Discovery and Design of Multifunctional Materials: Integration of Database Mining and First-Principles Calculations

Dr. Joseph W. Bennett

Dept. of Physics and Astronomy, Rutgers, The State University of New Jersey
bennett@physics.rutgers.edu
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.
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
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

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 Canonical Family

Moving Beyond the Perovskites

The $\textit{ABC}$ Half-Heuslers

Casting a Wider Net

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 coordinate)
O octahedron are corner-sharing
The Perovskites: A Canonical Family

ABO$_3$ solid oxide perovskites:

A at corners (12-fold coordinate)
B inside of O octahedron (6 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

**ABO₃** solid oxide *perovskites*:

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

**O octahedron are corner-sharing**

**Flexible structure** with choice of A and B sites combinations almost unlimited

- PbTiO₃, BaZrO₃, LiNbO₃

**Solid solutions** as well

- **AA’BB’O₃**
- Pb(Zr,Ti)O₃

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

- SONAR
- ultrasound positioning
- sensors and actuators
BiFeO$_3$: A Multifunctional Perovskite

Cubic perovskite oxides are space group 221, $\textit{Pm3barm}$ symmetry.

Then, distortions lower the symmetry.

Bi in BiFeO$_3$ distort along (111) as O$_6$ tilt to generate $R_3c$ symmetry, another space polar group.

Wang et al., Science 2003, 1719
BiFeO₃: A Multifunctional Perovskite

Cubic perovskite oxides are space group 221, \textit{Pm3barm} symmetry.

Then, \textit{distortions lower the symmetry}.

Bi in BiFeO₃ distort \textit{along (111) as O₆ tilt} to generate \textit{R₃c} symmetry, another space \textit{polar} group.

These polar distortions lead to an electromechanical response, and the polarization is reversible!

Wang \textit{et al.}, Science 2003, 1719
BiFeO₃: A Multifunctional Perovskite

Cubic perovskite oxides are space group 221, $Pm3barm$ symmetry.

Then, distortions lower the symmetry.

Bi in BiFeO₃ distort along (111) as O₆ tilt to generate $R_3c$ symmetry, another space polar group.

AND...Fe³⁺ is magnetic
This means that we can couple polarization and magnetization in one material!

Wang et al., Science 2003, 1719
BiFeO$_3$: A Multifunctional Perovskite

Cubic perovskite oxides are space group 221, $Pm3barm$ symmetry.

Then, distortions lower the symmetry.

Bi in BiFeO$_3$ distort along (111) as O$_6$ tilt to generate $R_3c$ symmetry, another space polar group.

AND...Fe$^{3+}$ is magnetic
This means that 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?

*Bennewitz et al.,* JACS 2008, 17409
Band Gaps of Solid Solutions of BaTiO$_3$

(Survey of expt. literature and DFT)

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!**

*Bennett et al., Phys. Rev. B., 2009, 235115*
High-Throughput Search For New Perovskites

So far, we’ve only discussed studying a few materials at one time... but what about many at once?
High-Throughput Search For 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.

Hautier et al., Chem. Mater. 3762 (2010)
Jain et al., Comp. Mat. Sci. 2295 (2011)
High-Throughput Search For 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*

The $ABC$ Half-Heuslers

Casting a Wider Net

Concluding Thoughts
What About These “New” Materials?

Previous efforts are all based on perovskites, mostly oxides...
Incremental modifications to existing, well-studied systems
What About These “New” Materials?

Previous efforts are all based on perovskites, mostly oxides...
Incremental modifications to existing, well-studied systems

What about other systems? Main group elements, magnetic sites...

How to find them?

Design principles...structural criterion for functionality?

Are there any promising underdeveloped families?
What About These “New” Materials?

Previous efforts are all based on perovskites, mostly oxides... Incremental modifications to existing, well-studied systems

What about other systems? Main group elements, magnetic sites...

How to find them?

Design principles...structural criterion for functionality?

Are there any promising underdeveloped families?

Can we find many at once (perform high-throughput searches)?

Where do we go to find structures of known compounds?
Inorganic Crystal Structural Database

Database of completely identified inorganic structures. 142,000 peer-reviewed entries, dating back to 1913. 7,000 added annually, in conjunction with NIST databases

http://www.fiz-karlsruhe.de/icsd.html
Inorganic Crystal Structural Database

Database of completely identified inorganic structures.
142,000 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
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**
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**
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)

Bennett and Rabe: http://arxiv.org/abs/1201.2743
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: http://arxiv.org/abs/1201.2743
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)

This is 3/4 of the polar entries.
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%
Strategies

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

Why? More attention to these systems could lead to:
improved sample quality, complete characterization, and identification of new representatives with enhanced properties.

Integration of first-principles methods and crystallographic database searches for new ferroelectrics: Strategies and explorations
by J. W. Bennett and K. M. Rabe: JSSC, in press

http://dx.doi.org/10.1016/j.jssc.2012.05.013
Outline

The $ABO_3$ Perovskites

Moving Beyond the Perovskites

The $ABC$ Half-Heuslers
A New Class of Piezoelectrics

Casting a Wider Net

Concluding Thoughts
Target For Our High-Throughput Study

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!

topological insulators, thermoelectrics, spintronics...

Can we make them ferroelectric?
Target For Our High-Throughput Study

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!

topological insulators, thermoelectrics, spintronics...

Unfortunately, it’s really difficult.

Large strain produces a weak polarization (not switchable).
Target For Our High-Throughput Study

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!

topological insulators, thermoelectrics, spintronics...

*\( F4bar3m \) space group means piezoelectricity!*

But no mention of this in the literature!

How many \( ABC \) are known? *Go to the ICSD!*
Searching the ICSD for $ABC$

$F_{4}\bar{3}m$ (#216), cubic nonpolar: 269 total (260 LiAlSi)
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
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, *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 more? We can create 900 combinations, most of which are as yet to be synthesized...
High-Throughput Study Using 900 Combinations

How do we get 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
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
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

YAlO₃

3.80

LaSrAlO₄

NdGaO₃

LaAlO₃

3.90

LaSrGaO₄

NdGaO₃

NdScO₃

3.95

LSAT

TbScO₃

SrTiO₃

4.00

DyScO₃

GdScO₃

EuScO₃

4.10

PrScO₃

KTaO₃

SmScO₃

4.20

BaTiO₃

PMN-PT

4.30

BiScO₃

(Ba,Sr)TiO₃

Pb(Zr,Ti)O₃

(Ba,K)BiO₃

Substrate lattice (Å)
Why Is This Important?

$E_{\text{gap}}$ (eV)

$a_0$ (Å)
Why Is This Important?

The range of the perovskites!
In Addition....

We have piezoelectricity that can potentially be coupled to:

- Metal-insulator transitions (Resistive switching, spintronics?)
  - Topological Insulators
    - Thermoelectrics
    - Photovoltaics
    - Buffer layers
  - Insulators (high-K dielectrics)
  - $E_{\text{gap}}$

- 0-0.2 eV
- 0.2-1.2 eV
- 1.2-1.8 eV
- 2.0-3.0 eV
- 3.0-4.0 eV

All this from one family!
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 Ten Half-Heuslers

<table>
<thead>
<tr>
<th></th>
<th>$a_{\text{calc}}$ (Ang.)</th>
<th>$E_{\text{gap}}$ (eV)</th>
<th>$d_{14}$ (pC/N)</th>
<th>$k_{14}$</th>
<th>$\varepsilon_{\text{inf.}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrAlGa</td>
<td>6.87</td>
<td>0.13</td>
<td>742.22</td>
<td>0.81</td>
<td>47.7</td>
</tr>
<tr>
<td>CaAgSb</td>
<td>6.93</td>
<td>0.63</td>
<td>467.50</td>
<td>0.89</td>
<td>13.3</td>
</tr>
<tr>
<td>NaZnP</td>
<td>6.07</td>
<td>0.37</td>
<td>384.31</td>
<td>0.94</td>
<td>12.0</td>
</tr>
<tr>
<td>NaBGe</td>
<td>5.56</td>
<td>0.43</td>
<td>342.86</td>
<td>0.81</td>
<td>17.6</td>
</tr>
<tr>
<td>MgSrSi</td>
<td>7.09</td>
<td>0.87</td>
<td>266.67</td>
<td>0.83</td>
<td>15.5</td>
</tr>
<tr>
<td>MgSrGe</td>
<td>7.11</td>
<td>0.36</td>
<td>224.72</td>
<td>0.79</td>
<td>17.1</td>
</tr>
<tr>
<td>CuYC</td>
<td>5.92</td>
<td>0.11</td>
<td>245.84</td>
<td>0.90</td>
<td>15.0</td>
</tr>
<tr>
<td>NaMgN</td>
<td>5.46</td>
<td>0.72</td>
<td>180.93</td>
<td>0.92</td>
<td>6.3</td>
</tr>
<tr>
<td>LiCaP</td>
<td>6.63</td>
<td>1.73</td>
<td>124.16</td>
<td>0.81</td>
<td>6.2</td>
</tr>
<tr>
<td>BeScB</td>
<td>5.39</td>
<td>0.33</td>
<td>122.31</td>
<td>0.73</td>
<td>9.3</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 $d_{14}=58$ pC/N)
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.**
### Ten Best Half-Heuslers

<table>
<thead>
<tr>
<th>Ten Best</th>
<th>$a_{\text{calc}}$</th>
<th>$E_{\text{gap}}$</th>
<th>$d_{14}$</th>
<th>$k_{14}$</th>
<th>$\varepsilon_{\text{inf.}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaBGe</td>
<td>5.56</td>
<td>0.43</td>
<td>342.86</td>
<td>0.81</td>
<td>17.6</td>
</tr>
<tr>
<td>MgSrSi</td>
<td>7.09</td>
<td>0.87</td>
<td>266.67</td>
<td>0.83</td>
<td>15.5</td>
</tr>
<tr>
<td>LiCaP</td>
<td>6.63</td>
<td>1.73</td>
<td>124.16</td>
<td>0.81</td>
<td>6.2</td>
</tr>
<tr>
<td>LiCuS</td>
<td>5.47</td>
<td>0.84</td>
<td>97.77</td>
<td>0.63</td>
<td>7.9</td>
</tr>
<tr>
<td>LiNaS</td>
<td>6.18</td>
<td>2.90</td>
<td>96.22</td>
<td>0.84</td>
<td>3.6</td>
</tr>
<tr>
<td>LiNaSe</td>
<td>6.43</td>
<td>2.42</td>
<td>72.60</td>
<td>0.76</td>
<td>4.1</td>
</tr>
<tr>
<td>NaBaP</td>
<td>7.46</td>
<td>0.63</td>
<td>68.16</td>
<td>0.53</td>
<td>6.9</td>
</tr>
<tr>
<td>NaBaSb</td>
<td>7.97</td>
<td>0.83</td>
<td>55.19</td>
<td>0.44</td>
<td>7.7</td>
</tr>
<tr>
<td>LiYC</td>
<td>5.83</td>
<td>0.72</td>
<td>54.15</td>
<td>0.59</td>
<td>11.3</td>
</tr>
<tr>
<td>AgYSi</td>
<td>6.55</td>
<td>0.56</td>
<td>44.09</td>
<td>0.41</td>
<td>15.9</td>
</tr>
</tbody>
</table>

Only 3 of our top ten made the list!

**Half-Heusler semiconductors as piezoelectrics:**
A. Roy, J. W. Bennett, K. M. Rabe and D. Vanderbilt
arXiv.org/abs/1107.5078
Outline

The $ABO_3$ Perovskites

Moving Beyond the Perovskites

The $ABC$ Half-Heuslers

Casting a Wider Net
A New class of ferroelectrics

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)
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\(_2\)P)
\[P6barm2\] (#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

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
3) re-forming $sp^3$ bonds

This is more than 0.6 eV by DFT!

Our DFT results
$a=3.19$ Ang. (3.21 Ang.)
$c=5.15$ Ang. (5.25 Ang.)
$u=0.379$ (0.375)
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 $P6_3mmc$ phase...

There’s at least 6 combinations reported in both space groups.
A Polar Distortion!

LiGaGe, or “stuffed wurtzite” is the polar $P6_3mc$ phase. ZrBeSi in the layered non-polar $P6_3mmc$ 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 of compounds. 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</td>
<td>0.80</td>
</tr>
<tr>
<td>CuScSn</td>
<td>4.351</td>
<td>6.795</td>
<td>0.330</td>
<td>0.729</td>
<td>0</td>
<td>0.45</td>
</tr>
<tr>
<td>CuYSn</td>
<td>4.475</td>
<td>7.148</td>
<td>0.320</td>
<td>0.728</td>
<td>0</td>
<td>0.32</td>
</tr>
<tr>
<td>CuYPb</td>
<td>4.512</td>
<td>7.191</td>
<td>0.321</td>
<td>0.729</td>
<td>0</td>
<td>0.34</td>
</tr>
<tr>
<td>AgYSn</td>
<td>4.634</td>
<td>7.240</td>
<td>0.314</td>
<td>0.702</td>
<td>0</td>
<td>0.39</td>
</tr>
<tr>
<td>AuScGe</td>
<td>4.263</td>
<td>6.679</td>
<td>0.196</td>
<td>0.793</td>
<td>0</td>
<td>0.61</td>
</tr>
<tr>
<td>AuScSn</td>
<td>4.507</td>
<td>7.066</td>
<td>0.348</td>
<td>0.730</td>
<td>0</td>
<td>0.75</td>
</tr>
<tr>
<td>AuYSi</td>
<td>4.247</td>
<td>7.358</td>
<td>0.228</td>
<td>0.780</td>
<td>0</td>
<td>0.05</td>
</tr>
<tr>
<td>AuYSiGe</td>
<td>4.364</td>
<td>7.084</td>
<td>0.219</td>
<td>0.789</td>
<td>0</td>
<td>0.26</td>
</tr>
<tr>
<td>AuYSn</td>
<td>4.614</td>
<td>7.293</td>
<td>0.173</td>
<td>0.774</td>
<td>0</td>
<td>0.70</td>
</tr>
<tr>
<td>LiBeSb</td>
<td>4.091</td>
<td>6.636</td>
<td>0.350</td>
<td>0.733</td>
<td>1.45</td>
<td>0.79</td>
</tr>
<tr>
<td>LiZnSb</td>
<td>4.327</td>
<td>7.024</td>
<td>0.290</td>
<td>0.668</td>
<td>0.99</td>
<td>0.93</td>
</tr>
<tr>
<td>CaAgBi</td>
<td>4.730</td>
<td>7.564</td>
<td>0.318</td>
<td>0.715</td>
<td>0</td>
<td>0.36</td>
</tr>
<tr>
<td>CaZnSn</td>
<td>4.595</td>
<td>7.331</td>
<td>0.218</td>
<td>0.813</td>
<td>0</td>
<td>0.32</td>
</tr>
<tr>
<td>CaHgSn</td>
<td>4.754</td>
<td>7.547</td>
<td>0.289</td>
<td>0.686</td>
<td>0</td>
<td>0.53</td>
</tr>
<tr>
<td>SrHgSn</td>
<td>4.878</td>
<td>7.801</td>
<td>0.305</td>
<td>0.712</td>
<td>0</td>
<td>0.36</td>
</tr>
<tr>
<td>SrHgPb</td>
<td>4.894</td>
<td>8.054</td>
<td>0.311</td>
<td>0.719</td>
<td>0</td>
<td>0.19</td>
</tr>
</tbody>
</table>

We have 17 combinations with reliable structural data.
### 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>(4.175)</td>
<td>6.713</td>
<td>6.783</td>
<td>0.314 (0.312)</td>
<td>0.698 (0.700)</td>
</tr>
<tr>
<td>CuScSn</td>
<td>4.351</td>
<td>(4.388)</td>
<td>6.795</td>
<td>6.830</td>
<td>0.330 (0.326)</td>
<td>0.729 (0.229)</td>
</tr>
<tr>
<td>CuYSn</td>
<td>4.475</td>
<td>(4.543)</td>
<td>7.148</td>
<td>7.274</td>
<td>0.320 (0.316)</td>
<td>0.728 (0.733)</td>
</tr>
<tr>
<td>CuYPb</td>
<td>4.512</td>
<td>(4.559)</td>
<td>7.191</td>
<td>7.334</td>
<td>0.321 (0.323)</td>
<td>0.729 (0.729)</td>
</tr>
<tr>
<td>AgYSn</td>
<td>4.634</td>
<td>(4.683)</td>
<td>7.240</td>
<td>7.372</td>
<td>0.314 (0.308)</td>
<td>0.702 (0.719)</td>
</tr>
<tr>
<td>AuScGe</td>
<td>4.263</td>
<td>(4.308)</td>
<td>6.679</td>
<td>6.846</td>
<td>0.196 (0.200)</td>
<td>0.793 (0.798)</td>
</tr>
<tr>
<td>AuScSn</td>
<td>4.507</td>
<td>(4.593)</td>
<td>7.066</td>
<td>7.202</td>
<td>0.348 (0.340)</td>
<td>0.730 (0.731)</td>
</tr>
<tr>
<td>AuYSi</td>
<td>4.247</td>
<td>(4.288)</td>
<td>7.358</td>
<td>7.546</td>
<td>0.228 (0.234)</td>
<td>0.780 (0.775)</td>
</tr>
<tr>
<td>AuYSb</td>
<td>4.140</td>
<td>(4.410)</td>
<td>7.084</td>
<td>7.309</td>
<td>0.219 (0.216)</td>
<td>0.789 (0.791)</td>
</tr>
<tr>
<td>AuYSn</td>
<td>4.614</td>
<td>(4.636)</td>
<td>7.293</td>
<td>7.373</td>
<td>0.173 (0.194)</td>
<td>0.774 (0.821)</td>
</tr>
<tr>
<td>LiBeSb</td>
<td>4.091</td>
<td>(4.152)</td>
<td>6.636</td>
<td>6.738</td>
<td>0.350 (0.341)</td>
<td>0.733 (0.732)</td>
</tr>
<tr>
<td>LiZnSb</td>
<td>4.327</td>
<td>(4.431)</td>
<td>7.024</td>
<td>7.157</td>
<td>0.290 (0.304)</td>
<td>0.668 (0.689)</td>
</tr>
<tr>
<td>CaAgBi</td>
<td>4.730</td>
<td>(4.811)</td>
<td>7.564</td>
<td>7.827</td>
<td>0.318 (0.312)</td>
<td>0.715 (0.721)</td>
</tr>
<tr>
<td>CaZnSn</td>
<td>4.595</td>
<td>(4.655)</td>
<td>7.331</td>
<td>7.628</td>
<td>0.218 (0.220)</td>
<td>0.813 (0.805)</td>
</tr>
<tr>
<td>CaHgSn</td>
<td>4.754</td>
<td>(4.800)</td>
<td>7.547</td>
<td>7.760</td>
<td>0.289 (0.310)</td>
<td>0.686 (0.720)</td>
</tr>
<tr>
<td>SrHgSn</td>
<td>4.878</td>
<td>(4.893)</td>
<td>7.801</td>
<td>8.217</td>
<td>0.305 (0.300)</td>
<td>0.712 (0.720)</td>
</tr>
<tr>
<td>SrHgPb</td>
<td>4.894</td>
<td>(4.995)</td>
<td>8.054</td>
<td>8.172</td>
<td>0.311 (0.300)</td>
<td>0.719 (0.720)</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.
A New Class of Ferroelectrics Based on Wurtzite!

Difference in energy between paraelectric and ferroelectric structures for all 17 polar combinations. Of these, 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 **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!
New Platforms for Functionality

These new $ABC$ materials have additional 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.

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? (phase-change materials, carrier physics, etc.)

Some of the $ABC$ tetragonal variants are 1-1-1 superconductors. (Josephson physics? metal-insulator transitions? optics?)
More Importantly...

I believe that we have found the "new perovskite oxides".
More Importantly...

I believe that we have found the “new perovskite oxides”.

But it was not easy.

It took us at least two years to efficiently combine database searching and first-principles methods.

So, before you attempt this, you should know a few of the challenges that we have faced.
Outline

The $\text{ABO}_3$ Perovskites

Moving Beyond the Perovskites

The $\text{ABC}$ Half-Heuslers

Casting a Wider Net

Concluding Thoughts

*So, you want to try this yourself*
With Regards to the Calculations

High throughput studies:
Pseudopotential testing is a must!
Do they match all electron (AE) calculations?
Set up a few test calculations before your high-throughput study!
PSP Test of Known $ABC$ Lattice Constants

% Error (PSP-AE)

TM PSP set
HGH PSP set

38 Known Half-Heuslers

38 Known Half-Heuslers
PSP Test of Known $ABC$ Lattice Constants

BR is the Bennett-Rappe library of LDA potentials

38 Known Half-Heuslers
What About the Hypothetical ABC?

% Error (PSP-AE)

40 Unknown Half-Heuslers

-6 -4 -2 0 2 4 6 8

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

![Graph showing % Error (PSP-AE) for 40 Unknown Half-Heuslers with TM PSP set and HGH PSP set compared to Bennett-Rappe (BR set).]
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, \( E_{\text{cut}} \), etc.

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

Some Calculations Simply Fail:
This is most times a hardware issue, sometimes software (dilatmx)
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!
Tetragonal Sr(Sb$_{1/2}$Mn$_{1/2}$)O$_3$ example: see our JSSC paper
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: see our JSSC paper
Polar chemical elements: see our JSSC paper

Some entries are simply missing information:
Missing 1 of 3 elements: where’s the C in ABC?
What We’re Working on Now

1) Other ways to stuff wurtzite:
   Two additional structure types: KSnAs and La$_2$O$_3$

2) Efficient solar harvesting chalcogenides:
   Elements common to Cu(In,Ga)Se$_2$ in overlooked polar groups

3) The inverse perovskite:
   Can we stabilize a “polar” $BXA_3$ with common $ABX_3$ elements?

4) $ABC$ compounds with more than one reported space group:
   New insights into first order phase transitions?

5) Search for Dirac semimetals (with Young, Rappe, Kane)
   Can we find examples of already synthesized compounds?
Acknowledgements

At Rutgers University:
Dr. Anindya Roy (currently at UCSB)
Qibin Zhou, Dr. Kevin Garrity
Dr. Don Hamann
Prof. David Vanderbilt
Prof. Karin Rabe

At Univ. Penn.:
Prof. Sara E. Mason (UI)
Dr. Valentino Cooper (ORNL)
Dr. Eric J. Walter (William and Mary)
Dr. Ilya Grinberg, Prof. Peter Davies
Prof. Andrew M. Rappe

Funding: DoD, HPCMP, DOE, ONR

At Cambridge:
Prof. Jim Scott

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
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.