3$As$_5$S$_4$ (56)</td>
<td>157 (41.8%)</td>
</tr>
<tr>
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<td>30</td>
<td>20</td>
<td>0</td>
<td>2</td>
<td>3</td>
<td>5</td>
<td>9</td>
<td>Fe$_3$(PO$_4$)$_2$·H$_2$O</td>
<td>19 (95.0%)</td>
</tr>
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<td>29</td>
<td>305</td>
<td>1</td>
<td>11</td>
<td>83</td>
<td>124</td>
<td>86</td>
<td>boracite (16)</td>
<td>184 (60.3%)</td>
</tr>
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<td>28</td>
<td>30</td>
<td>0</td>
<td>6</td>
<td>12</td>
<td>2</td>
<td>10</td>
<td>AuTe$_2$ (5)</td>
<td>20 (66.7%)</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>5</td>
<td>0</td>
<td>1</td>
<td>3</td>
<td>1</td>
<td>0</td>
<td>V$_4$H$_3$ (1)</td>
<td>4 (80.0%)</td>
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<tr>
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<td>26</td>
<td>133</td>
<td>0</td>
<td>9</td>
<td>37</td>
<td>59</td>
<td>28</td>
<td>NaNbO$_3$ (5)</td>
<td>88 (66.2%)</td>
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<tr>
<td></td>
<td>25</td>
<td>47</td>
<td>0</td>
<td>17</td>
<td>12</td>
<td>12</td>
<td>6</td>
<td>GaAs (7)</td>
<td>29 (61.7%)</td>
</tr>
</tbody>
</table>

## Mono and Triclinic Polar Groups

<table>
<thead>
<tr>
<th>$m$</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
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<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>460</td>
<td>6</td>
<td>52</td>
<td>118</td>
<td>150</td>
<td>134</td>
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<tr>
<td>2</td>
<td>5</td>
<td>430</td>
<td>1</td>
<td>30</td>
<td>123</td>
<td>152</td>
<td>124</td>
<td>199</td>
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<tr>
<td>3</td>
<td>45</td>
<td>2</td>
<td>4</td>
<td>11</td>
<td>13</td>
<td>15</td>
<td>292</td>
<td>292</td>
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<tr>
<td>4</td>
<td>722</td>
<td>10</td>
<td>35</td>
<td>151</td>
<td>282</td>
<td>244</td>
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<td>30</td>
<td>103</td>
<td>116</td>
<td>101</td>
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<td>189</td>
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<tr>
<td>6</td>
<td>307</td>
<td>0</td>
<td>51</td>
<td>68</td>
<td>108</td>
<td>80</td>
<td>Pb(Ti,Zr)O$_3$ (14)</td>
<td>339 (54.6%)</td>
</tr>
<tr>
<td>7</td>
<td>59</td>
<td>0</td>
<td>7</td>
<td>13</td>
<td>22</td>
<td>17</td>
<td>Ca$_5$(BO$_3$)$_3$F (17), Pb$_2$FeNbO$_6$ (48)</td>
<td>199 (56.9%)</td>
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<tr>
<td>8</td>
<td>9</td>
<td>621</td>
<td>0</td>
<td>40</td>
<td>159</td>
<td>215</td>
<td>207</td>
<td>WO$_3$ (32)</td>
</tr>
</tbody>
</table>

PMN-PT and (Na,K)NbO$_3$ (17) | 42 (71.2%) |

Landolt-Bornstein database

Some materials are very well characterized! And decent!

Class 3m \((C3v)\) \(k_{31} k_{33} k_{15} d_{31} d_{33} d_{15} e_{31} e_{33} e_{15}\)

<table>
<thead>
<tr>
<th>Material</th>
<th>(k_{31})</th>
<th>(k_{33})</th>
<th>(k_{15})</th>
<th>(d_{31})</th>
<th>(d_{33})</th>
<th>(d_{15})</th>
<th>(e_{31})</th>
<th>(e_{33})</th>
<th>(e_{15})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ag}_3\text{SbS}_3)</td>
<td>0.17</td>
<td>0.4</td>
<td>0.3</td>
<td>23</td>
<td>35</td>
<td>32</td>
<td>0.2</td>
<td>1.1</td>
<td>0.4</td>
</tr>
<tr>
<td>(\text{LiNbO}_3)</td>
<td>0.02</td>
<td>0.2</td>
<td>0.6</td>
<td>1</td>
<td>18</td>
<td>75</td>
<td>0.7</td>
<td>1.8</td>
<td>3.8</td>
</tr>
</tbody>
</table>

But most really aren’t

Class 622 \((D6)\) \(k_{14} d_{14} e_{14}\)

<table>
<thead>
<tr>
<th>Material</th>
<th>(k_{14})</th>
<th>(d_{14})</th>
<th>(e_{14})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CsCuCl}_3)</td>
<td>0.12</td>
<td>7.2</td>
<td>0.04</td>
</tr>
<tr>
<td>(\text{SiO}_2)</td>
<td>?</td>
<td>2</td>
<td>?</td>
</tr>
</tbody>
</table>

Class 3 \((C3)\) \(k_{31} k_{33} e_{31} e_{33}\)

<table>
<thead>
<tr>
<th>Material</th>
<th>(k_{31})</th>
<th>(k_{33})</th>
<th>(e_{31})</th>
<th>(e_{33})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Pb}_5\text{Ge}<em>3\text{O}</em>{11})</td>
<td>0.08</td>
<td>0.13</td>
<td>0.61</td>
<td>0.77</td>
</tr>
</tbody>
</table>

Class 4bar3m \(k_{14} d_{14} e_{14}\)

<table>
<thead>
<tr>
<th>Material</th>
<th>(k_{14})</th>
<th>(d_{14})</th>
<th>(e_{14})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{AlSb})</td>
<td>0.10</td>
<td>1.6</td>
<td>0.07</td>
</tr>
<tr>
<td>(\text{CdTe})</td>
<td>0.03</td>
<td>1.7</td>
<td>0.04</td>
</tr>
<tr>
<td>(\text{GaAs})</td>
<td>0.09</td>
<td>2.6</td>
<td>0.16</td>
</tr>
<tr>
<td>(\text{Tl}_3\text{TaS}_4)</td>
<td>0.55</td>
<td>58</td>
<td>0.32</td>
</tr>
<tr>
<td>(\text{ZnS})</td>
<td>0.09</td>
<td>3.2</td>
<td>0.15</td>
</tr>
<tr>
<td>(\text{ZnSe})</td>
<td>0.03</td>
<td>1.1</td>
<td>0.05</td>
</tr>
<tr>
<td>(\text{ZnTe})</td>
<td>0.02</td>
<td>0.9</td>
<td>0.03</td>
</tr>
</tbody>
</table>

where’s the \(d_{ij}\) values?
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 $d_{ij}$

$$e_{i\alpha} = \frac{\partial P_i'}{\partial \eta_\alpha}$$

$$d_{i\alpha} = S_{\alpha\beta} e_{i\beta}$$
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 $d_{ij}$

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

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