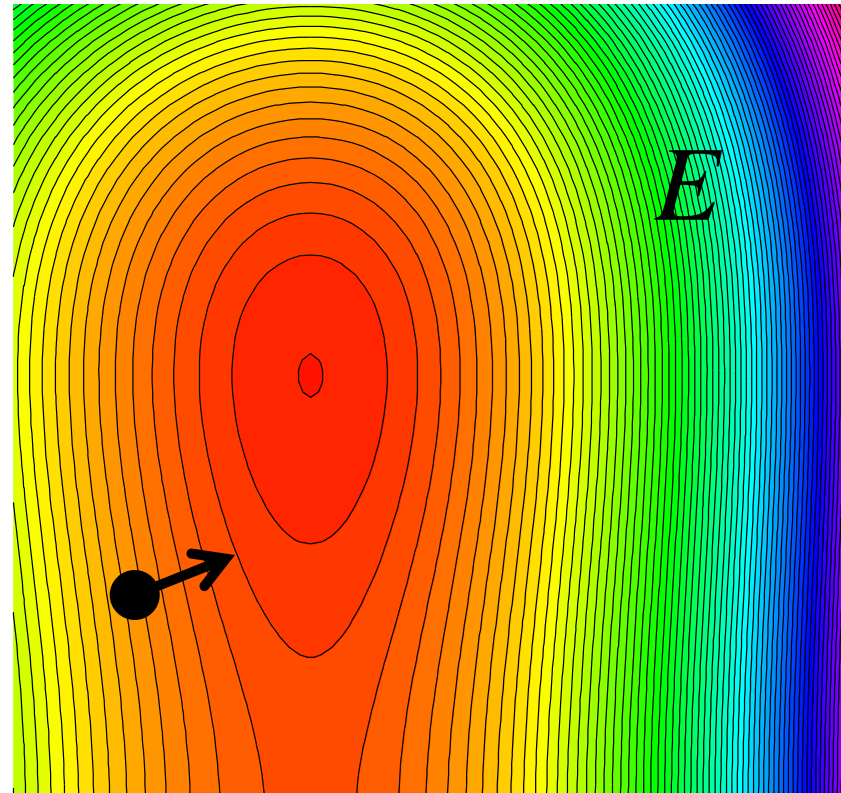


Applications of Structure Optimization and Forces in the LAPW Method

David J. Singh
Oak Ridge National Laboratory

$$F_i = -\nabla_i E$$



Exploring Complex Energy Surfaces

Suppose we want to know about $h(x,y)$ by making measurements on a set of points $x_i, y_i \quad i=1 \dots n$



Measure h at each point
→ n pieces of information.

Measure $F = -\nabla h$
→ $2n$ pieces of information.

Measure both
→ $3n$ pieces of information.

If we want to know F at a given location we need 3 measurements of h (finite difference)

Medical Imaging

Ultrahigh strain and piezoelectric behavior in relaxor based ferroelectric single crystals

Seung-Eek Park^{a)} and Thomas R. Shrout

Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802

(Received 20 March 1997; accepted for publication 12 May 1997)

1804 J. Appl. Phys. **82** (4), 15 August 1997

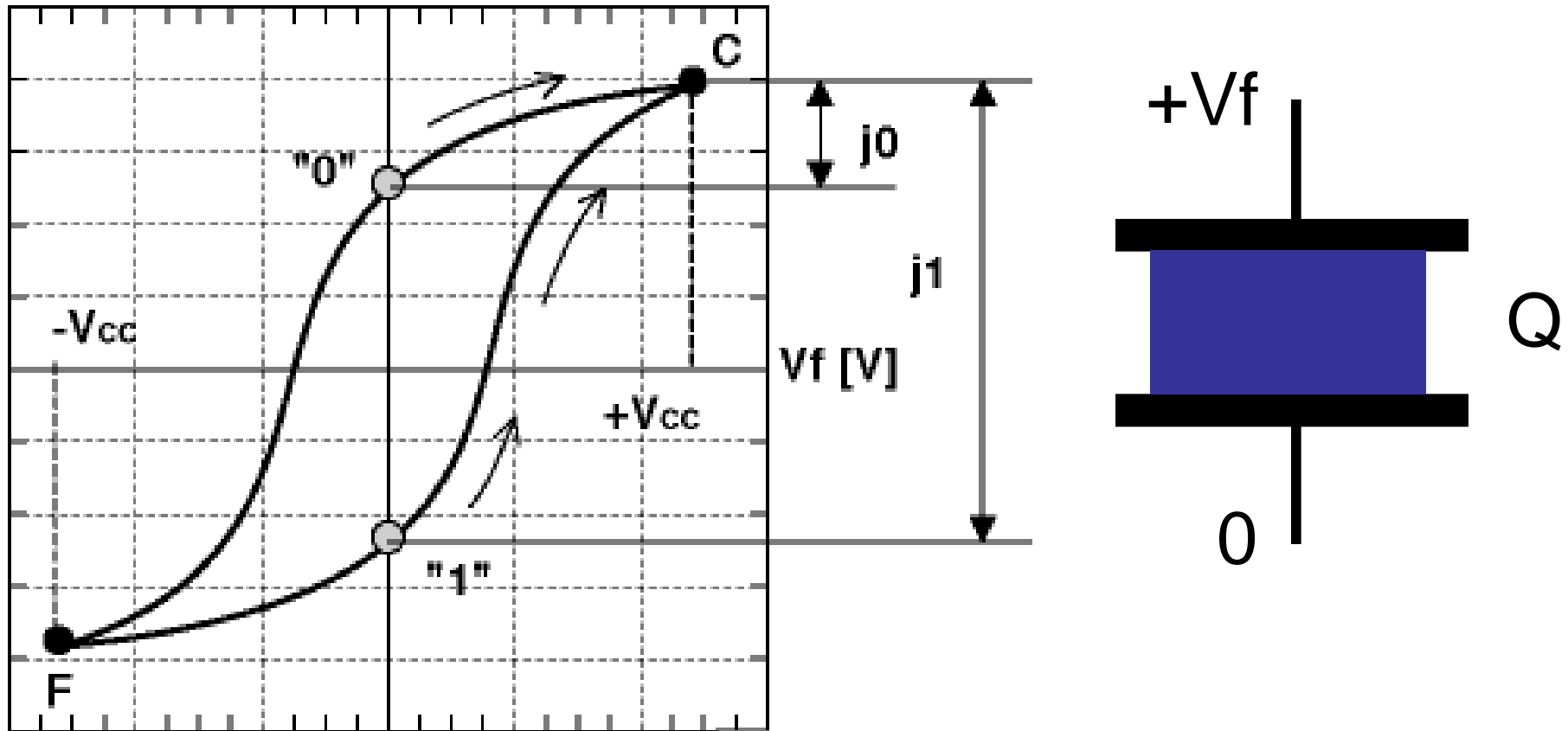
Materials discovery to commercial products in less than seven years



PHILIPS
sense and simplicity

Live 3D imaging enables clear visualization of thickened ventricular cardiomyopathy and pericardial effusion, while also providing valve, chamber and muscle detail.

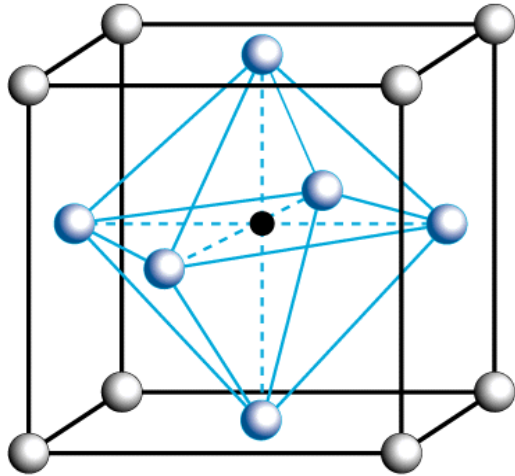
What are Ferroelectrics?



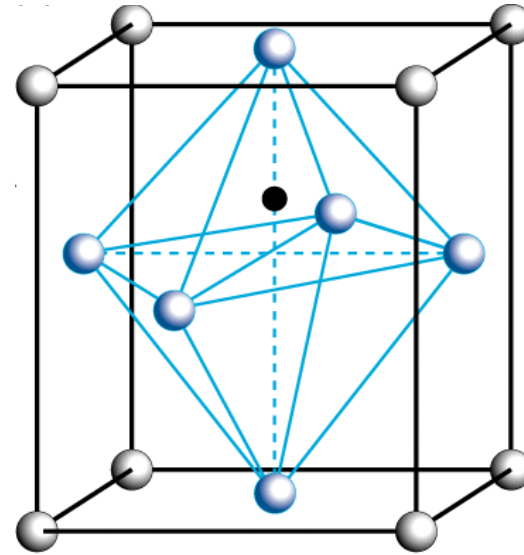
Note analogy with Ferromagnets

How Does PZT Work?

Cubic Perovskite Structure

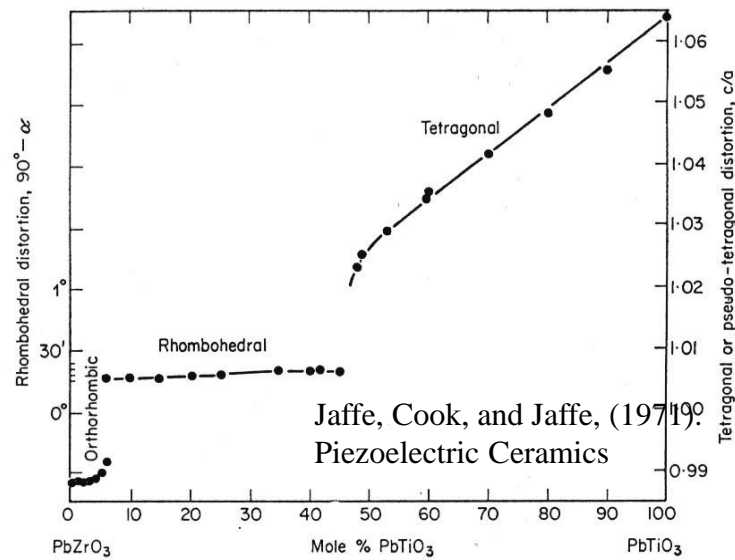
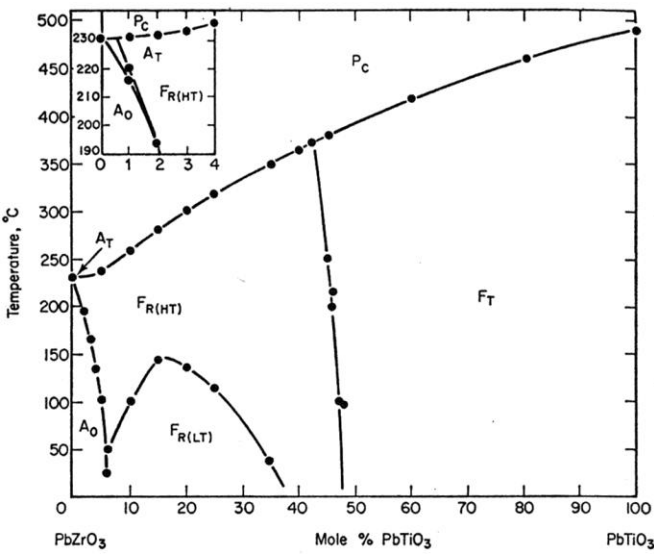


Tetragonal FE



TO(Γ) unstable phonon
(Ferroelectric)

Ground state can be tetragonal, orthorhombic, rhombohedral or monoclinic.



Jaffe, Cook, and Jaffe, (1971)
Piezoelectric Ceramics

PZT near the morphotropic phase boundary is the basis of current devices

Forces in Periodic Solids

- N atoms in the unit cell:
 - $E(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ 1 piece of information
 - $F_i(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = -\nabla_i E(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ $3N-3$ pieces of information

n.b. acoustic sum rule requires $\Sigma F_i = 0$

Calculation of forces provides much more information than calculation of the energy alone, especially as one goes to more and more complex materials

➔ enabling for many applications, e.g. determination of structures.

Example: Zone Center Phonons

Harmonic approximation: N atoms

$\mathbf{r} = \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\}$ ($3N$ component vector); \mathbf{r}_0 is the equilibrium.

$$E(\mathbf{r}) = E_0 + 1/2(\mathbf{r}-\mathbf{r}_0)^T \mathbf{k}(\mathbf{r}-\mathbf{r}_0)$$

$$\mathbf{F}(\mathbf{r}) = \mathbf{K}(\mathbf{r}-\mathbf{r}_0)$$

Can readily determine \mathbf{K} and \mathbf{r}_0 with $N+1$ calculations around the expected position of \mathbf{r}_0 (one less if the acoustic sum rule is used) \rightarrow equilibrium position and phonon frequencies and polarization vectors.

Doing this with energies alone would require at least $(3N+1)(3N+2)/2$ calculations (\mathbf{k} is symmetric).

Molecular Dynamics

VOLUME 55, NUMBER 22

PHYSICAL REVIEW LETTERS

25 NOVEMBER 1985

Unified Approach for Molecular Dynamics and Density-Functional Theory

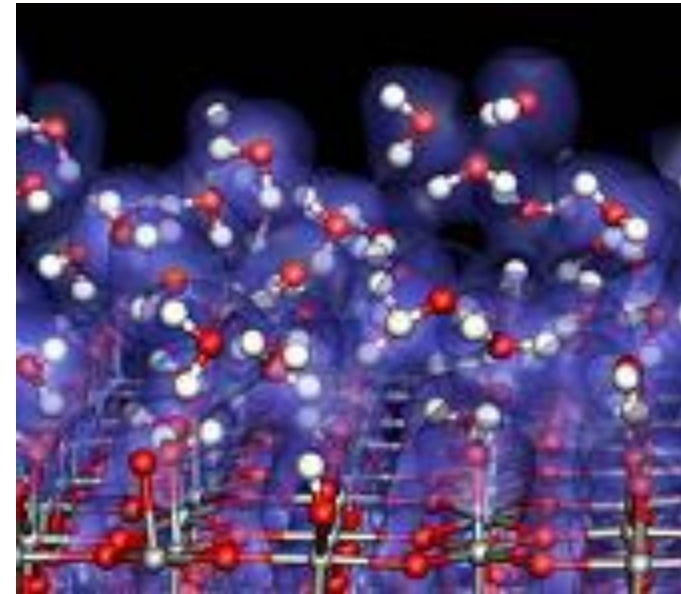
R. Car

International School for Advanced Studies, Trieste, Italy

and

M. Parrinello

- Molecular dynamics using force from DFT rather than empirical potentials.
- Advantage: the interesting regions often are places where empirical potentials are most in doubt, e.g. bond breaking ...
- First principles MD is efficient if one can solve the Kohn-Sham equations quickly starting from the solution at the prior step
→ true for planewaves (CP).
- Not very efficient in methods like LAPW where the complex basis depends on the atom positions.



Snapshot of a first-principles molecular dynamics simulation of water molecules reacting on the 110 surface of titanium oxide. (P.R.C. Kent).

*Not common with LAPW
but this could change.*

Thermal Conductivity

Heat transport in solids is a central problem in technology:

- Thermal Barrier Coatings.
- Electronics.
- Heat Exchangers.
- Cookware.
- Nuclear Reactor Fuel.
- Thermoelectrics.

Often calculated with classical molecular dynamics, but not with first principles.



Turbine blade with coating
(wikipedia)

Thermal Conductivity (con't)

Kubo Formula:

R. Kubo, M. Yokota and S. Nakajima, J. Phys. Soc. Jpn. **12**, 1203 (1957).

$$\kappa = \frac{V}{3k_B T^2} \int_0^\infty \langle \mathbf{q}(t) \cdot \mathbf{q}(0) \rangle dt,$$

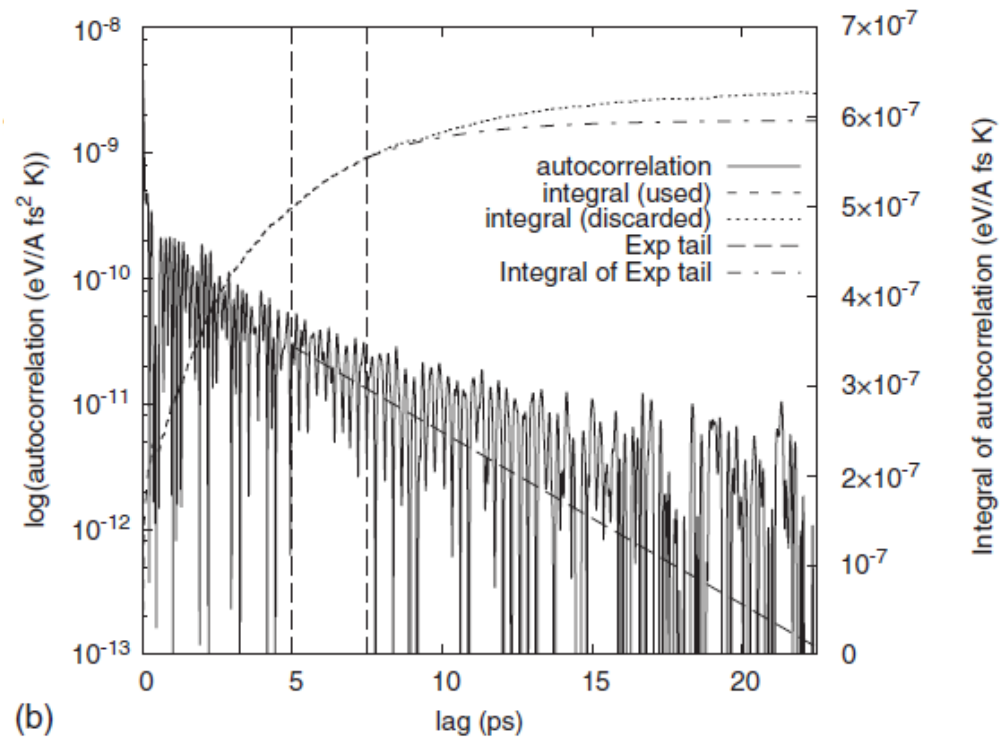
$\mathbf{q}(t)$ is the heat current

$$\mathbf{q}V = \frac{1}{2} \sum_{i>j} (\mathbf{v}_i + \mathbf{v}_j) \cdot \mathbf{F}_{ij} \mathbf{r}_{ij}^0$$

volume

“power”

distance



Problem:

This requires F_{ij} not just F_i

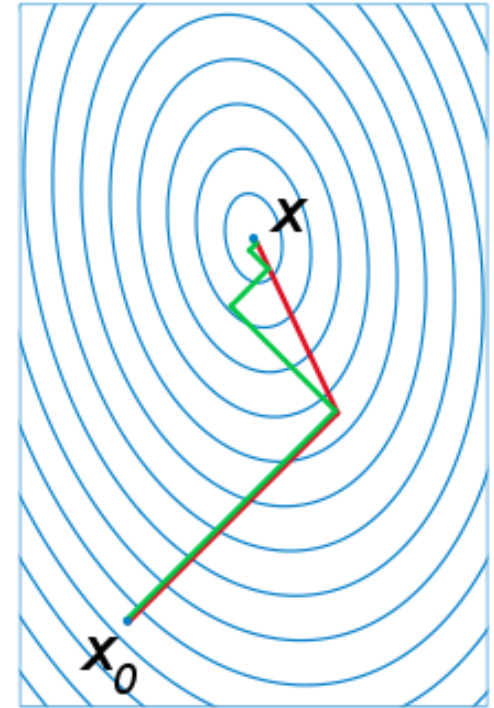
Structure Optimization

- Key to problems like ferroelectricity where ground state structures play the central role.
- Well developed area of mathematics: tractable algorithms rely on forces.

Some Algorithms:

Steepest Descent:

- At each step, proceed in the direction of the gradient to the minimum.
- Each direction is orthogonal to the previous one → very slow convergence.
- Can modify by not going all the way to the minimum on each step, but using e.g. some mixing parameter.



wikipedia: conjugate gradient method (shows problem with steepest descent)

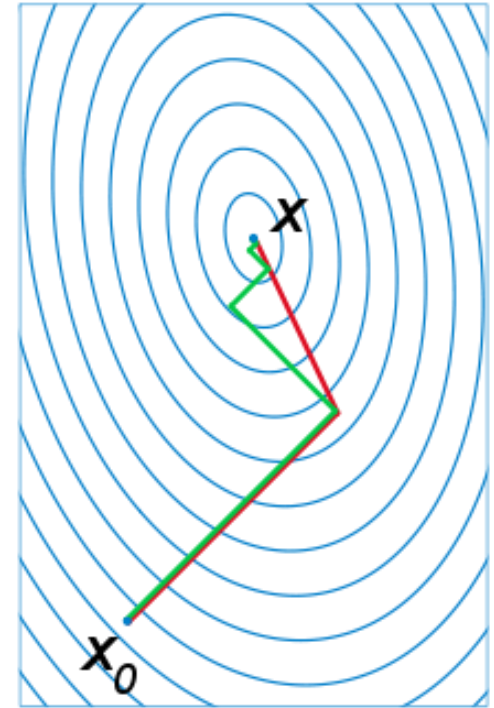
Structure Optimization (con't)

Damped Dynamics (simulated annealing):

- Molecular dynamics algorithm but with a portion of the kinetic energy removed at each step.
- Can overcome local minima on complex energy surfaces.

Conjugate Gradient:

- Very fast convergence for nearly harmonic surfaces.
- Like steepest descent, but line minimizations are along “conjugate directions” rather than the direction of the force.



wikipedia: conjugate gradient method

Wikipedia: Conjugate Gradient Method

1. Calculate the steepest direction: $\Delta x_n = -\nabla_x f(x_n)$,
2. Compute β_n according to one of the formulas below,
3. Update the conjugate direction: $\Lambda x_n = \Delta x_n + \beta_n \Lambda x_{n-1}$
4. Perform a line search: optimize α_n , $\arg \min_{\alpha_n} f(x_n + \alpha_n \Lambda x_n)$,
5. Update the position: $x_{n+1} = x_n + \alpha_n \Lambda x_n$,

- Fletcher–Reeves:

$$\beta_n^{FR} = \frac{\Delta x_n^\top \Delta x_n}{\Delta x_{n-1}^\top \Delta x_{n-1}}$$

- Polak–Ribière:

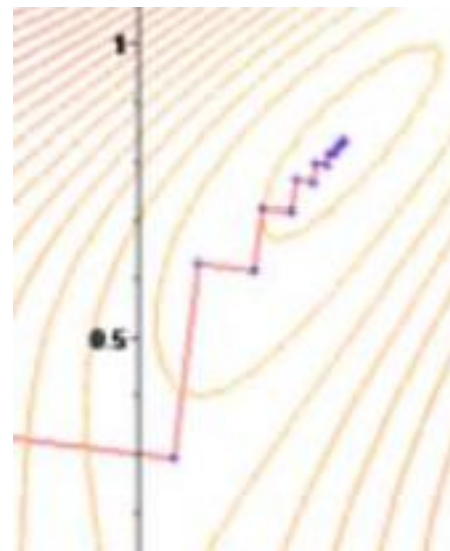
$$\beta_n^{PR} = \frac{\Delta x_n^\top (\Delta x_n - \Delta x_{n-1})}{\Delta x_{n-1}^\top \Delta x_{n-1}}$$

- Hestenes–Stiefel:

$$\beta_n^{HS} = \frac{\Delta x_n^\top (\Delta x_n - \Delta x_{n-1})}{\Delta x_{n-1}^\top (\Delta x_n - \Delta x_{n-1})}$$

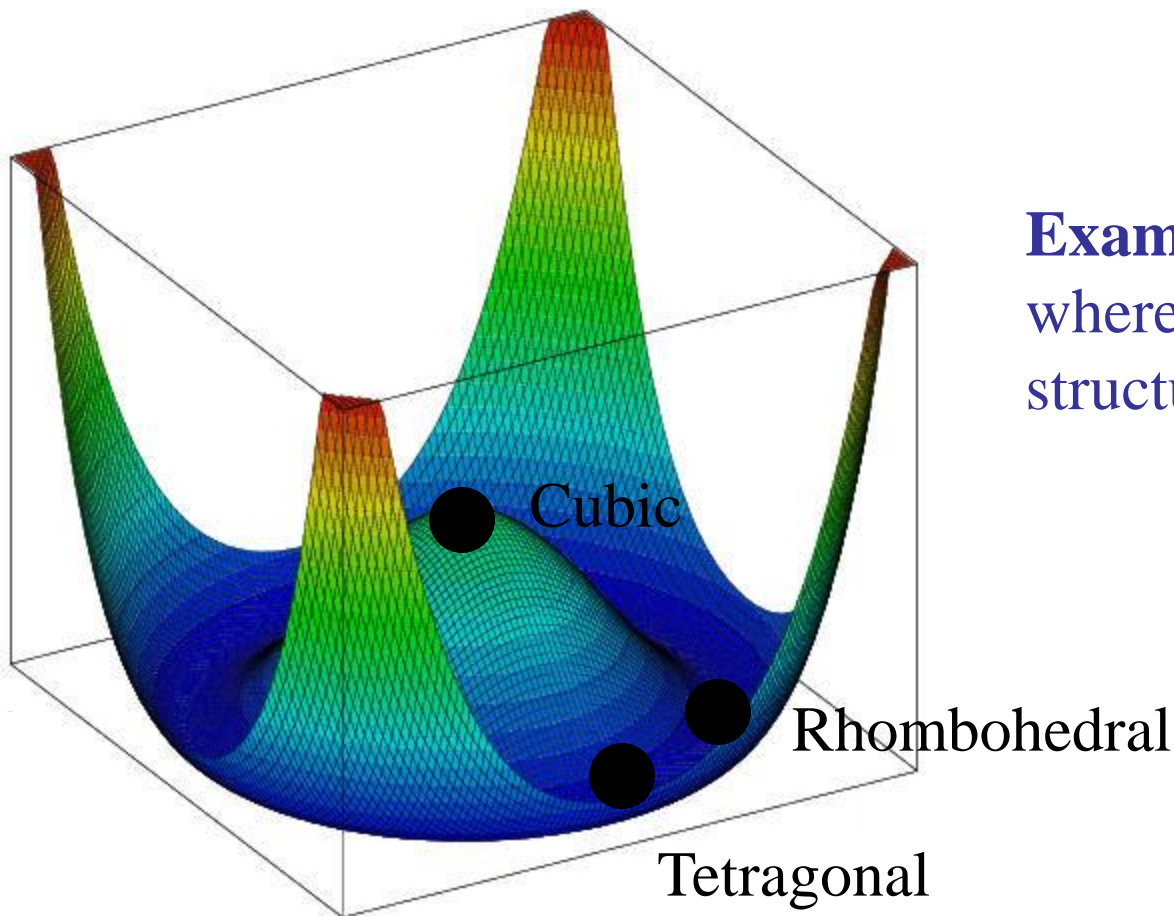
These are not the steepest descent directions after the first iteration.

Avoid sawtooth path down a valley



Caution

- Force convergence and structure convergence are not the same thing.
 - There can be soft degrees of freedom even in stiff materials → you can get small forces and be far from the true structure.



Example: Ferroelectrics where very different structures are close in energy.

References for Forces

- J.M. Soler and A.R. Williams, Phys. Rev. B **40**, 1560 (1989).
- J.M. Soler and A.R. Williams, Phys. Rev. B **42**, 9728 (1990).
- R.C. Yu, D. Singh and H. Krakauer, Phys. Rev. B **43**, 6411 (1991).

PART 2

Ferroelectricity in Perovskites

How much of a good thing is enough?

Co-workers:

Valentino Cooper

Shigeyuki Takagi

Alaska Subedi

D.I. Bilc

S.V. Halilov

M. Fornari

The Size of an Atom

Acta Cryst. (1976). A32, 751

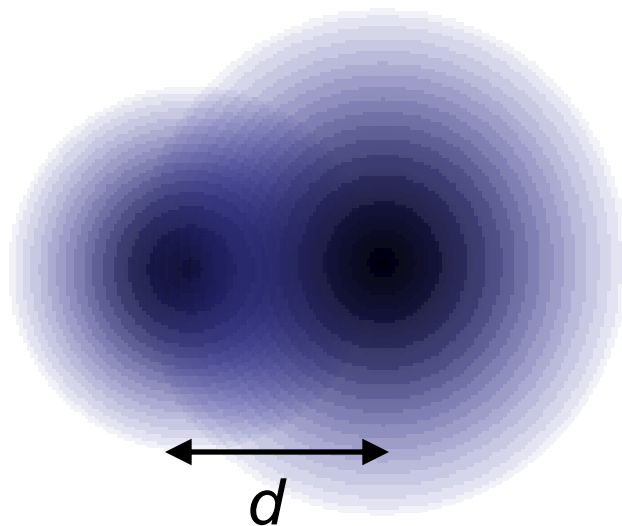
Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides

BY R. D. SHANNON

Central Research and Development Department, Experimental Station, E. I. Du Pont de Nemours and Company, Wilmington, Delaware 19898, U.S.A.

(Received 30 October 1975; accepted 9 March 1976)

The effective ionic radii of Shannon & Prewitt [*Acta Cryst.* (1969), B25, 925–945] are revised to include more unusual oxidation states and coordinations. Revisions are based on new structural data, empirical bond strength–bond length relationships, and plots of (1) radii *vs* volume, (2) radii *vs* coordination number, and (3) radii *vs* oxidation state. Factors which affect radii additivity are polyhedral distortion, partial occupancy of cation sites, covalence, and metallic character. Mean Nb⁵⁺–O and Mo⁶⁺–O octahedral distances are linearly dependent on distortion. A decrease in cation occupancy increases mean Li⁺–O, Na⁺–O, and Ag⁺–O distances in a predictable manner. Covalence strongly shortens Fe²⁺–X, Co²⁺–X, Ni²⁺–X, Mn²⁺–X, Cu⁺–X, Ag⁺–X, and M–H[–] bonds as the electronegativity of X or M decreases. Smaller effects are seen for Zn²⁺–X, Cd²⁺–X, In³⁺–X, Pb²⁺–X, and Tl⁺–X. Bonds with delocalized electrons and therefore metallic character, *e.g.* Sm–S, V–S, and Re–O, are significantly shorter than similar bonds with localized electrons.



Inter-atomic distance,

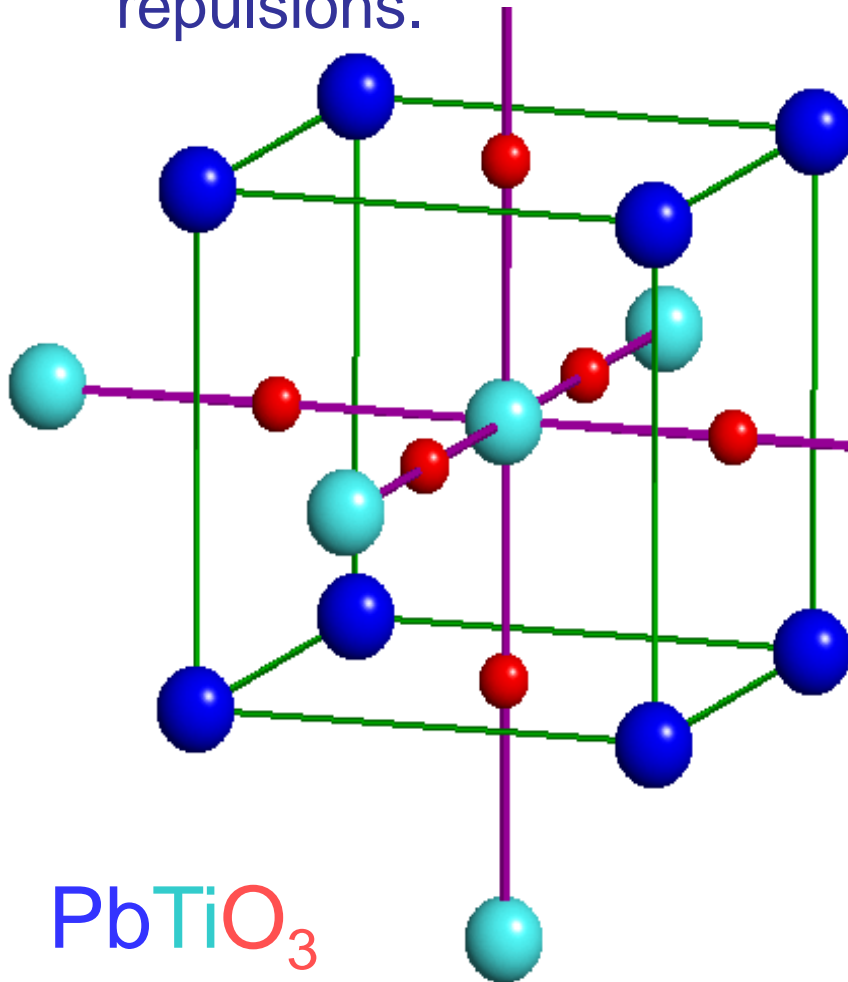
$$d = r_A + r_B$$

Crystallographic data
“defines” the “sizes” of
atoms.

INSTABILITIES OF PEROVSKITES

Chemical Understanding:

- Main interactions are (1) Coulomb (ionic) and (2) Closed shell repulsions.



Competition of bond lengths drives most perovskite instabilities.

Tolerance Factor:

$$t = (r_A + r_O) / \sqrt{2}(r_B + r_O)$$

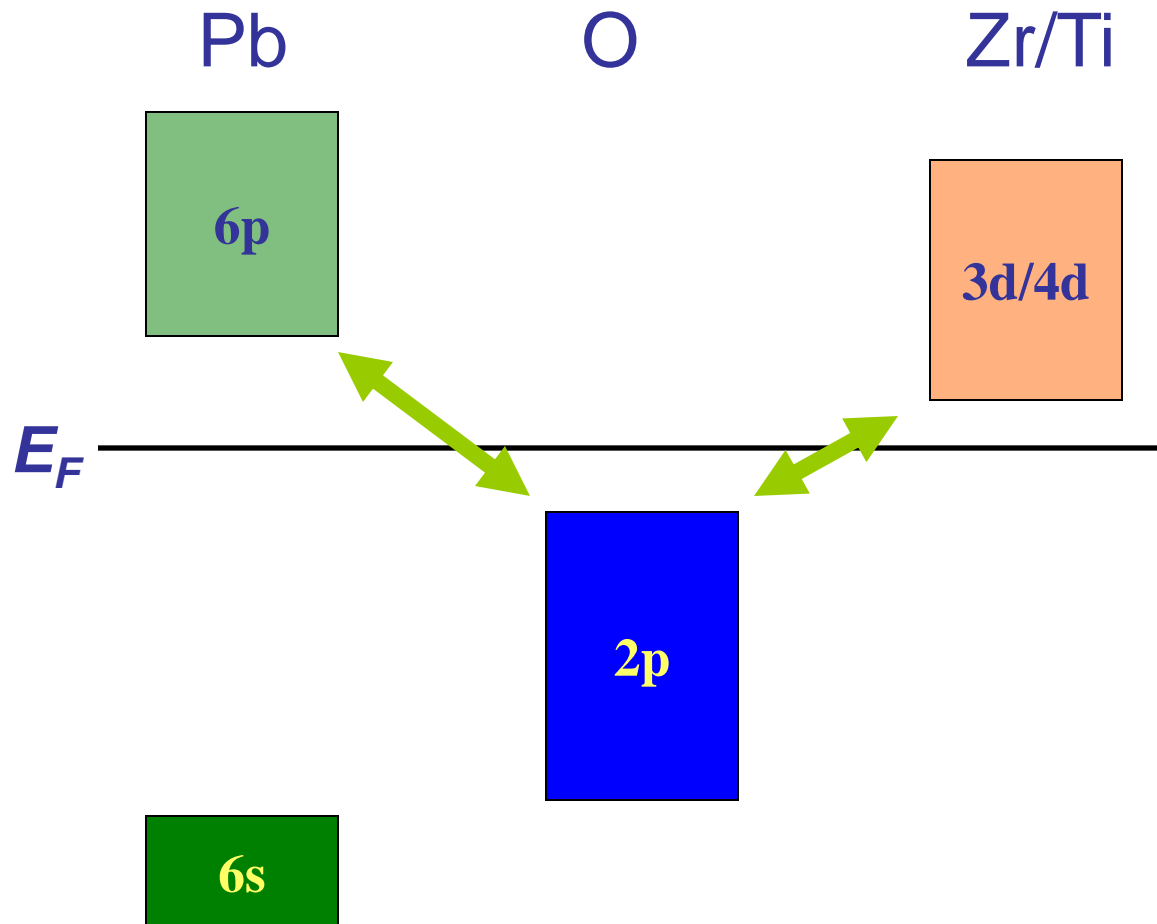
- (a) $t > 1$ (B ion [Ti] is too small)
→ B site off-centering and ferroelectricity (BaTiO₃, KNbO₃)
- (b) $t < 1$ (A ion [Pb] is too small)
→ Rotation of octahedra, e.g. CaTiO₃, GdFeO₃, LaMnO₃... (the great majority of perovskites).

Role of Pb on the Perovskite A-Site

- Pb allows $t < 1$ perovskites to be ferroelectric instead of *Pnma* or similar.

Electronic Structure:

R.E. Cohen, 1992



Cross-gap hybridization:

- Increases Z^*
- Softens interactions
- Increases polarizability
- Favors Ferroelectricity

DIRECTIVE 2002/95/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL
of 27 January 2003

on the restriction of the use of certain hazardous substances in electrical and electronic equipment

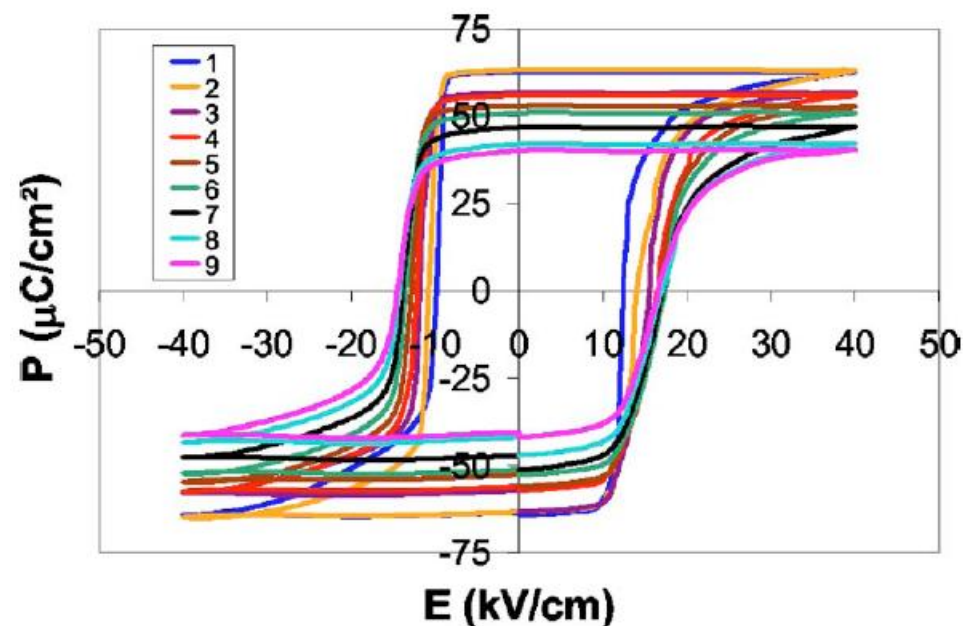
Are there Pb-free materials that are as good as or even better than the Pb-based materials, e.g. PZT?

Answer was long thought to be no...

... but results in the last decade for materials such as BiFeO_3 suggest a closer look.

BiFeO_3 :

- A very high polarization material based on structure (Tomashpol'skii, 1967), but not usable due to conductivity.

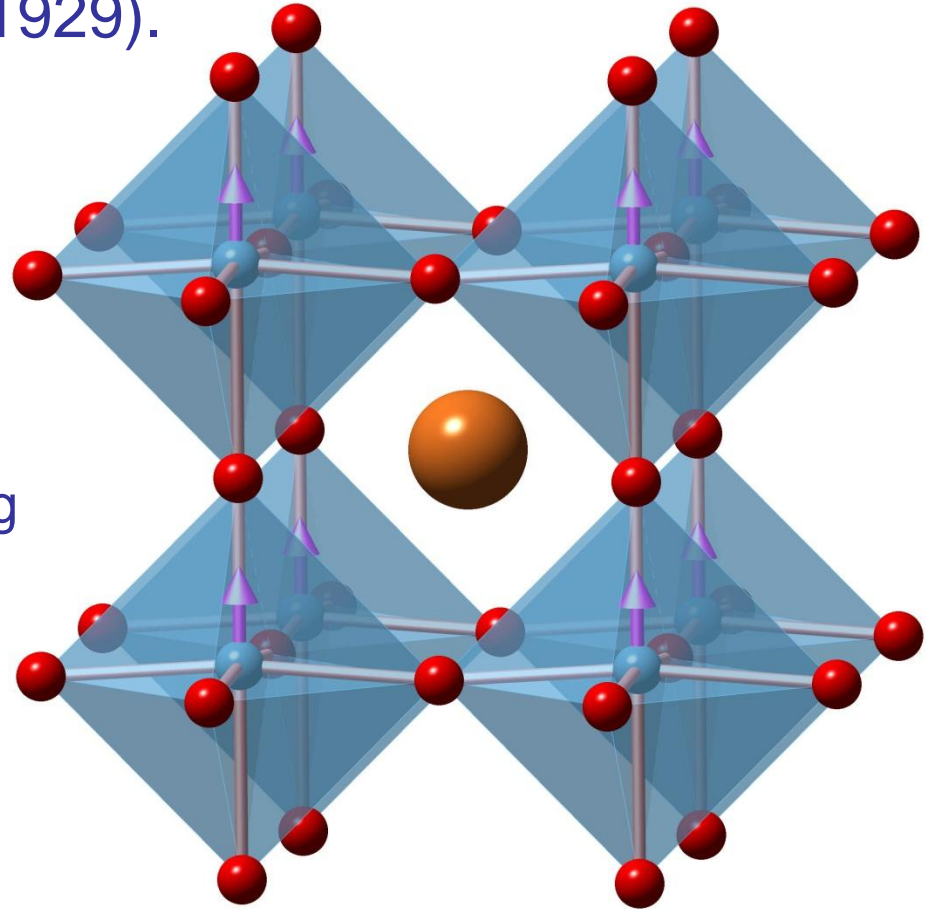


Lebeugle et al., APL 2007, room temp.

The Perovskite Structure

Pauling Rules - JACS **51**, 1010 (1929).

1. “the cation-anion distance being determined by the radius sum and the coordination number of the cation by the radius ratio”
2. “charge of each anion tends to compensate the strength of the electrostatic valence bonds reaching it”
3. “shared edges and particularly shared faces ... decreases stability; this effect is large for cations with large valence ...”



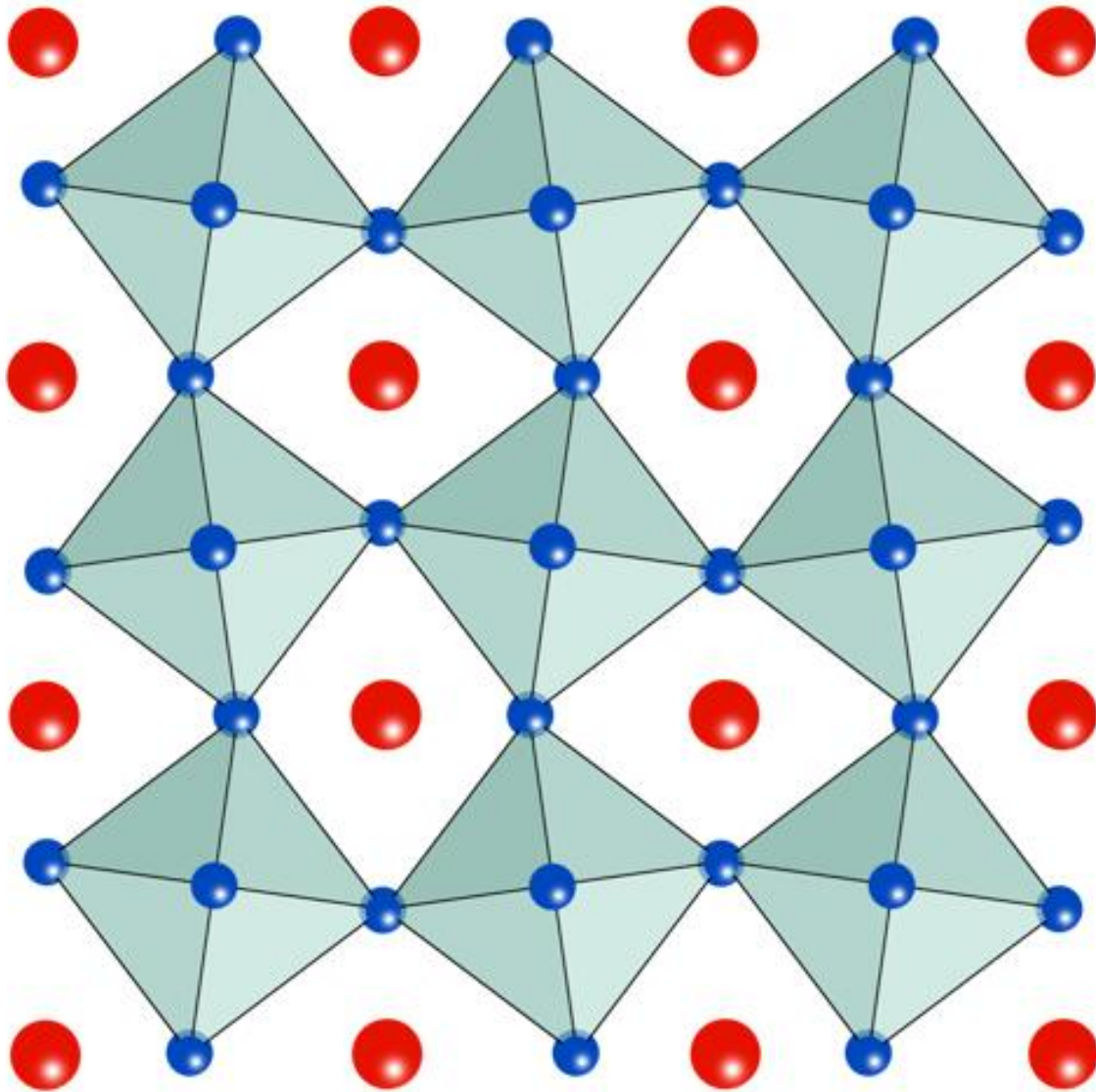
from www.crystallmaker.co.uk

Problem:

- Bi^{3+} vs. Pb^{2+} implies lower average B-site charge.
- Bi^{3+} has c.r. $\sim 1.3 \text{ \AA}$ \ll Pb^{2+} (1.63 \AA).

\rightarrow *Bi perovskites are often difficult to make.*

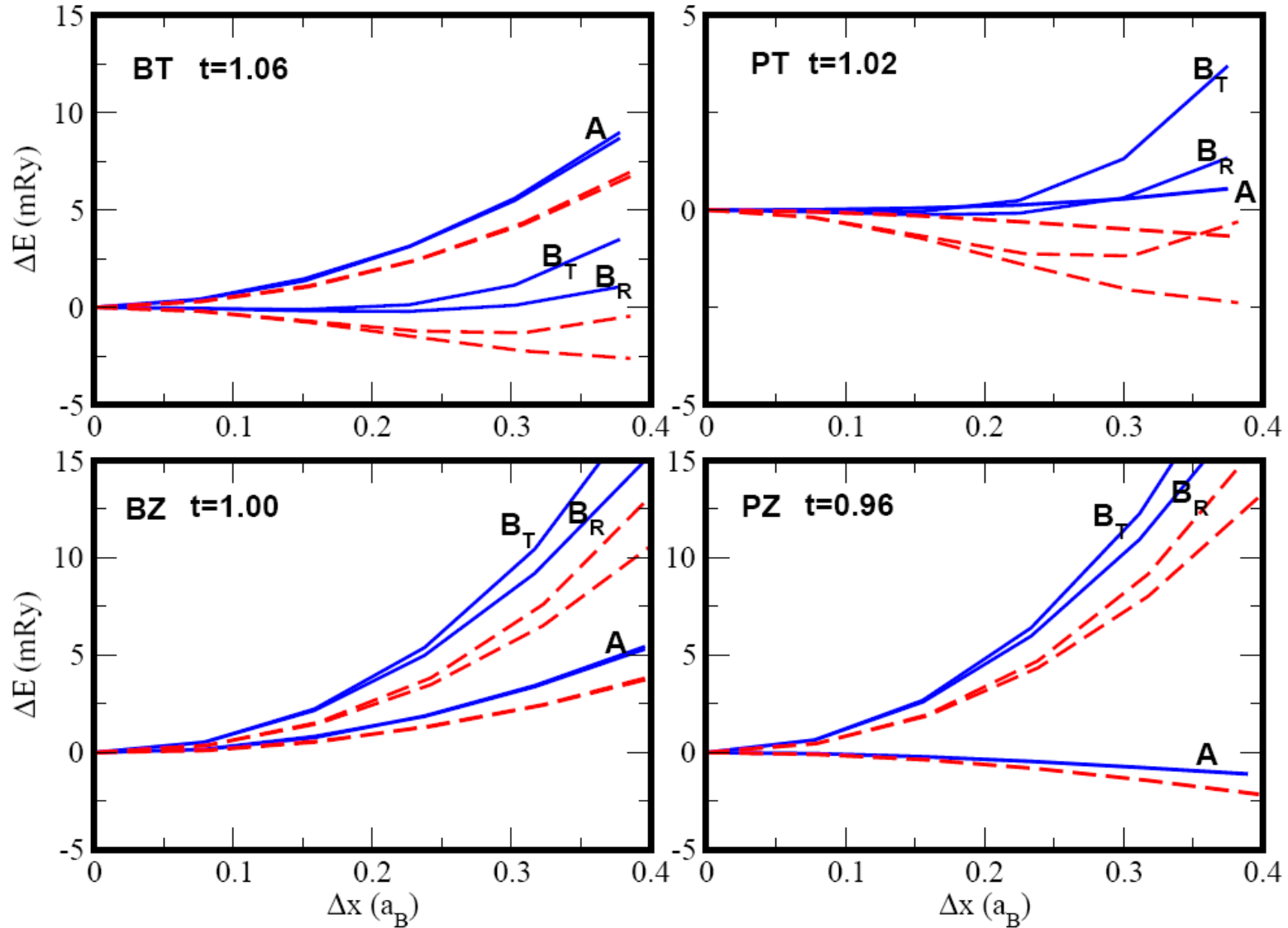
ROTATIONAL MODE



- Distortion around A (A -O bond lengths)
- Bends B -O- B bonds but only bond lengths in second order. (*n.b.* breathing mode is usually stiff).
- Driven by pressure and/or tolerance factor ***if octahedra are stiff.***
- Alternate is A -site off-centering (Pb).

INSTABILITIES OF PEROVSKITES

Single sub-lattice off-centering (LDA):



Expt. Volume: —————

6% Expansion: - - - - -

INSTABILITIES OF PEROVSKITES

LDA calculations constrained to rhombohedral ferroelectric

Displacements in Bohr along x direction ($0.529 \sqrt{3} \rightarrow$ Ang. disp.)

	A_x	B_x	O_x	O_z	r
V_{expt}					
BT	0.095	0.211	0.021	-0.042	0.45
BT(exp)	0.104	0.200	0.021	-0.042	0.52
PT	0.479	0.295	-0.015	0.029	1.63
PZ	0.643	0.281	-0.077	0.153	2.29

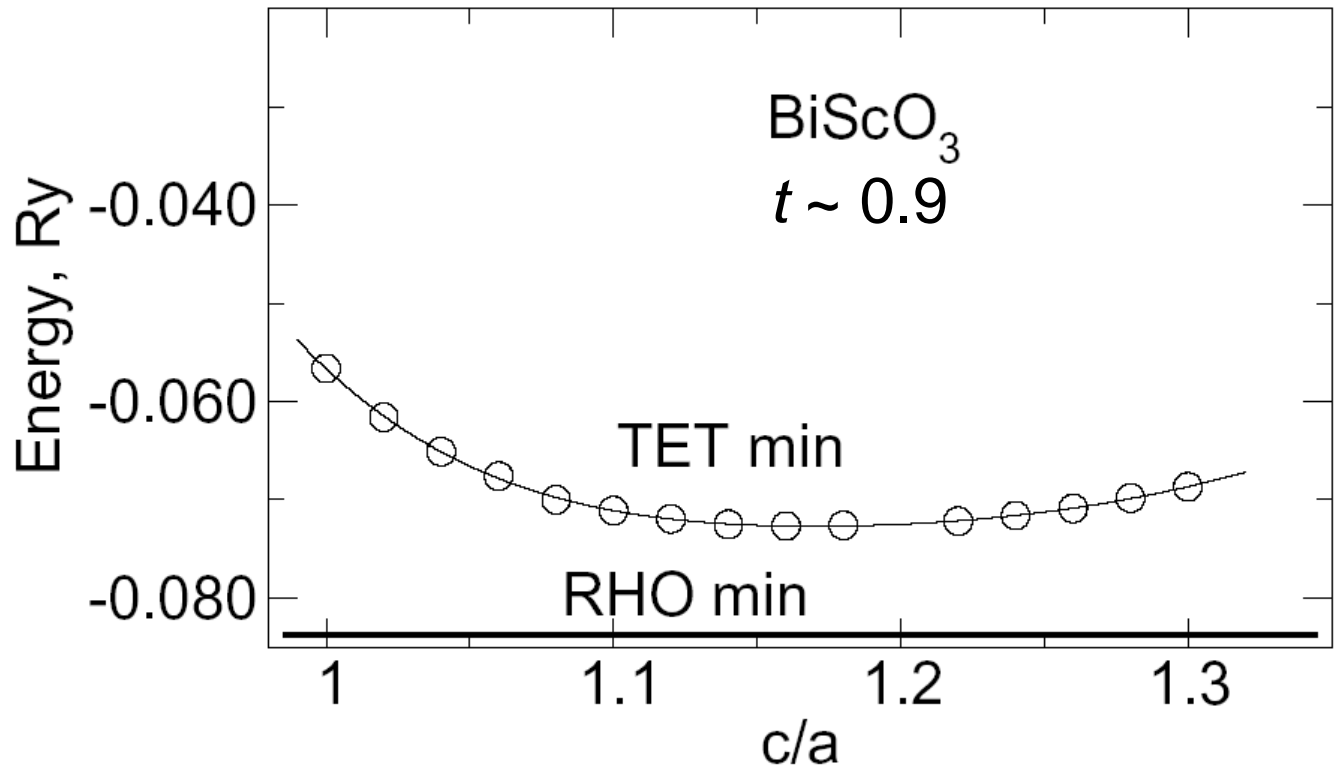
Cooperative A-site and B-site displacements characterize good perovskite ferroelectrics

also Grinberg & Rappe (2004) showing T_C in relation to cooperativity.

Strain Coupling

Allowing only ferroelectric states & at the LDA lattice parameter:

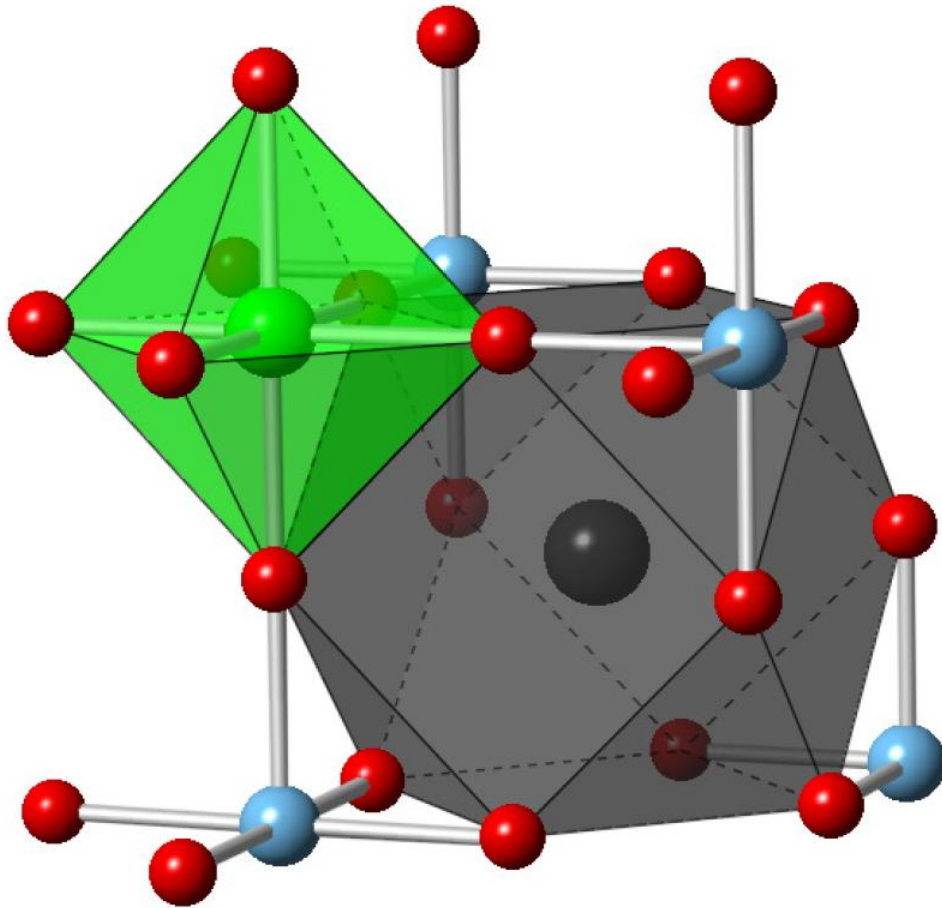
*Why are these
so different*



- Note rhombohedral ferroelectric phase is very much more stable than tetragonal.
- Note large ferroelectric energy.
- Also note the large c/a of the tetragonal.

R-FE vs. T-FE LDA ENERGETICS

- A site ion is 12-fold coordinated (very isotropic).
- B site ion is 6-fold (octahedral).



B-site responds to *A*-site off-centering, and the *B*-site off-centering favors the rhombohedral state. This is why we have MPB's in *A*-site driven materials.

Halilov, Fornari, Singh, PRB **67**, 174107 (2004)

Ghita, Fornari, Singh, Halilov, PRB **72**, 054114 (2005)

What If ...

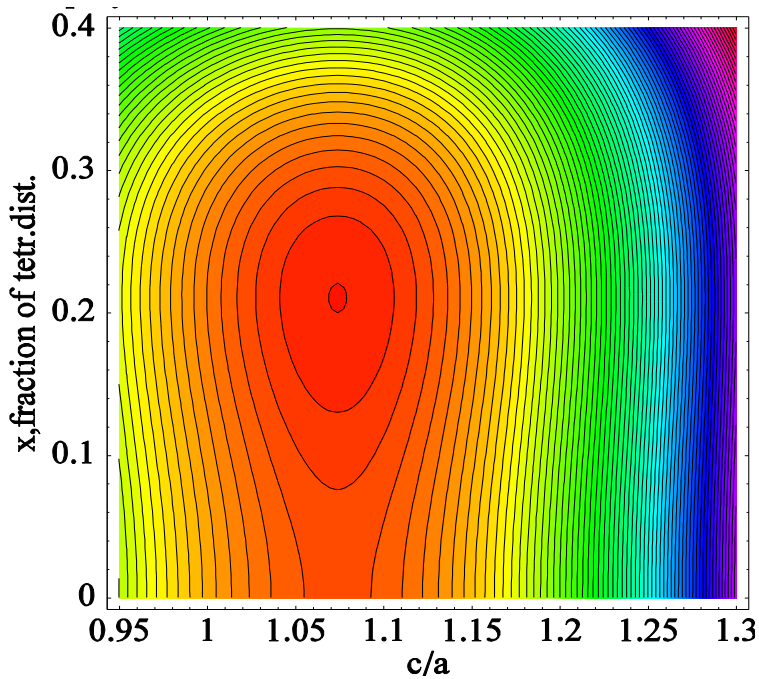
... we could eliminate the tilt instability from arbitrary $t < 1$ perovskites?

According to first principles ferroelectricity would result.

- This is found universally for low t .
- It consists of A-site off-centering.

CdTiO₃ and Alloys with PbTiO₃

Density functional calculations for CdTiO₃ (small tolerance factor, possibly interesting chemistry)



“Ferroelectric CdTiO₃”

- CdTiO₃ has antiferroelectric ground state.
- If forced ferroelectric it has a large tetragonal strain in the tetragonal FE state, and high energy scale.
- Supercells for 50-50 CdTiO₃-PbTiO₃ are borderline ferroelectric and tetragonal and have a large c/a~1.08 (higher than PbTiO₃).

Experimental Confirmation

APPLIED PHYSICS LETTERS

VOLUME 82, NUMBER 19

12 MAY 2003

Structure and phase stability of the $\text{CdTiO}_3\text{--PbTiO}_3$ system

D. Y. Suárez-Sandoval and P. K. Davies^{a)}

Department of Materials Science and Engineering, University of Pennsylvania, 3231 Walnut Street, Philadelphia, Pennsylvania 19104

(Received 20 February 2003; accepted 14 March 2003)

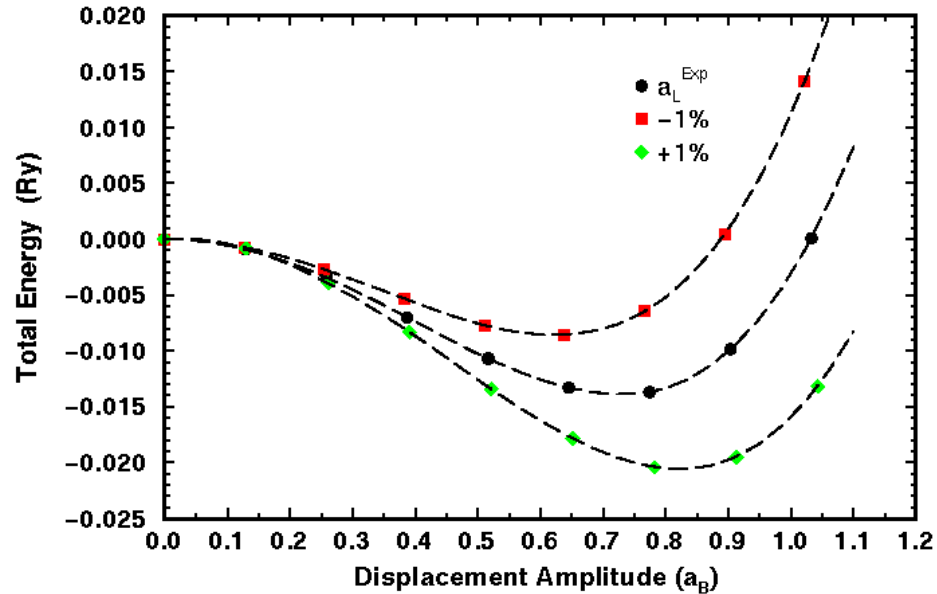
The formation of solid solutions in the $\text{CdTiO}_3\text{--PbTiO}_3$ system has been examined using x-ray diffraction (XRD) and differential scanning calorimetry. The XRD data showed two solid-solution ranges for the $(\text{Pb}_{1-x}\text{Cd}_x)\text{TiO}_3$ system at 1170 °C; orthorhombic on the cadmium-rich side and tetragonal on the lead-rich side, separated by a two-phase region for $0.08 < x < 0.85$. Despite the limited range of solubility the tetragonal $(\text{Pb}_{1-x}\text{Cd}_x)\text{TiO}_3$ solid solutions show a $>10\%$ increase in the c/a ratio, demonstrating that the role of Cd in this structure is quite unique. The enthalpy of the tetragonal-to-cubic phase transformation also increases with increasing Cd substitution, although the temperature of the transition is $\sim 20^\circ$ lower than that found in pure PbTiO_3 . © 2003 American Institute of Physics. [DOI: 10.1063/1.1573362]

This was the second example of an alloy with PbTiO_3 that increases c/a .

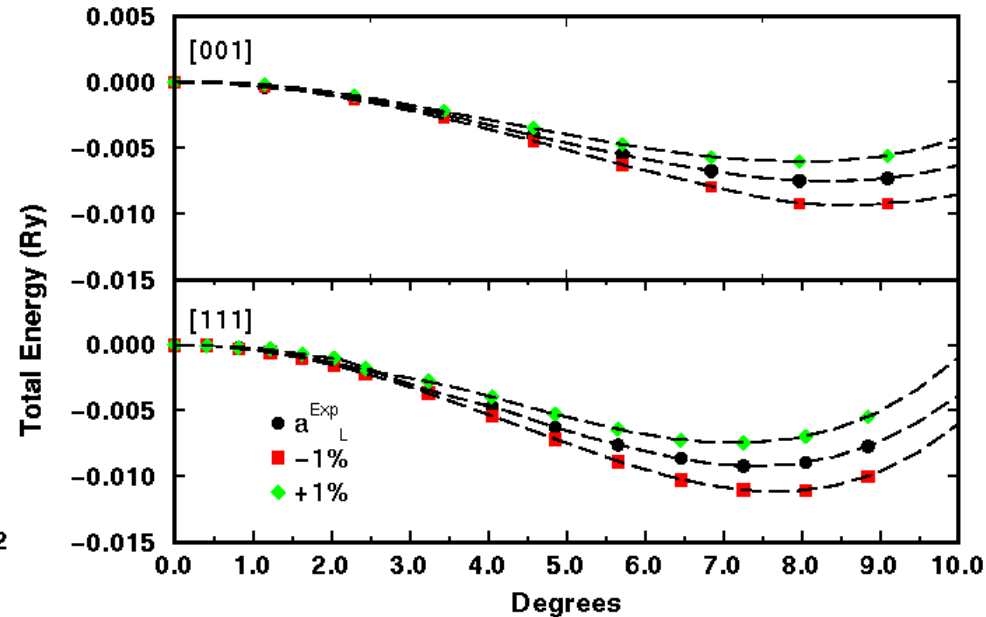
Volume Dependence of Modes (50-50 PZT)

•Fornari and Singh, 2000.

Ferroelectric Mode (Γ)

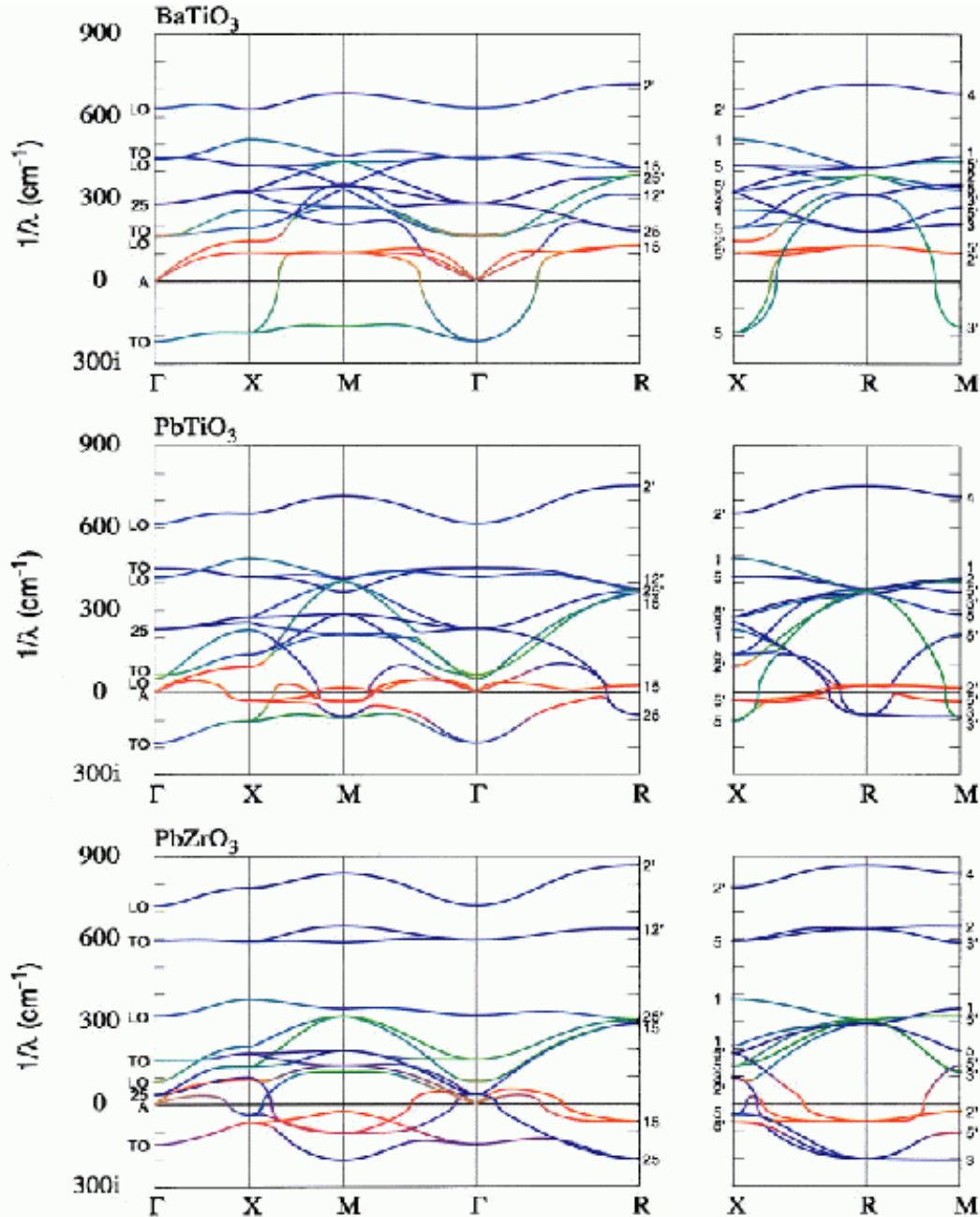


Rotational Mode (R)



- Volume dependence of FE and Rotational Instabilities is large and opposite.
- Implies co-existence in disordered alloys due to local stress fields.
- Tilts are active in PZT even at the MPB.
- **Generally in low tolerance factor perovskites, tilts and ferroelectricity compete with tilts “winning” unless there are stereochemically active A-site ions.**

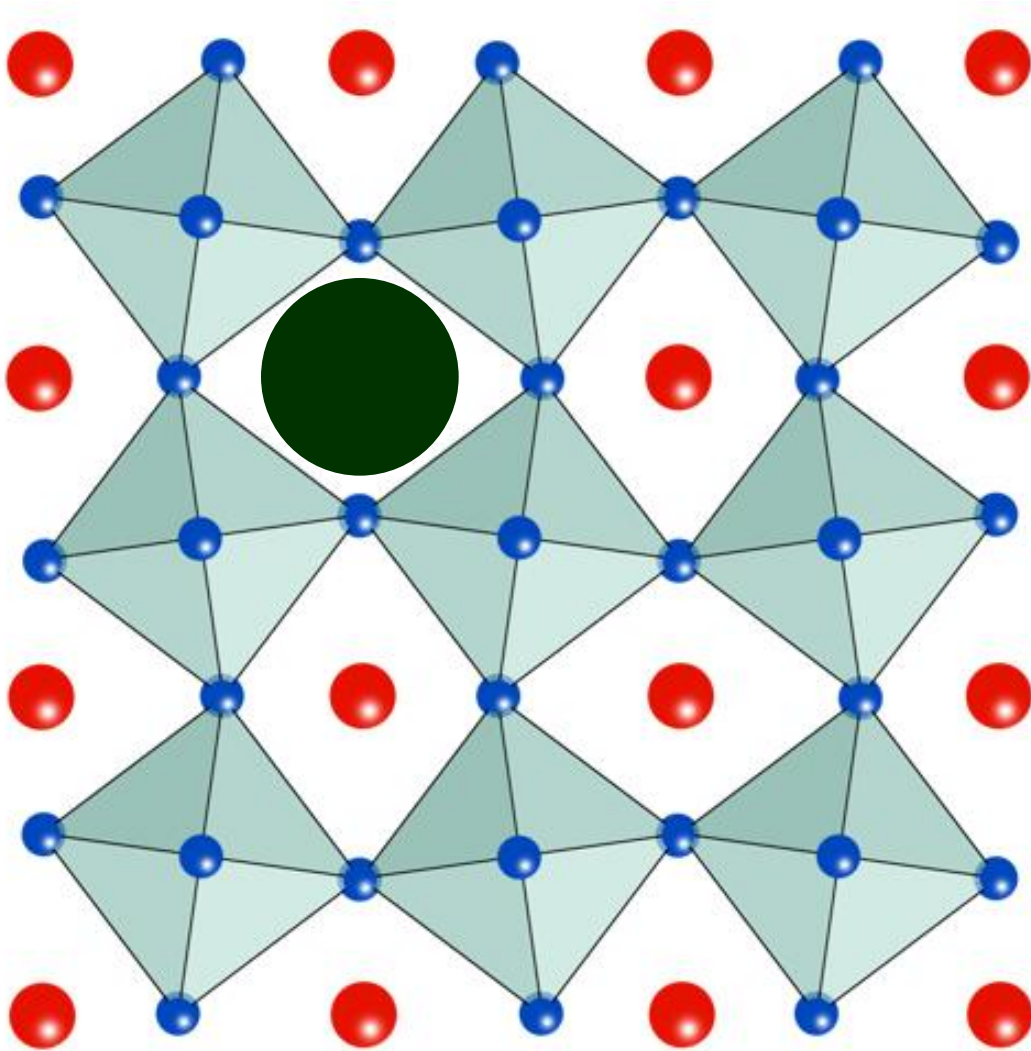
Phonons In Ferroelectric Perovskites



First Principles Calculations of Ghosez et al. (1999):

- note R point instabilities in *PZ* and *PT* but not *BT*.
- Note different coherence lengths for zone center and zone boundary instabilities.

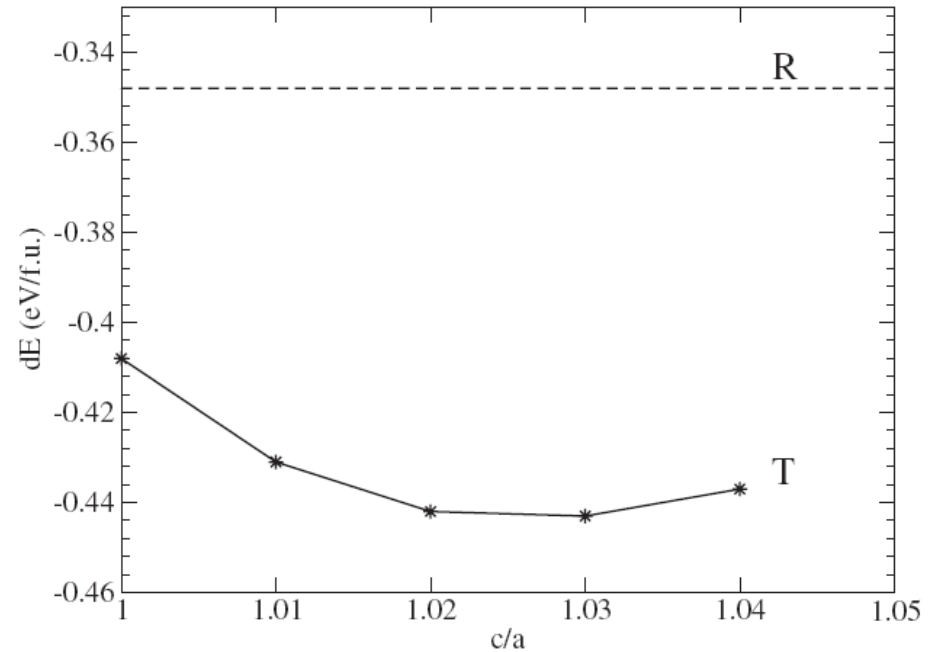
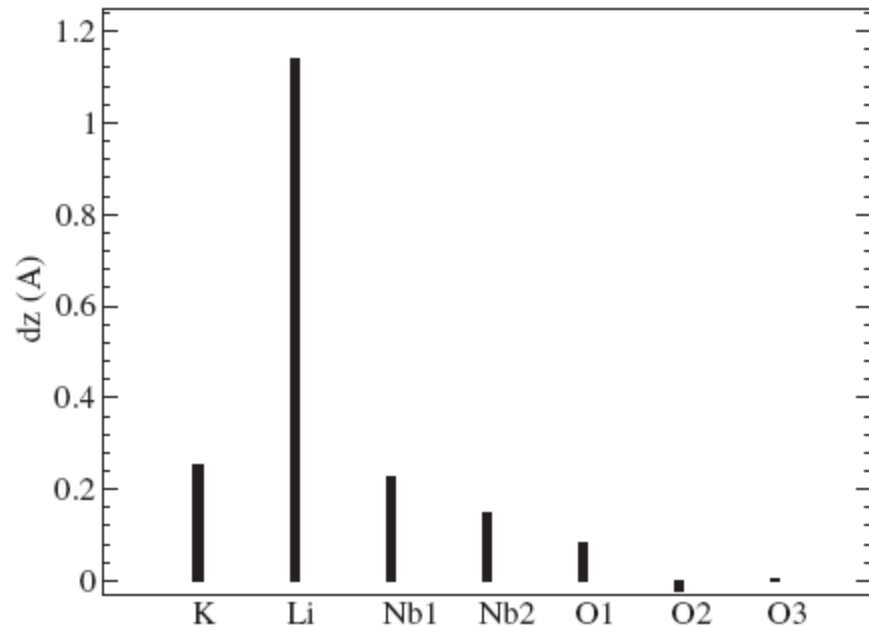
ROTATIONAL MODE



Can we use disorder to exploit the difference in coherence length between rotational and ferroelectric instabilities?

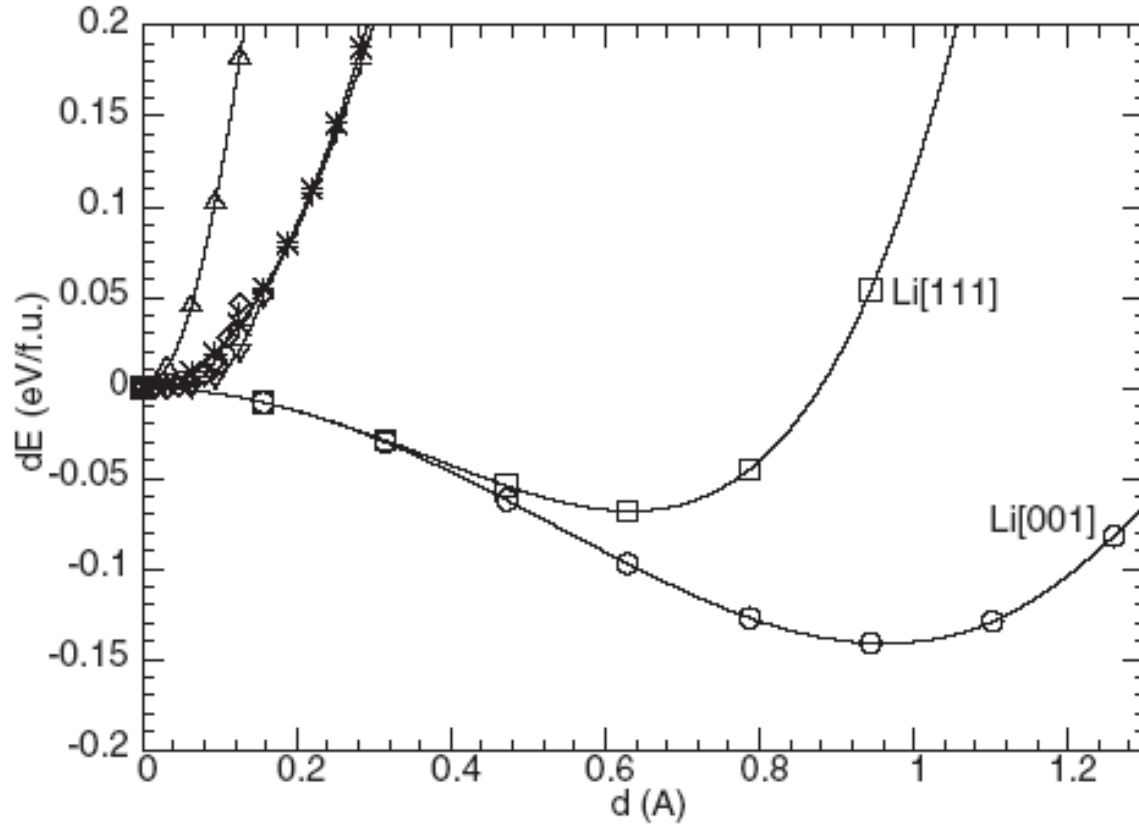
Hypothetical Perovskite: $\text{K}_{0.5}\text{Li}_{0.5}\text{NbO}_3$

- K and Li have very different sizes (1.8Å vs. 1.1Å).
- What if we make a perovskite alloying K and Li on the A-site?



- Strong off-centering of Li (A-site driven ferroelectric) – Tilt does not happen.

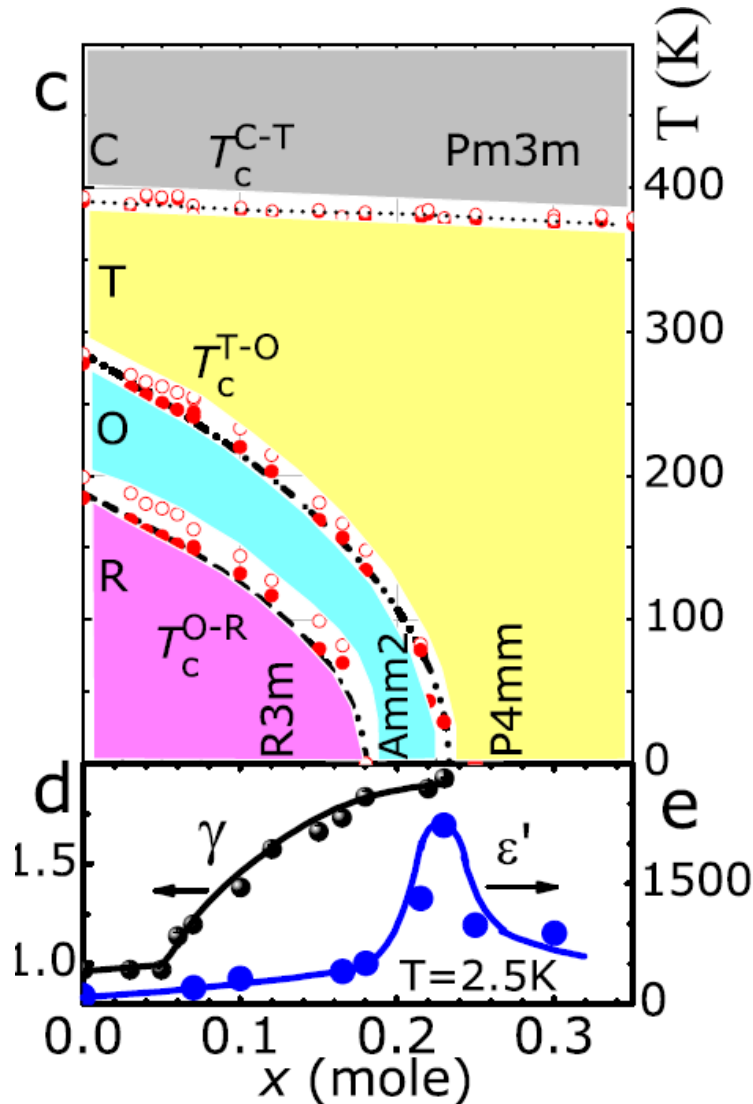
Single ion off-centering



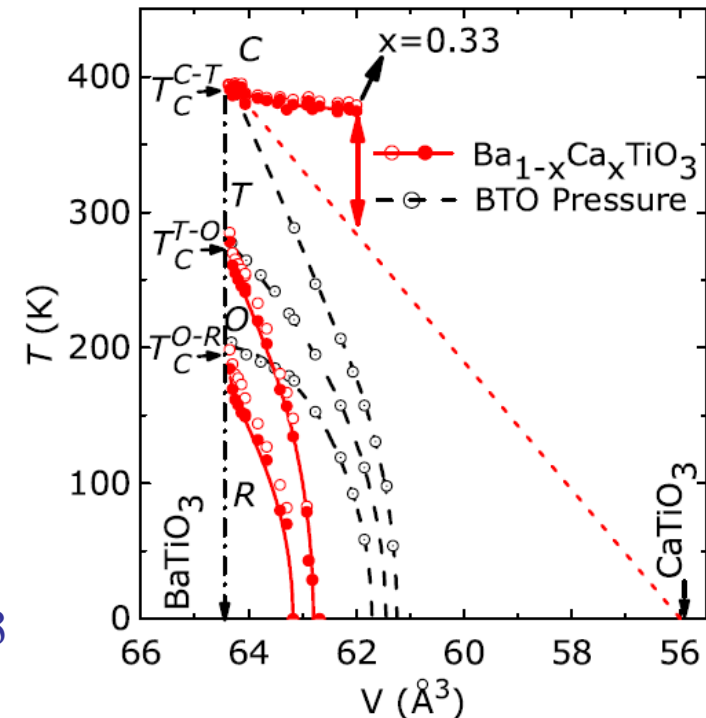
- Reason for tetragonal state is the very large displacement of Li.

Anomalous Phase Diagram of Ferroelectric (Ba, Ca)TiO₃ Single Crystals with Giant Electromechanical Response

Desheng Fu,^{1,2} Mitsuru Itoh,² Shin-ya Koshihara,^{1,3,4} Taichi Kosugi,⁵ and Shinji Tsuneyuki⁵



- 1) T_c is maintained high under Ca alloying even though the average tolerance factor is strongly decreasing.
- 2) The system becomes much more tetragonal as Ca is added.

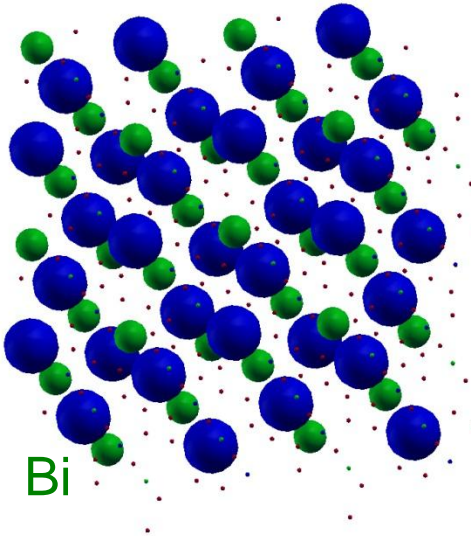


A-Site Alloys with Bi

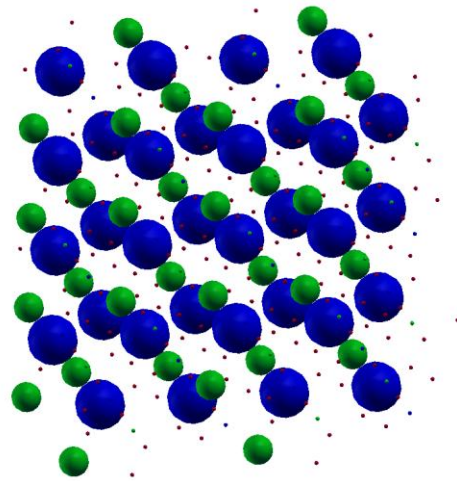
- $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{Zn}_{0.5}\text{Nb}_{0.5}\text{O}_3$ was reported in perovskite structure by Kosyachenko *et al.* [Neorg. Mater. **18**, 1352 (1982)] and evidence pointing towards ferroelectricity was found.
- $\text{Bi}_{0.5}\text{Pb}_{0.5}\text{Zn}_{0.5}\text{Nb}_{0.5}\text{O}_3$ would be the 50-50 solid solution of PZN with hypothetical $\text{BiZn}_{2/3}\text{Nb}_{1/3}\text{O}_3$.
- $(\text{Na},\text{Bi})\text{TiO}_3$ is a known material that has been investigated alone and in alloys with PbTiO_3 and KNbO_3 .
- $\text{Bi}(\text{Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3$ was shown to be a super tetragonal ferroelectric with very high polarization by Suchomel and Davies [APL **86**, 262905 (2005)].

(Bi,Pb)₂ZnNbO₆ Supercells

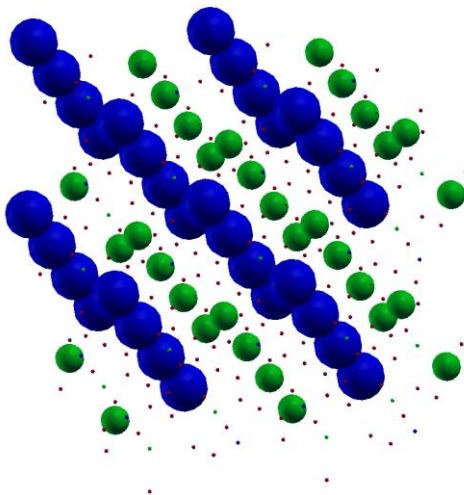
NaCl (111) layers



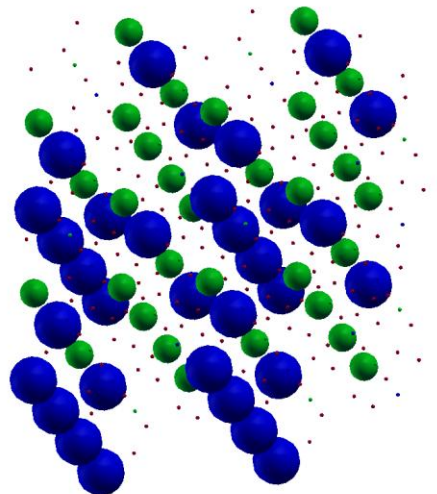
A-type (100) layers



C-type [001] chains



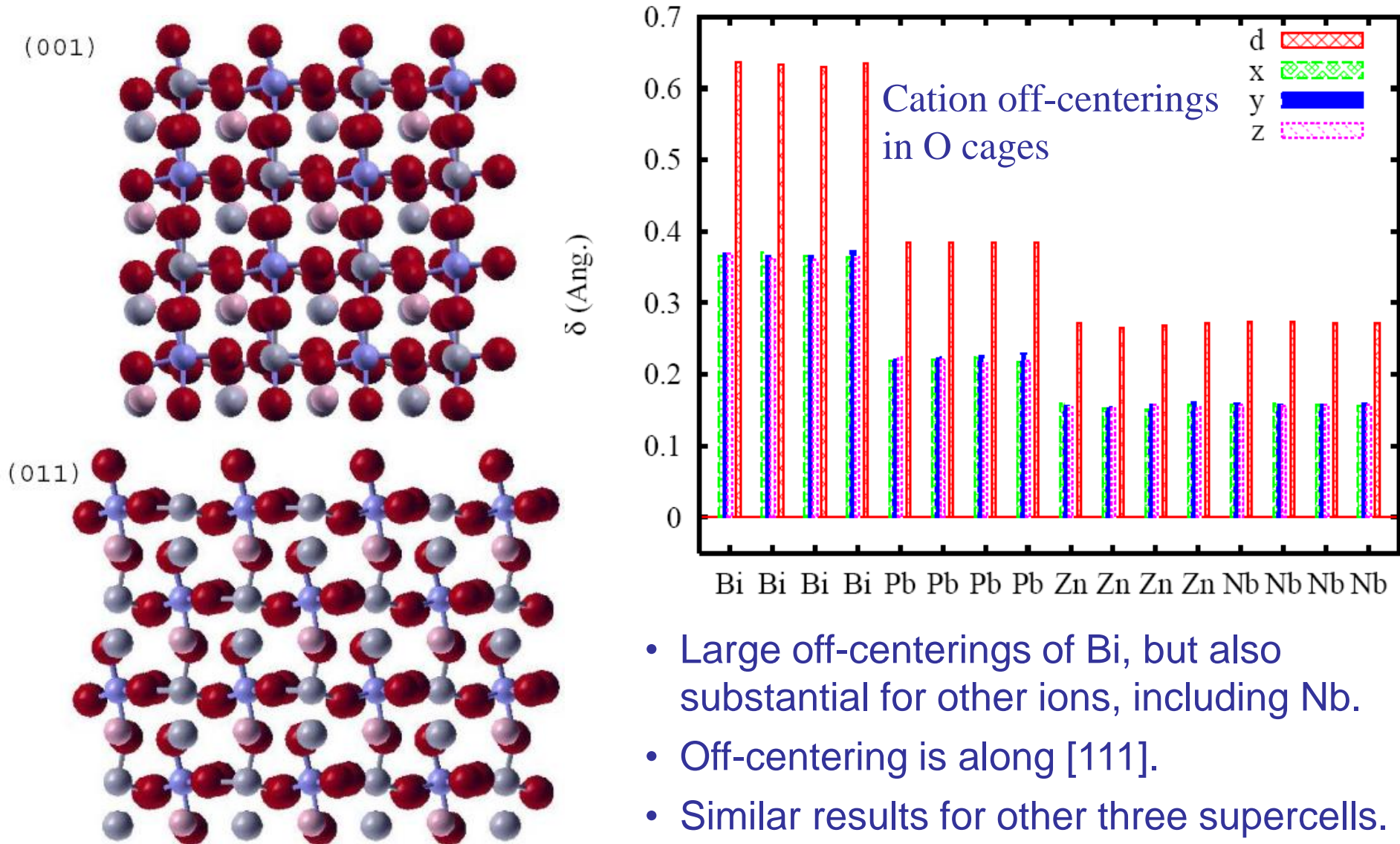
Clusters



- Charge difference of Nb⁵⁺ and Zn²⁺ is 3 → favors chemical ordering.
- PbZn_{1/3}Nb_{2/3}O₃ (PMN) has a two sub-lattice (double perovskite based) structure → should be stronger for Zn:Nb ratio at 1:1.
- Done at LDA lattice parameter → somewhat compressed [3.99 Å for Pb and 3.97 Å for Sr]
- LDA calculations for 40-atom double perovskite supercells with various Bi/Pb orderings and rocksalt Bi/Sr ordering.

BiPbZnNbO₆

Relaxed G-type cell at LDA lattice parameter (3.99 Å), pseudo-cubic



BiPbZnNbO₆

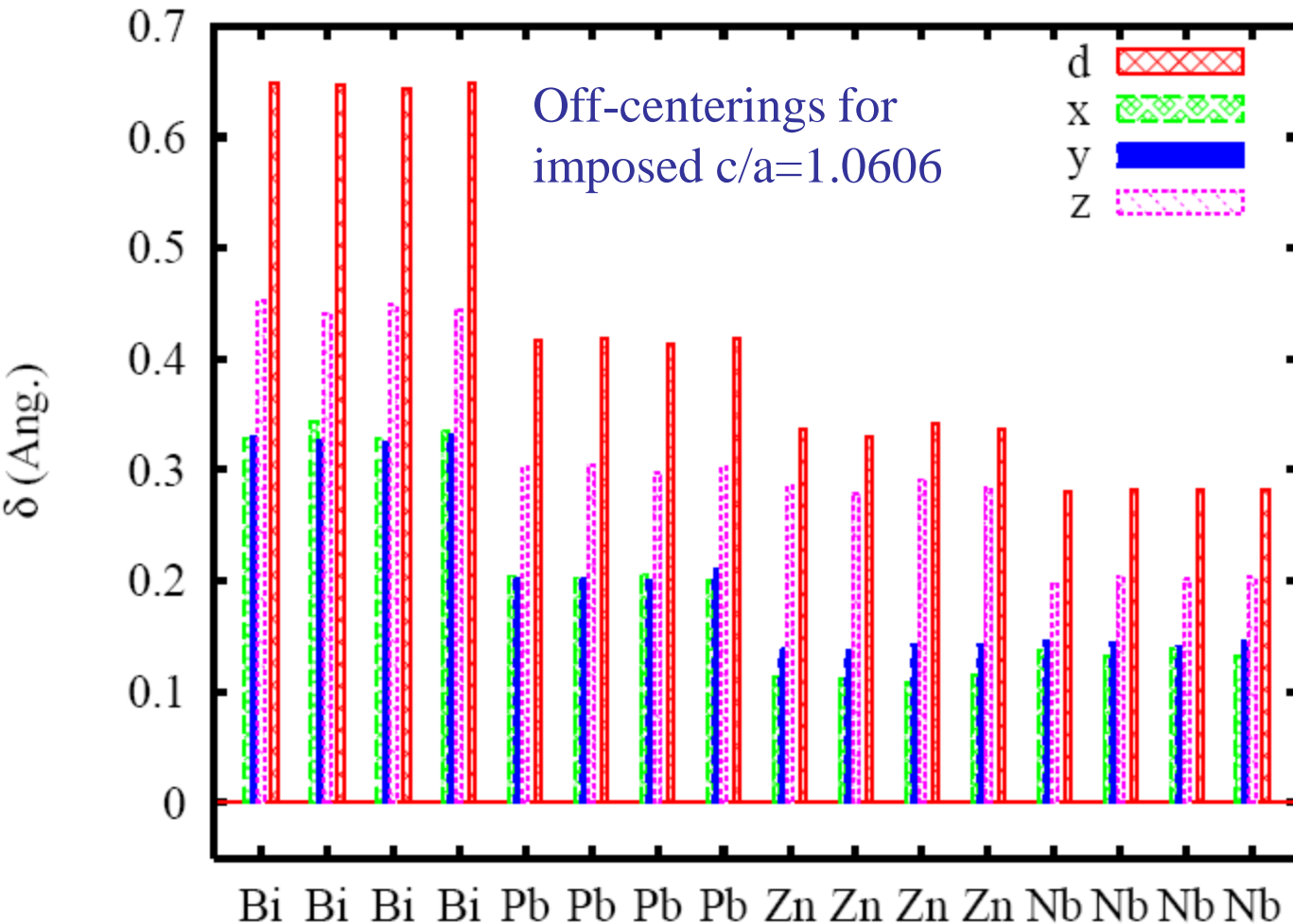
G-type supercell as a function of pseudo-cubic lattice parameter:

$a(\text{\AA})$	$\delta_{\text{Bi}}(\text{\AA})$	$\delta_{\text{Pb}}(\text{\AA})$	$\delta_{\text{Zn}}(\text{\AA})$	$\delta_{\text{Nb}}(\text{\AA})$
3.88	0.50	0.28	0.20	0.22
3.92	0.54	0.31	0.23	0.24
3.98	0.62	0.38	0.26	0.27
3.99	0.64	0.39	0.27	0.27
4.03	0.69	0.44	0.30	0.30
4.07	0.75	0.50	0.35	0.32

- Increasing off-centering with increasing volume, as usual (LDA may underestimate).
- Substantial off-centerings of Nb.

BiPbZnNbO₆

- G-type cell was relaxed as a function of tetragonal strain
- Minimum energy was at a c/a ratio of ~1.015, but this appears to be due to tilts, not ferroelectricity (supercell artifact)



Note that off-centering does not switch to [001] even with large imposed strain.

Polarization: BiSrZnNbO₆ and the Role of Pb

	BiPbZnNbO ₆	BiSrZnNbO ₆
$a(\text{LDA})$	3.99 Å	3.97 Å
$\delta(\text{Bi})$	0.64 Å	0.62 Å
$z^*(\text{Bi})$	4.4	4.4
$\delta(\text{Pb/Sr})$	0.39 Å	0.33 Å
$z^*(\text{Pb/Sr})$	3.6	2.6
$\delta(\text{Zn})$	0.27 Å	0.25 Å
$z^*(\text{Zn})$	2.9	2.8
$\delta(\text{Nb})$	0.27 Å	0.25 Å
$z^*(\text{Nb})$	5.8	5.8
$P(111)$	85 $\mu\text{C}/\text{cm}^2$	79 $\mu\text{C}/\text{cm}^2$

BiSrZnNbO₆

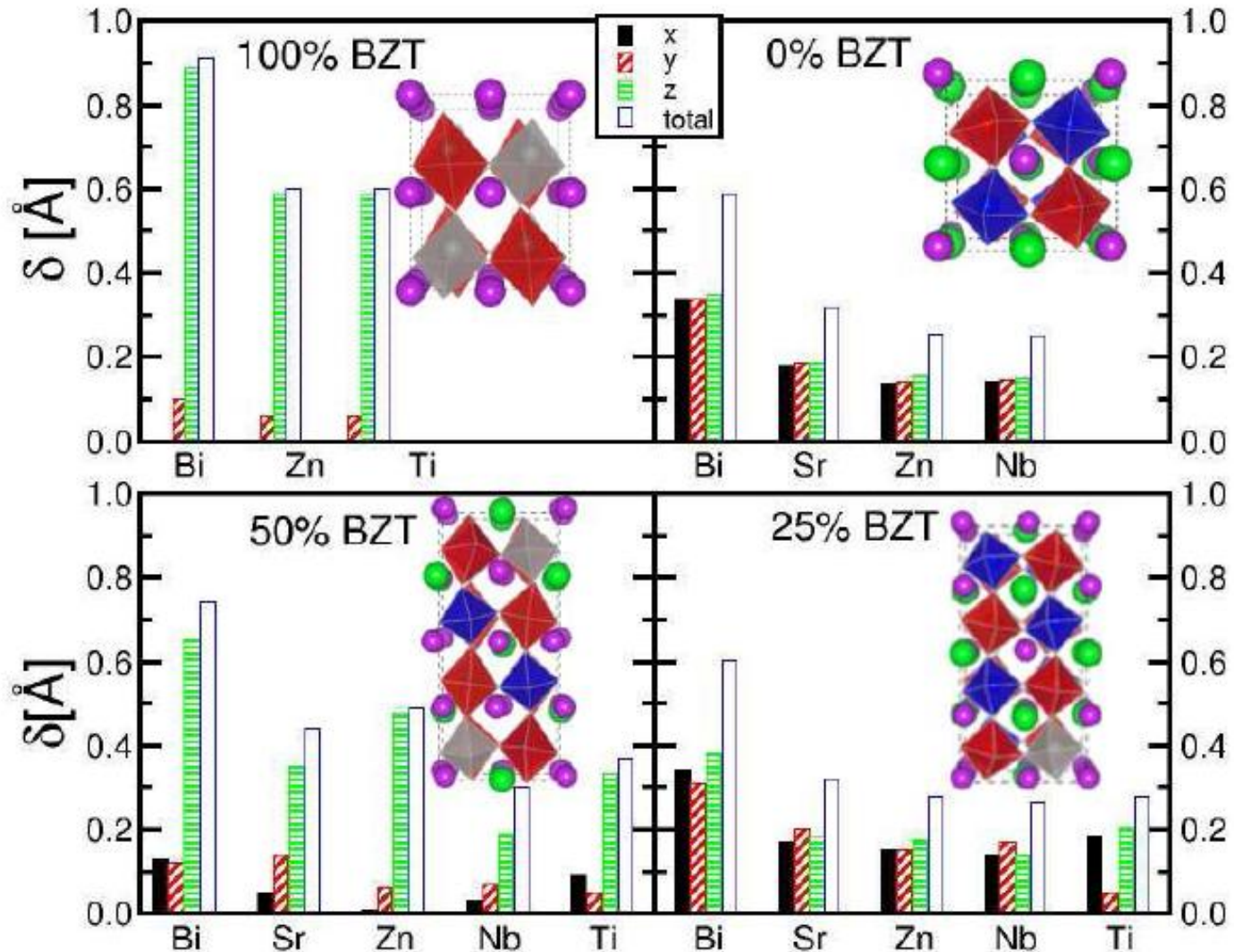
- Known compound that readily forms in perovskite structure.
- Average A-site charge is +2.5 → Av. B-site is +3.5 (better for stability of perovskite).
- Polarization is comparable to pure Bi compounds even though there is only 50% Bi.
- Reason is large Bi displacement & Nb off-centering.

BiSrZnNbO₆ – Bi₂ZnTiO₆ Solid Solution

- Bi(Zn,Ti)O₃ has a very large polarization ~150 μC/cm² but is essentially non-switchable due to super-tetragonality, c/a ~ 1.2 (Suchomel, 2006).
- Can we produce a useful MPB by alloying – key may be to alloy with a strongly R material that produces an MPB far from the BZT end so that it can be switchable.
- We did supercell calculations for the pseudo-binary solid solution with BiSrZnNbO₆.
- We used 40 and 80 atom cells with Zn and (Ti,Nb) on separate sublattices (i.e. double perovskite).

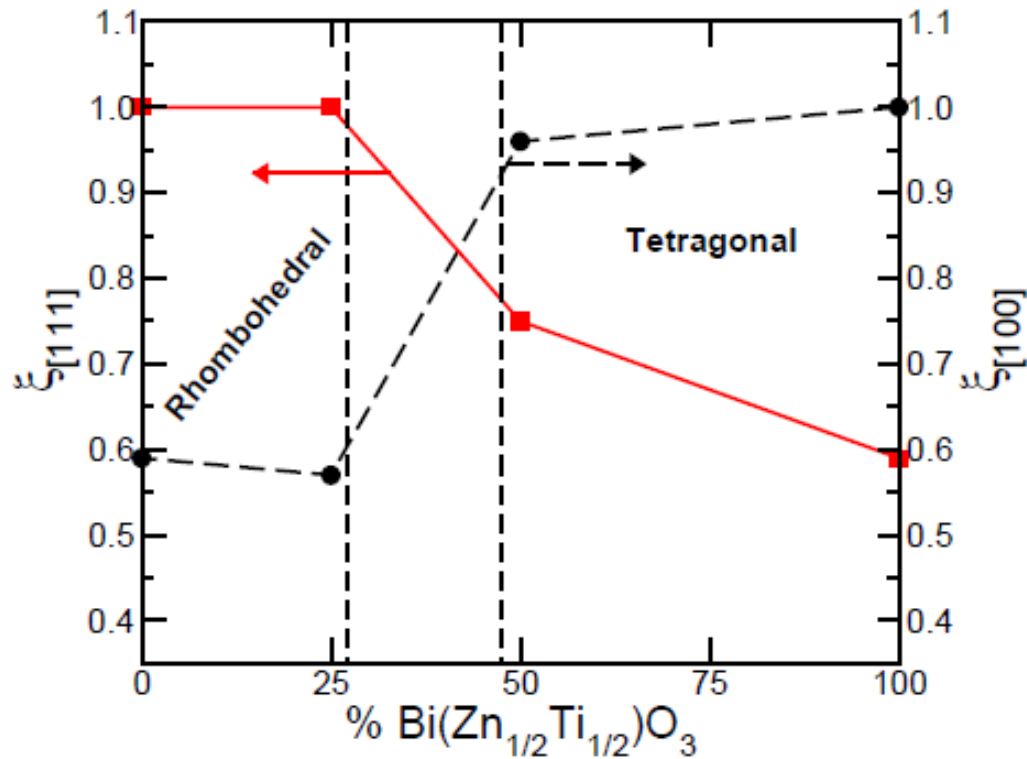
BiSrZnNbO₆ – Bi₂ZnTiO₆ Solid Solution

Average cation off-centerings in supercells:



Proposed Phase Diagram

Direction of P relative to 111 and 100:



% BZT	a [Å]	c/a	P [$\mu\text{C}/\text{cm}^2$]
100	3.74	1.22	142
50	3.84	1.11	114
25	3.95	1.01	81
0	3.95	1.01	77

- We find a region with a possible MPB and high polarization, although the tetragonality on the T side is still very high.

Summary and Conclusions

- It is possible to obtain ferroelectricity in $t < 1$ and $t = 1$ perovskites without relying on Pb or Pb analogues.
- Disorder on the A-site can also be used with Bi.
 - Can obtain high polarization ferroelectricity in materials like $(\text{Bi,Sr})(\text{Zn,Nb})\text{O}_3$
 - Provides a more opportunities for Pb-free materials than pure Bi compounds alone.
- Co-operativity between A-site and B-site off-centerings provides opportunities for new MPB systems.