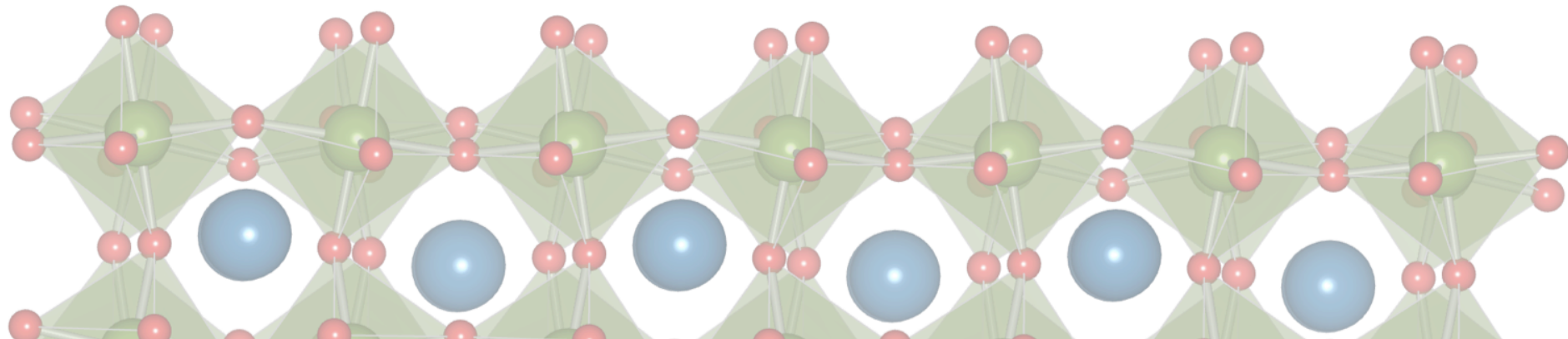# Exploring the Structures and Properties of Complex Oxides:
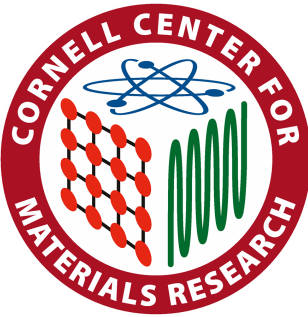# New Ideas and Insights from Theory and Simulation

Nicole A. Benedek

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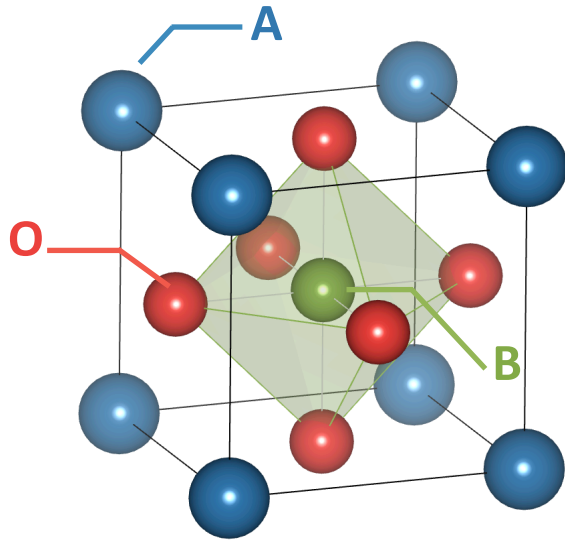
Collaborators (and $$)

Craig Fennie (Cornell)

DOE-BES-SISGR

Office of the Dean

Enormous diversity of properties in complex oxides, particularly in the ABO₃ perovskite family

A

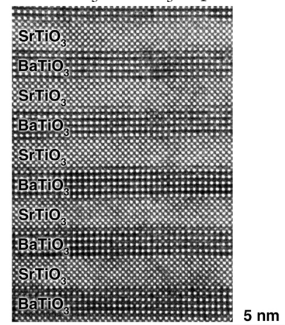**O**

B

Same basic structure, many physical properties:
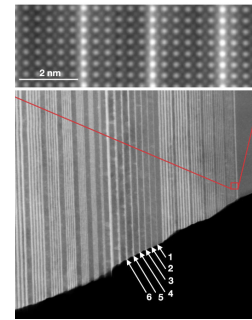
Dielectric	$CaTiO_3$, $SrTiO_3$
Ferroelectric	$BaTiO_3$, $PbTiO_3$
Magnetoelectric	$TbMnO_3$, $BiFeO_3$
Antiferroelectric	$PbZrO_3$
Antiferromagnetic	$LaMnO_3$
Ferromagnetic	$SrRuO_3$
Superconducting	doped $SrTiO_3$
Semiconducting	doped $SrTiO_3$

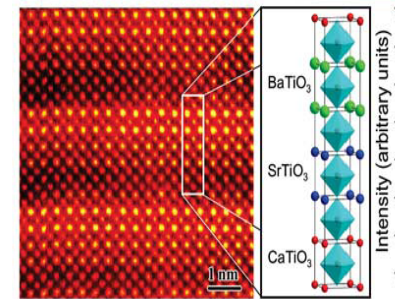**Advances in synthesis and characterization mean properties can be tailored at the nanoscale:**

• Now possible to grow oxide thin films with atomic-level precision

• Properties can be customized, new functionalities can be created

• Can grow thin-film interfaces that cannot be made by other methods

$(BaTiO_3)_6(SrTiO_3)_5$

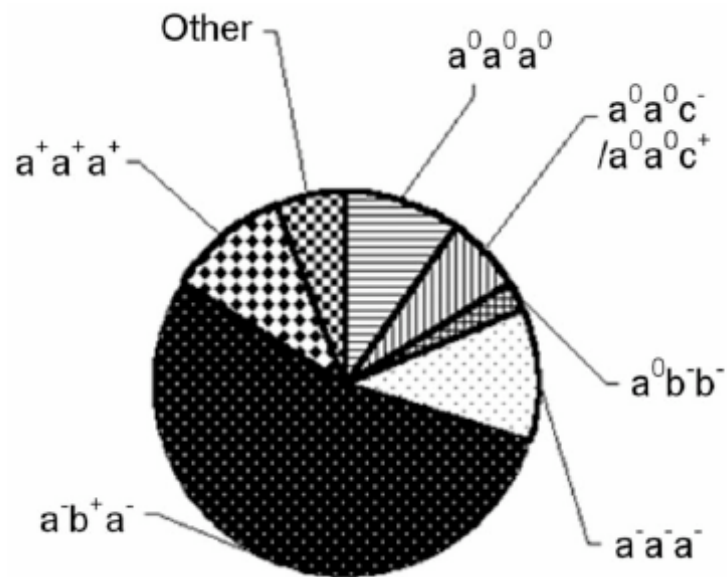Haeni, Schlom, Tian, & Pan
J. Mat. Res (2001)

$(LaTiO_3)_1(SrTiO_3)_n$

Ohtomo, Muller, Grazul, & Hwang
Nature (2002)

$(BaTiO_3)_n(SrTiO_3)_m(CaTiO_3)_k$

Lee, ORNL

Most perovskites do not have the cubic structure in their ground state

Figure 1
Distribution of tilt systems among known perovskites with a single octahedral cation.
Lufaso and Woodward Acta Cryst. **B57** 725 (2001)

- Majority of perovskites undergo octahedral rotation distortions

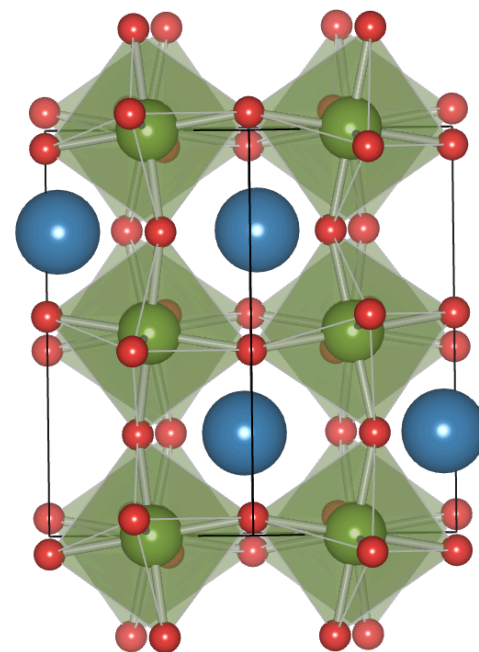- There are 23 different 'rotation patterns', leading to 15 unique space groups

Rotation patterns can be conveniently described using Glazer notation:

$$a^\# b^\# c^\#$$

Letters specify rotations about each cubic axis

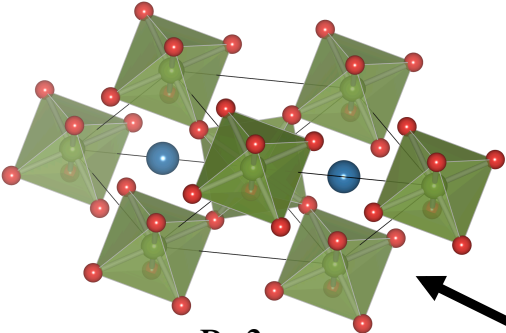Superscripts specify whether adjacent octahedra rotate in-phase (+) or out-of-phase (-)

Pnma

Most perovskites undergo some form of structural distortion

**Octahedral rotations
(not polar/ferroelectric)**
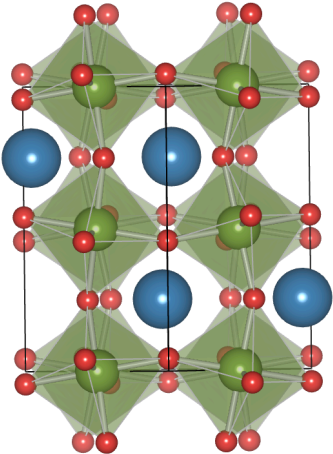
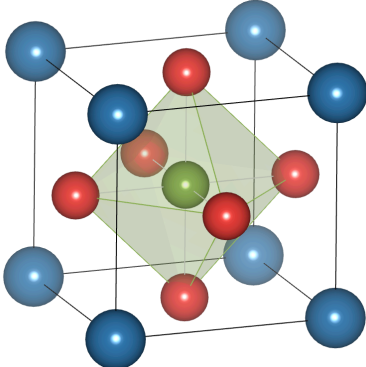$$t = \frac{R_{A-O}}{\sqrt{2}(R_{B-O})}$$

It is assumed that octahedral rotations and ferroelectricity compete with and suppress each other

R-3c

A-site underbonded

$$t < 1$$

$$t = 1$$
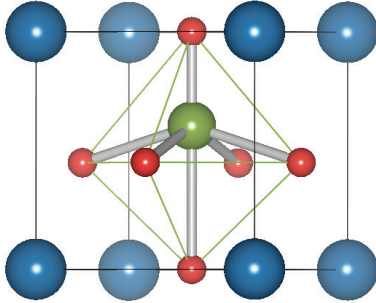
B-site underbonded

$$t > 1$$

Pnma

Polar/ferroelectric

How can we take advantage of structural distortions to create new functional materials?

We have known for some time that octahedral rotations can have a significant effect on material properties

• Changing octahedral rotation angle causes five orders of magnitude change in resistivity in doped $CaMnO_3$
Polli, et al. Nature Mat. **6** 643 (2007)

• Magnetic properties of ruthenates and rare earth manganites can be tuned by changing octahedral rotation angle
Jin, Zhou, Goodenough, et al. PNAS **105** 7115 (2008)

Woodward, et al. Chem. Mater. **10** 3652 (1998) Kimura, et al. PRB **68** 060403(R) (2003)

Rotations alone cannot break all inversion symmetries in ABO_3 perovskites and rotations tend to suppress ferroelectricity

How can we manipulate these properties in a practical way?

$CaTiO_3$ and $CaMnO_3$ Ruddlesden-Popper phases as candidate multiferroics

n=2 $Ca_3Ti_2O_7$ and $Ca_3Mn_2O_7$ properties

- Crystallize in a polar space group, $A2_1am$

Guiblin et al, Acta Cryst. **C58**, i3, 2002
Elcombe et al, Acta Cryst **B47**, 305, 1991.

- $Ca_3Mn_2O_7$ is a (weak) ferromagnet

Guiblin et al, Acta Cryst. **C58**, i3, 2002

- Octahedral rotations induce ferroelectricity AND ferromagnetism (spin canted antiferromagnet)

- Both materials occur naturally in **BULK**

- Theory predicts that magnetization is electric field controllable

Ca
Ti/Mn
O

Perovskite blocks

CaO rocksalt layers

It is assumed that octahedral rotations and ferroelectricity suppress each other in ABO_3 perovskites…

Is this really true??

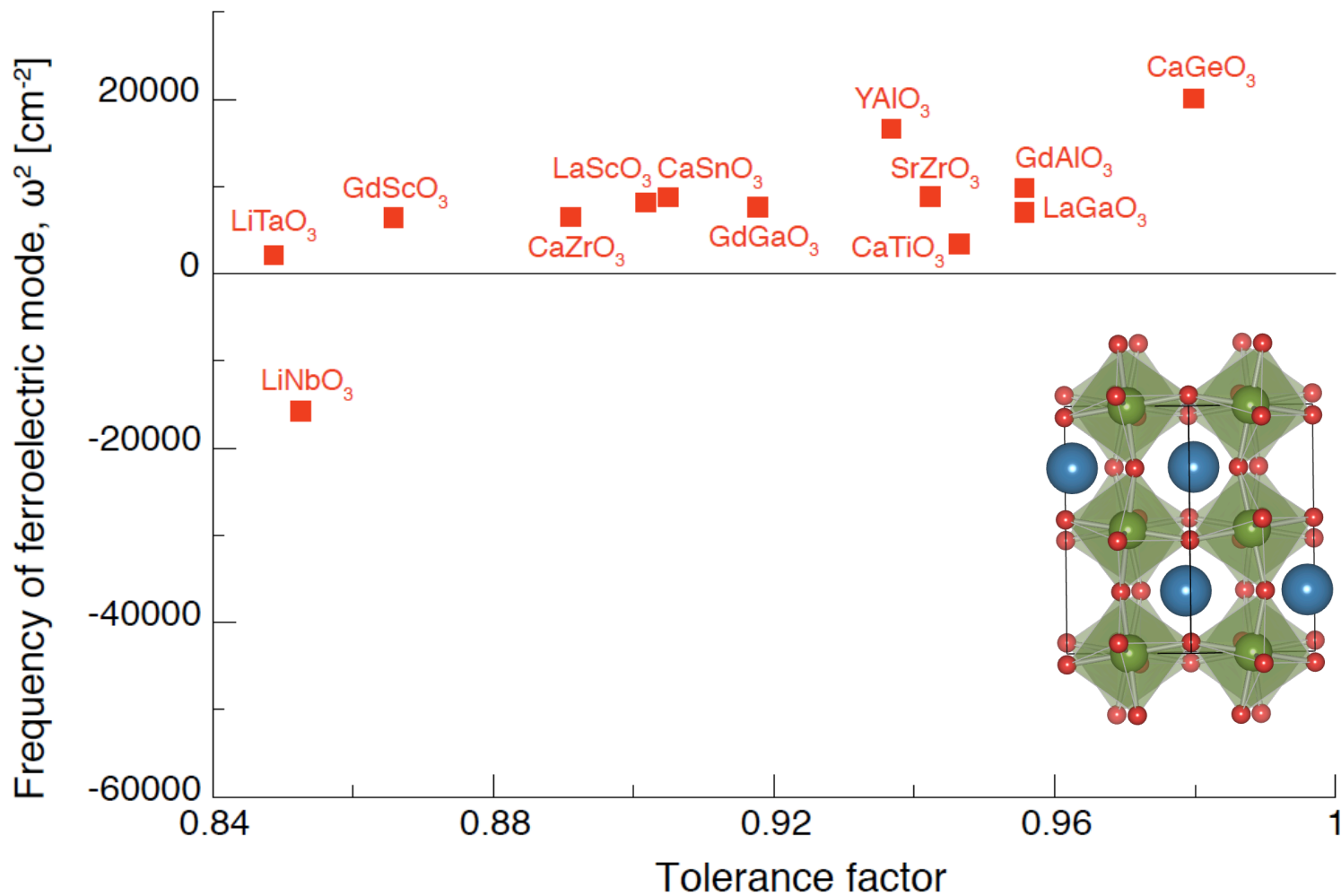# The structures of Pnma perovskites can be decomposed into contributions from five different modes

$Pnma$

R_4^+

M_3^+

X_5^+

- Two rotation modes makes largest contribution

- Of the modes that aren't rotations, anti-polar (X5+) A-site mode makes largest contribution

This plot shows the cumulative effect of all five modes on the FE mode frequency

What if we consider each mode individually?

Rotations alone do not suppress ferroelectricity in Pnma as tolerance factor decreases

Rotations alone do not suppress ferroelectricity in Pnma as tolerance factor decreases

Figure axes: Frequency of ferroelectric mode, ω^2 [cm^{-2}] vs Tolerance factor

Legend:
- ● Pm-3m
- ◆ Pnma, no A-site (Pm-3m volume)

Data point labels: GdAlO$_3$, LaGaO$_3$, YAlO$_3$, SrZrO$_3$, GdGaO$_3$, CaSnO$_3$, CaTiO$_3$, LaScO$_3$, CaZrO$_3$, GdScO$_3$

Rotations alone do not suppress ferroelectricity in Pnma as tolerance factor decreases

Plot of frequency of ferroelectric mode, ω^2 [cm^{-2}], versus tolerance factor. Data points labeled: GdAlO$_3$, LaGaO$_3$, YAlO$_3$, SrZrO$_3$, GdGaO$_3$, CaSnO$_3$, LaScO$_3$, CaTiO$_3$, CaZrO$_3$, GdScO$_3$.

Legend:
- ● Pm-3m
- ◆ Pnma, no A-site (Pm-3m volume)
- ■ Pnma, fully relaxed

Free energy expansion about cubic phase as a function of ferroelectric mode and rotation mode

$$\mathcal{F} = \alpha_{02} Q_{FE}^2 + \alpha_{20} Q_R^2 + \beta_{02} Q_{FE}^4 + \beta_{20} Q_R^4 + \beta_{22} Q_{FE}^2 Q_R^2$$

$$\omega_{FE}^2 \sim \alpha_{02} + \beta_{22} R^2$$

For materials with larger tolerance factors:
Ferroelectric energy scale, $\omega^2{}_{\mathrm{FE}}$, is much less negative than the positive contribution coming from rotations, $\beta_{22} R^2$, so the two distortions don't really compete

For materials with smaller tolerance factors:
As the tolerance factor decreases, α_{02} becomes increasingly negative and wins competition with rotations. However, A-site displacements, coupled to rotations, ultimately suppress ferroelectricity.

FE distortion can optimize A-site coordination environment in Pm-3m

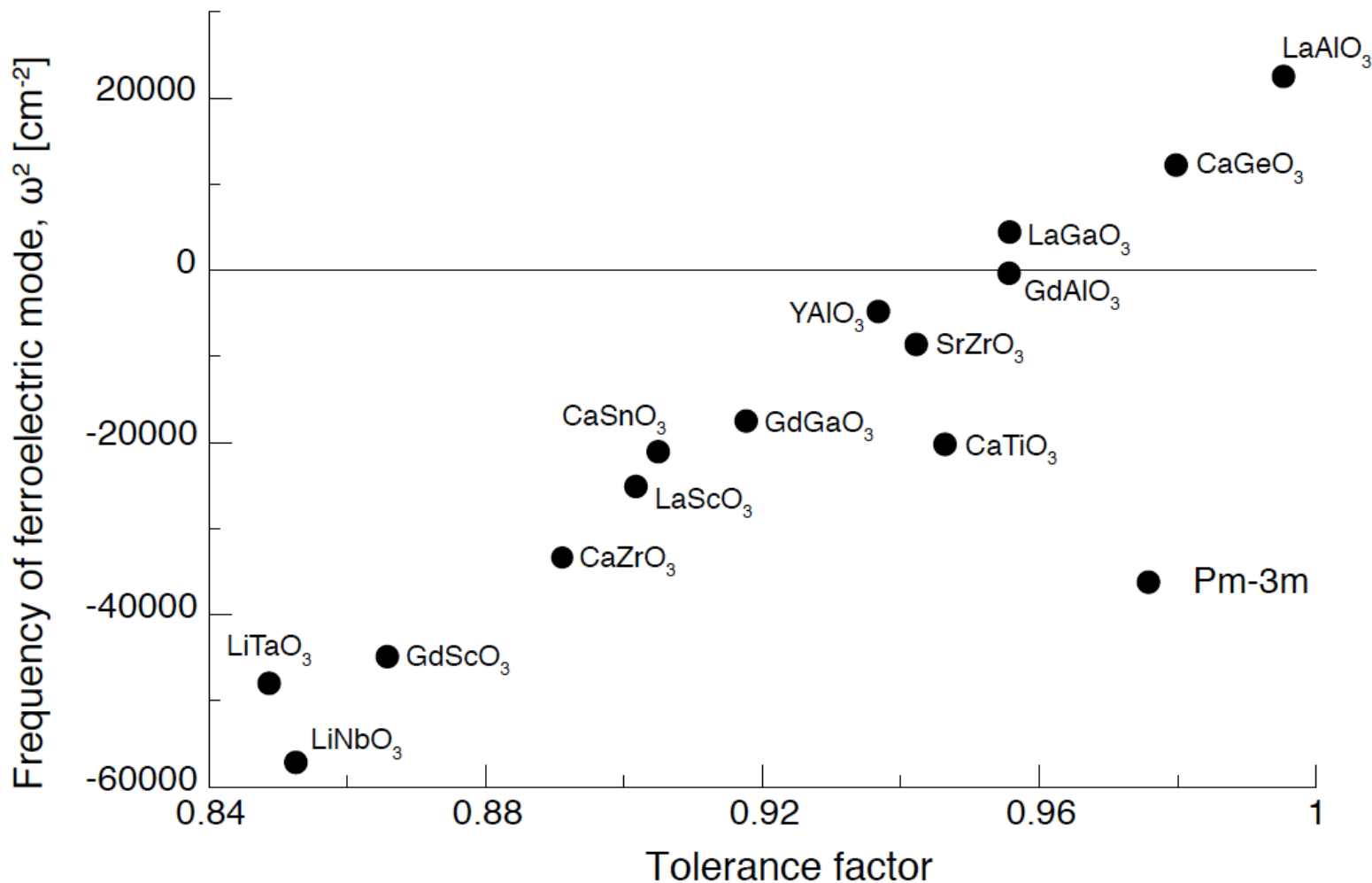- Main contribution to FE mode comes from the A-site for materials with Pnma ground states

Do rotations suppress ferroelectricity?
It depends: for larger tolerance factor materials, rotations alone are enough to suppress ferroelectricity. For smaller tolerance factor materials, A-site displacements are needed to completely suppress ferroelectricity.

Why are there so few perovskite ferroelectrics?
Because most perovskites adopt the Pnma structure, in which either rotations alone, or rotations plus A-site displacements suppress ferroelectricity.

In the absence of A-site displacements, most Pnma perovskites would be R3c

Negative numbers: *Pnma* more stable

Positive numbers: *R3c* more stable

Material	$Pnma$, fully relaxed
$YAlO_3$	-0.13
$GdAlO_3$	-0.08
$LaGaO_3$	-0.02
$GdScO_3$	-0.11
$CaZrO_3$	0.04
$CaSnO_3$	-0.07
$LaScO_3$	-0.11
$GdGaO_3$	-0.22
$SrZrO_3$	-0.19
$CaTiO_3$	-0.03

In the absence of A-site displacements, most Pnma perovskites would be R3c

Pnma, fully relaxed

R3c	Pnma	R-3c

$t \sim 0.8$ $t \sim 1$

Pnma, with $Q(X_5^+) = 0$

R3c		R-3c

$t \sim 0.8$ *Pnma* $t \sim 1$

How can we exploit these findings to create new functional materials?
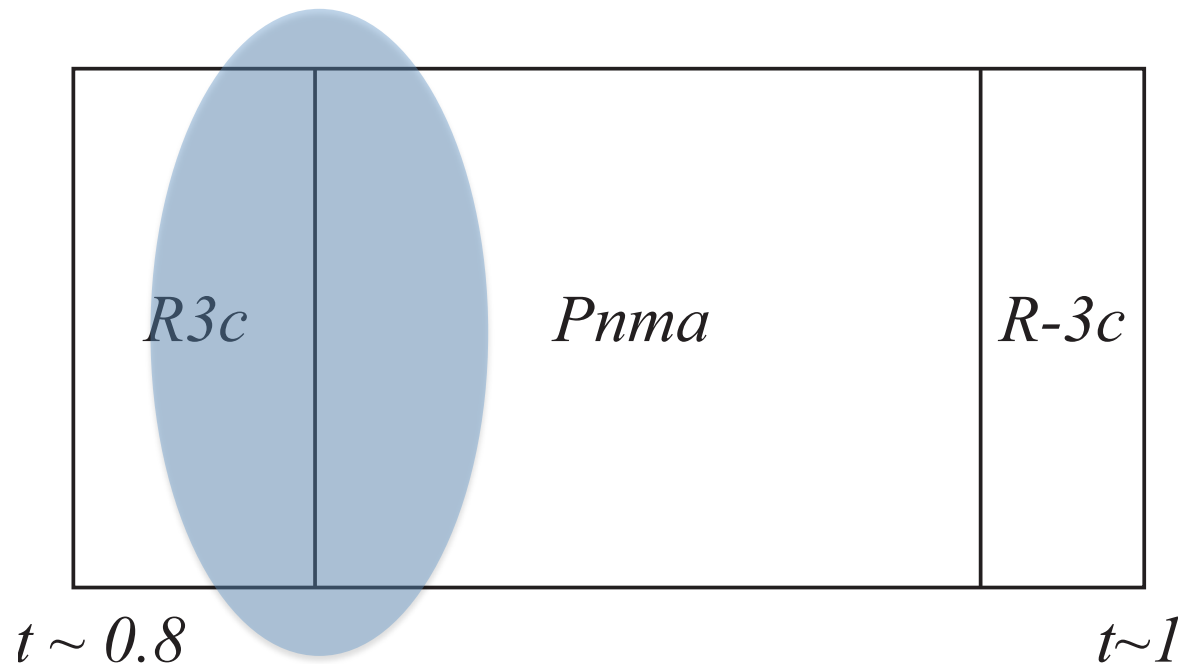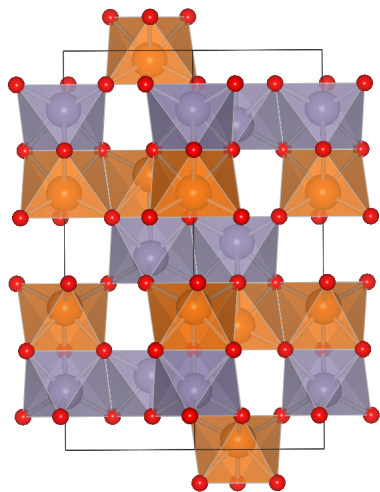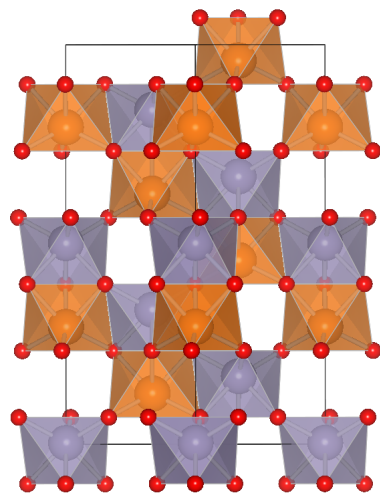
Select a material with a small tolerance factor and stabilize it in a rotation pattern that forbids A-site displacements, such that any further optimization of the A-site must come from a ferroelectric distortion

R3c   Pnma   R-3c

t ~ 0.8   *t~1*

The ABO$_3$ ilmenites — A new place to look for multifunctional materials?

Ilmenite — BORING

R3c — multiferroic

Multiferroics with R3c structure:

- FeTiO$_3$ Fennie PRL (2008); Varga PRL (2009)

- MnTiO$_3$ Aimi, et al Inorg. Chem. (2011)

- MnSnO$_3$ Aimi, et al Inorg. Chem. (2011)

All electric-field-switchable ferromagnets with large estimated polarization (~55 – 100 μC/cm^2)

Ferroelectrics with R3c structure:

- ZnSnO$_3$ Inaguma, et al JACS (2008); Son, et al JACS (2009)

- PbNiO$_3$ Inaguma, et al JACS (2011)

Large estimated polarization (~59 μC/cm^2) for ZnSnO$_3$

$$\Gamma_2^-$$

Polar displacements along [111]

$$Pm\bar{3}m \longrightarrow R\bar{3}c \longrightarrow R3c$$

Rotation of octahedra about [111]

$$R_4^+$$

A-site displacements forbidden by symmetry in R-3c

Test materials:

$MgSnO_3$	$MgGeO_3$	$MnTiO_3$
$MnSnO_3$	$ZnGeO_3$	$ZnTiO_3$
$FeSnO_3$		$FeTiO_3$
$ZnSnO_3$		$MgTiO_3$

Materials with Ilmenite ground states have small tolerance factors and large ferroelectric instabilities in R3c
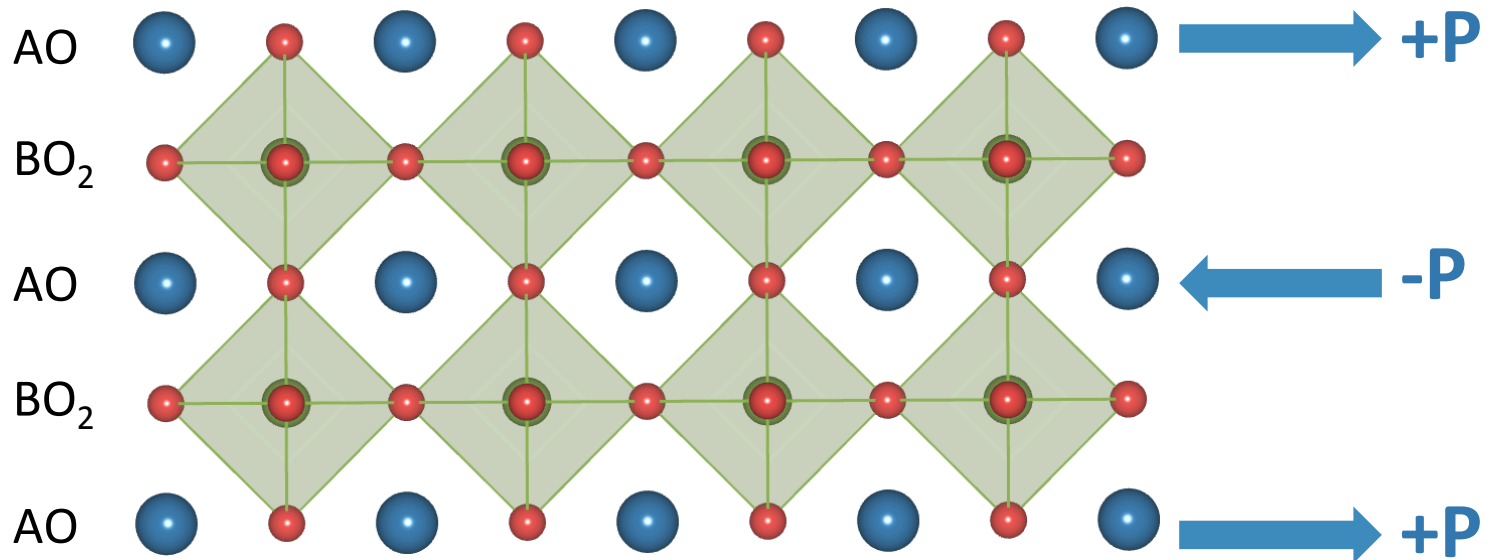
Strategy number 1:
Select a material with a small tolerance factor and stabilize it in a rotation pattern that forbids A-site displacements, such that any further optimization of the A-site must come from a FE distortion

Strategy number 2:
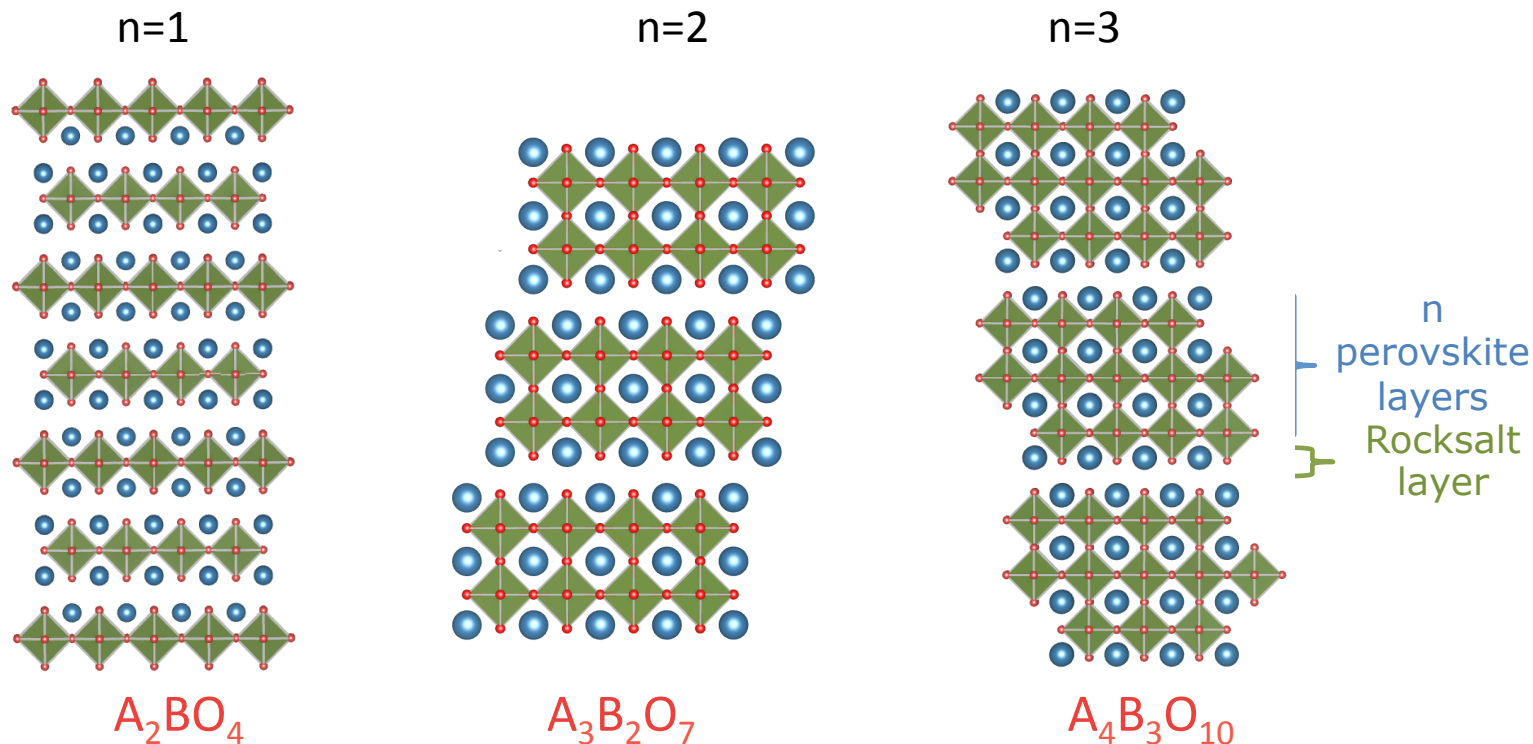Exploit anti-polar A-site displacements by breaking topology of perovskite lattice

Octahedral rotations induce antiferroelectric A-site cation displacements in the Pnma space group

- Displacements of A cations in successive AO layers are anti-parallel

- Polarization induced in one AO layer exactly canceled by polarization induced in next AO layer

Macroscopic polarization is zero

Ruddlesden-Popper phases are naturally occurring, bulk materials that may display the right properties

$A_{n+1}B_nO_{3n+1}$

n=1

n=2

n=3

A_2BO_4

$A_3B_2O_7$

$A_4B_3O_{10}$

n perovskite layers

Rocksalt layer

The properties of Ruddlesden-Popper phases can significantly differ from that of the parent perovskite, e.g. $SrTiO_3$ RP phases [Birol, Benedek and Fennie, Phys. Rev. Lett. **107** 257602 (2011)]
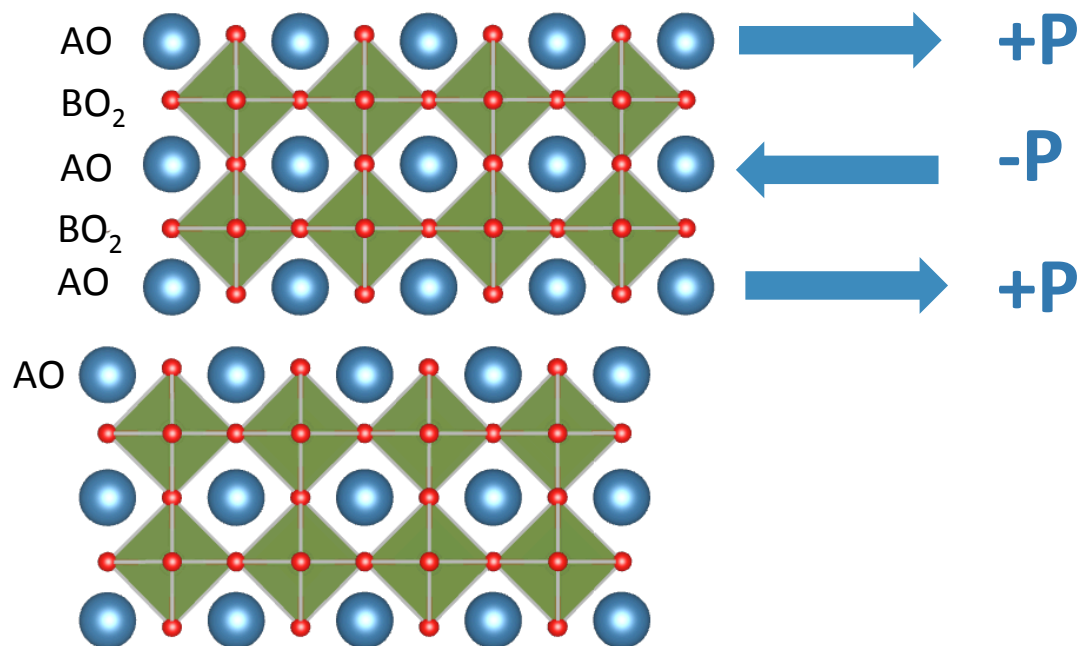
'Layering' plays a crucial role in allowing ferroelectricity to arise in Ruddlesden-Popper phases

Knapp and Woodward, J. Solid State Chem. **179** 1076 (2006)

King and Woodward, J. Mater. Chem. **20** 5785 (2010)

Benedek and Fennie, Phys. Rev. Lett. **106** 107204 (2011)

Mulder, Benedek, Rondinelli and Fennie, Adv. Funct. Mater. **In Press** (2013)

Octahedral rotations, together with A cation displacements, induce ferroelectricity in layered perovskites

Hybrid improper ferroelectricity

Benedek and Fennie, Phys. Rev. Lett. **106** 107204 (2011)

CaTiO$_3$ and CaMnO$_3$ Ruddlesden-Popper phases as candidate multiferroics

Benedek and Fennie, Phys. Rev. Lett. **106** 107204 (2011)

n=2 Ca$_3$Ti$_2$O$_7$ and Ca$_3$Mn$_2$O$_7$ properties

- Ferroelectric -- crystallize in a polar space group, A2$_1$am

  Guiblin et al, Acta Cryst. **C58**, i3, 2002
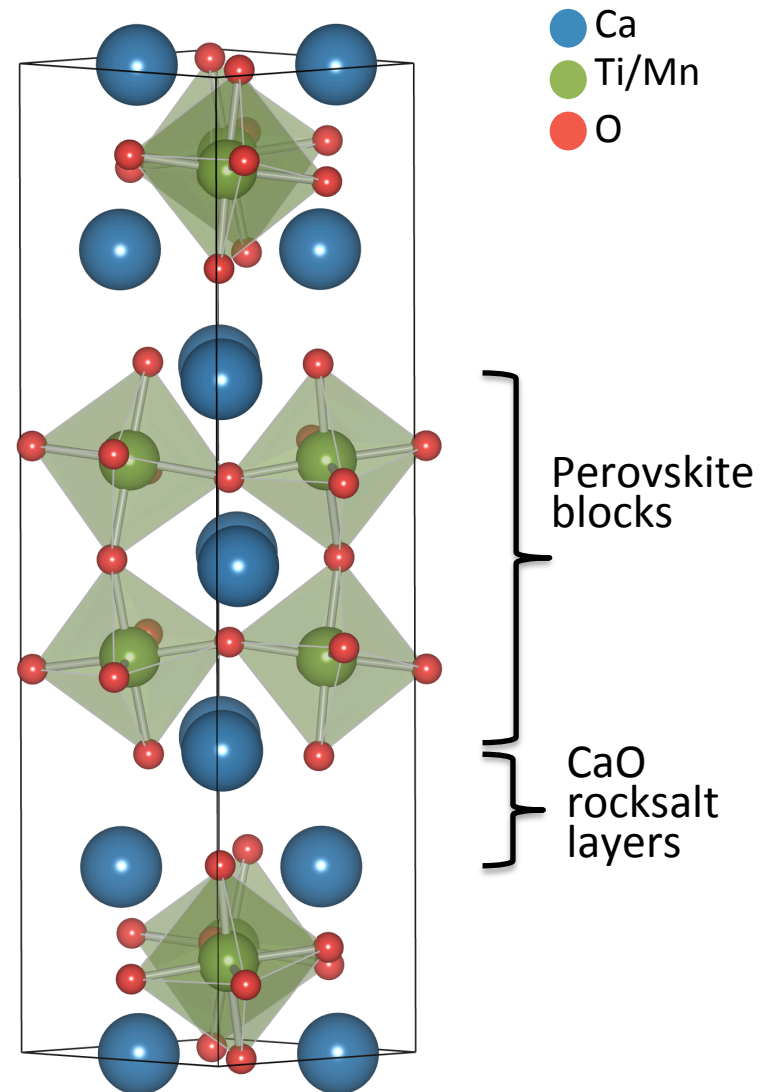 Elcombe et al, Acta Cryst **B47**, 305, 1991.

- Ca$_3$Mn$_2$O$_7$ is a (weak) ferromagnet

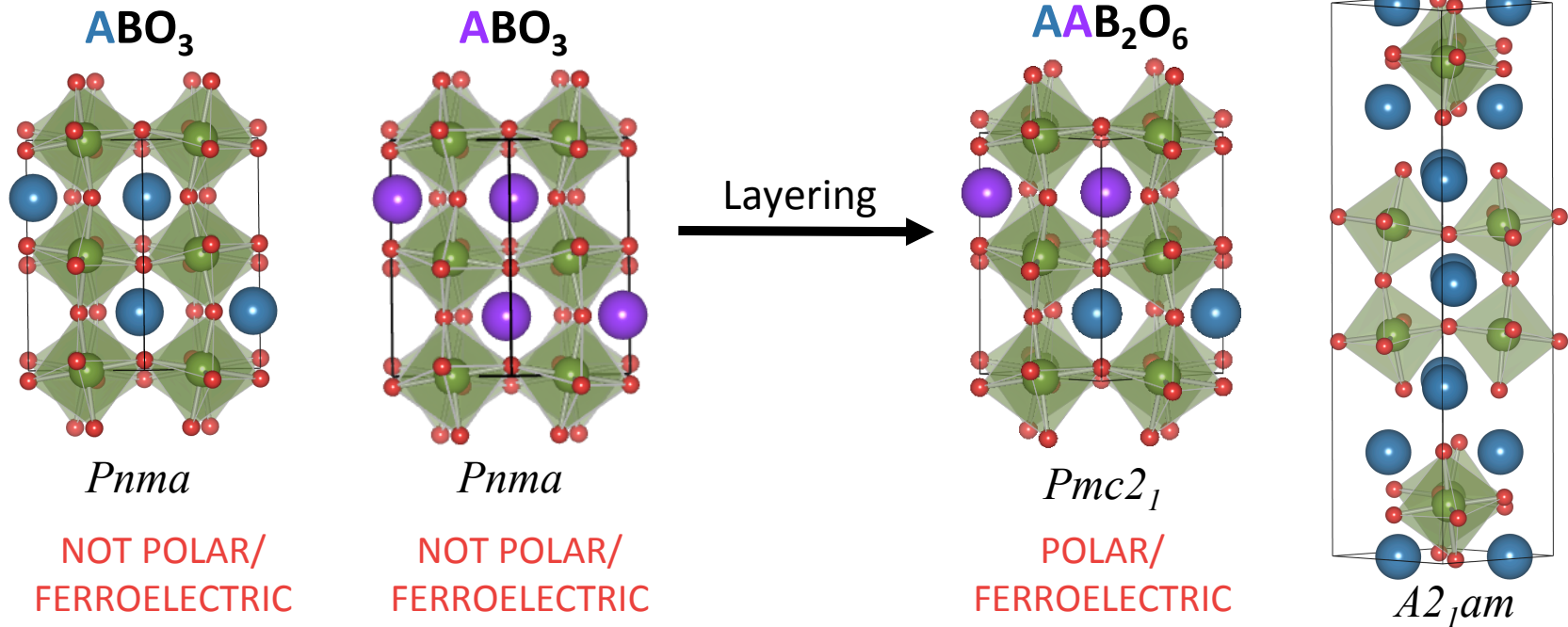 Guiblin et al, Acta Cryst. **C58**, i3, 2002

- Octahedral rotations induce ferroelectricity AND ferromagnetism (spin canted antiferromagnet)

- Both materials occur naturally in **BULK**

- Theory predicts that magnetization is electric field controllable

Ca
Ti/Mn
O

Perovskite blocks

CaO rocksalt layers

Layering, making rotations functional

ABO_3

$Pnma$

NOT POLAR/
FERROELECTRIC

ABO_3

$Pnma$

NOT POLAR/
FERROELECTRIC

Layering

AAB_2O_6

$Pmc2_1$

POLAR/
FERROELECTRIC

$A_3B_2O_7$

$A2_1am$

- A-site displacements are anti-ferroelectric → can exploite these to create ferroelectricity in A-site ordered double perovskites and Ruddlesden-Popper phases
  Knapp and Woodward, *J. Solid State Chem.* **179** 1076-1085 (2006).
  Benedek, Mulder, Fennie, *J. Solid State. Chem.* **195** 11-20 (2012).
  Mulder, Benedek, Rondinelli, Fennie, *Adv. Funct. Mat*. **In Press** (2013).

- ABO_3 perovskites can be used as 'building blocks' to create new functional materials

Ferroelectricity from anti-ferroelectricity

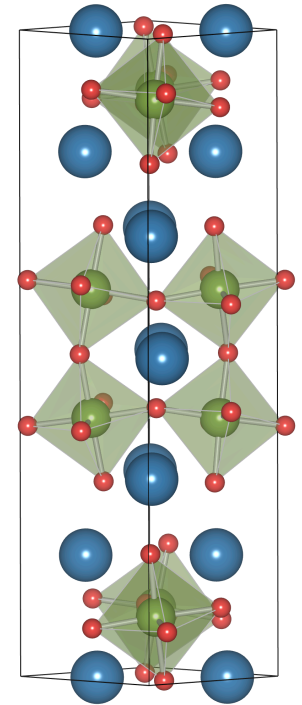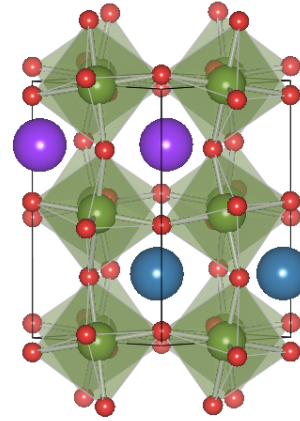Mulder, Benedek, Rondinelli, Fennie, *Adv. Funct. Mat.* **In Press** (2013)
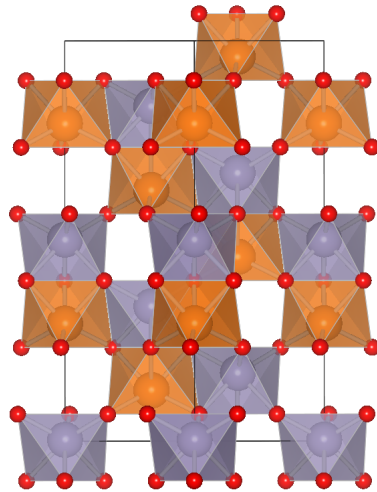
$$\mathcal{P} \propto \Delta \tau$$
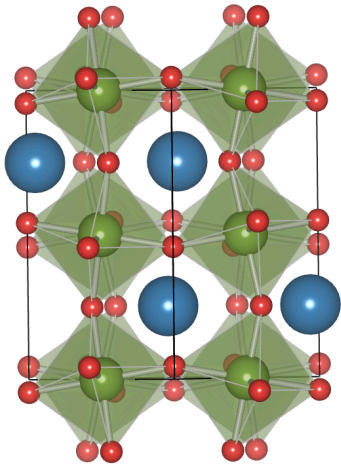
$$\mathcal{F} \sim \mathcal{P} R_1 R_2$$
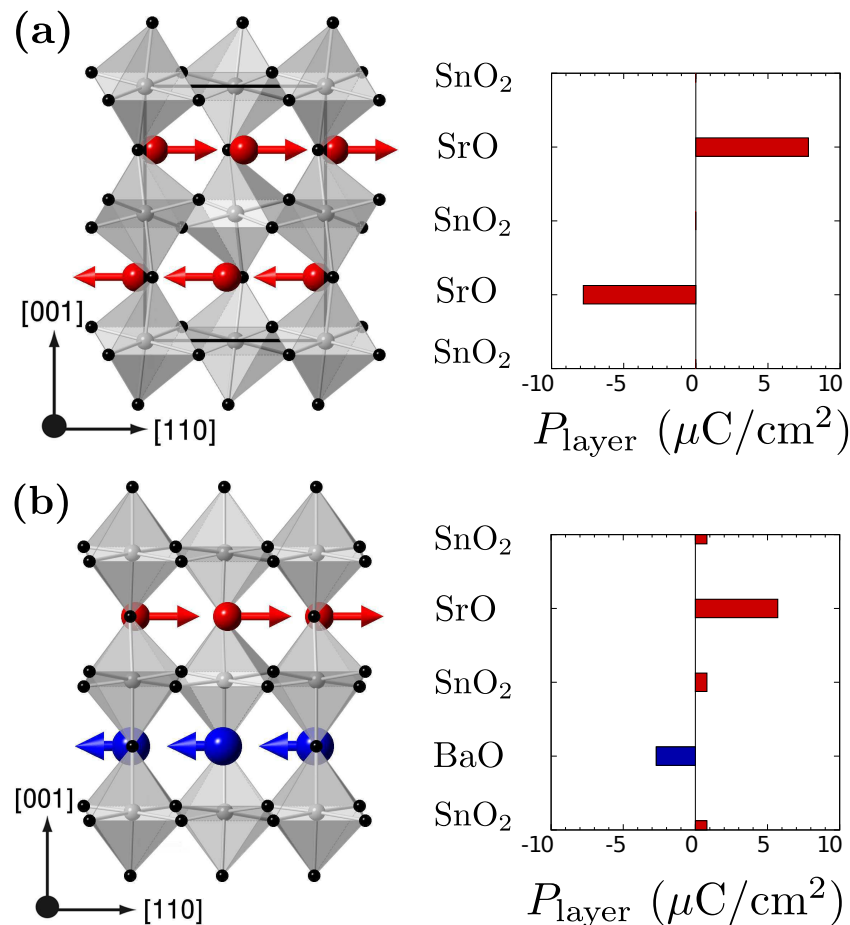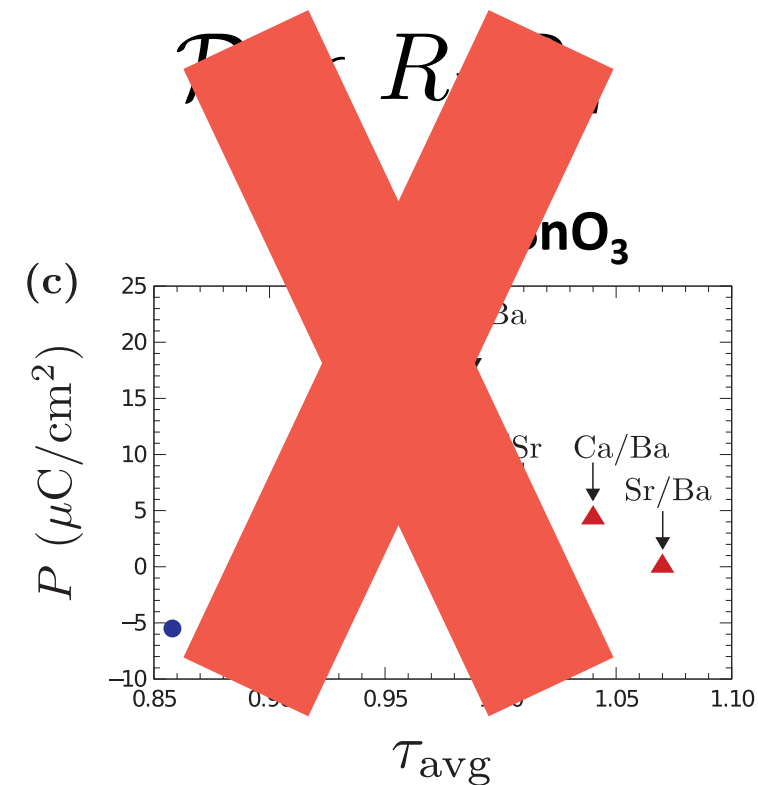
Relevant design criterion is difference in tendency of A-sites to displacements – large polarization and small switching barrier

The same structural distortion can manifest in different ways to produce different physics/chemistry depending on the material

Take-home message and references

- The ferroelectric mechanisms uncovered and investigated in recent years all involve octahedral rotations and/or A-site displacements

Although BaTiO$_3$ was the first known perovskite ferroelectric and has perhaps been the most intensively studied, it appears to be an exception rather than the rule and is not representative of the majority of perovskite and perovskite-like ferroelectrics.

For a review see:
Nicole A. Benedek, Andrew T. Mulder, & Craig J. Fennie, "Polar octahedral rotations: a path to new multifunctional materials," *Journal of Solid State Chemistry*, **195** 11-20 (2012). arXiv:1108.2915

"Why are there so few perovskite ferroelectrics?" Nicole A. Benedek and Craig J. Fennie, *J. Phys. Chem. C* **In Press** (2013).

"Turning ABO$_3$ antiferroelectrics into ferroelectrics: Design rules for practical rotation-driven ferroelectricity in double perovskites and A$_3$B$_2$O$_7$ Ruddlesden-Popper phases," Mulder, Benedek, Rondinelli, and Fennie, *Advanced Functional Materials* **In Press** (2013) arXiv:1205.5526.

App for calculating tolerance factors with the bond valence model (works on iPhone and Android). See 'Tools' at
http://www.me.utexas.edu/~benedekgroup/