FIRST-PRINCIPLES STUDY OF PIEZOELECTRIC $(Ba,Ca)(Ti,Zr)O_3$ SOLID SOLUTIONS

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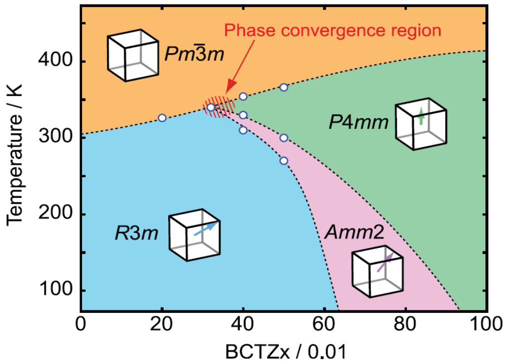
Because of the search of high-performing Pb-free piezoelectric materials ***W. Liu et X. Ren*** designed **$BaTiO_3$-$CaTiO_3$-$BaZrO_3$** pseudo-ternary system by discovering a large electromechanical response *[PRL **103**, 257602 (2009)]*

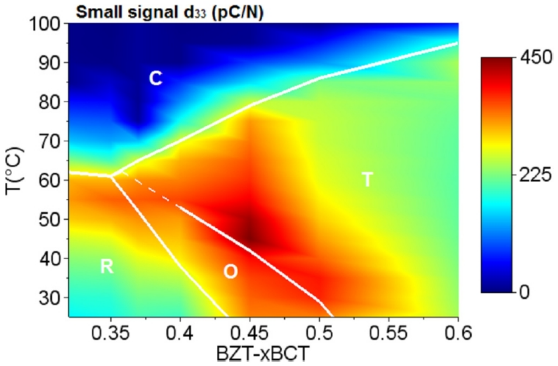
$(Ba_{0.85}Ca_{0.15})(Ti_{0.90}Zr_{0.10})O_3$

d_{33}≈600 pC/N for

existence of convergence region in the phase diagram



Keeble at *al.*,
Appl. Phys. Lett. **102**, 092903 (2013)



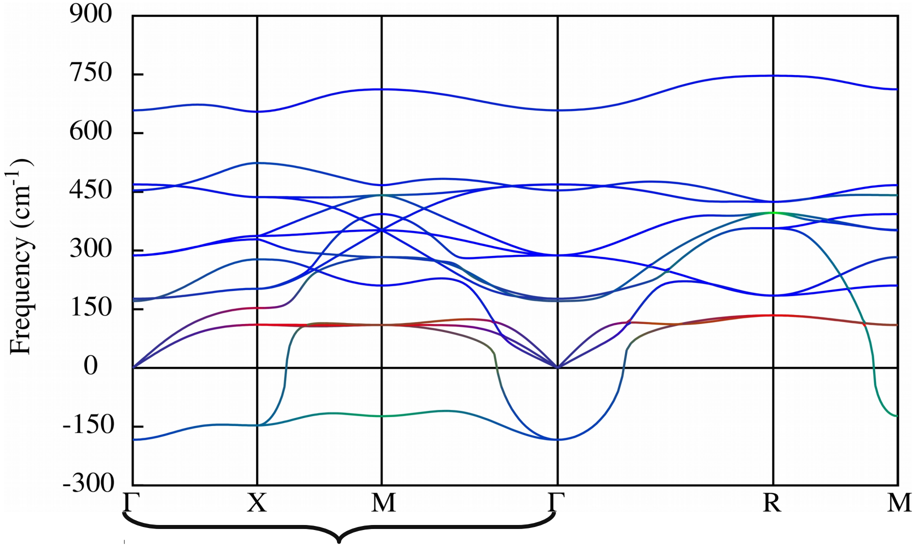
Acosta at *al.*,
Phys. Rev. B, **91**, 104108 (2015)

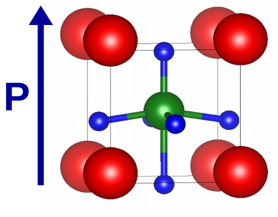
Great number of later experiments, but underlying physics still unclear

Step-by-step analysis
via first-principles calculations
based on DFT (GGA functional)
to unravel microscopic mechanisms
tuning ferroelectric properties
in $(Ba,Ca)(Ti,Zr)O_3$

Parent Compounds : $BaTiO_3$ & $CaTiO_3$

$BaTiO_3$ (a_c = 3.975 Å , *t* = 1.06)





Polar distortion
(Ti,O)-dominated

↓

cooperative atomic **motions**
along correlated **Ti-O-Ti-O chains**
[Ph. Ghosez *et al.*, *Ferroelectrics*, **206**, 205 (1998)]

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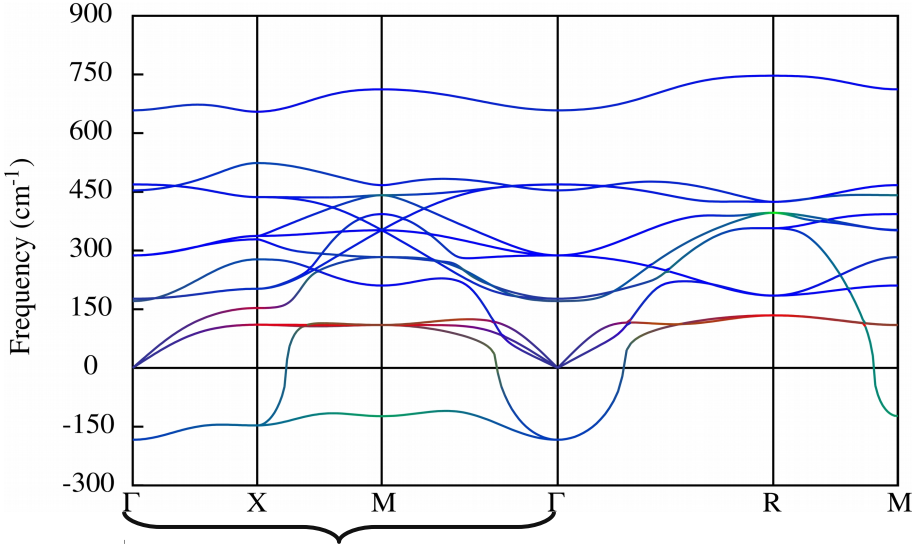

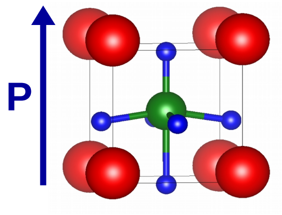

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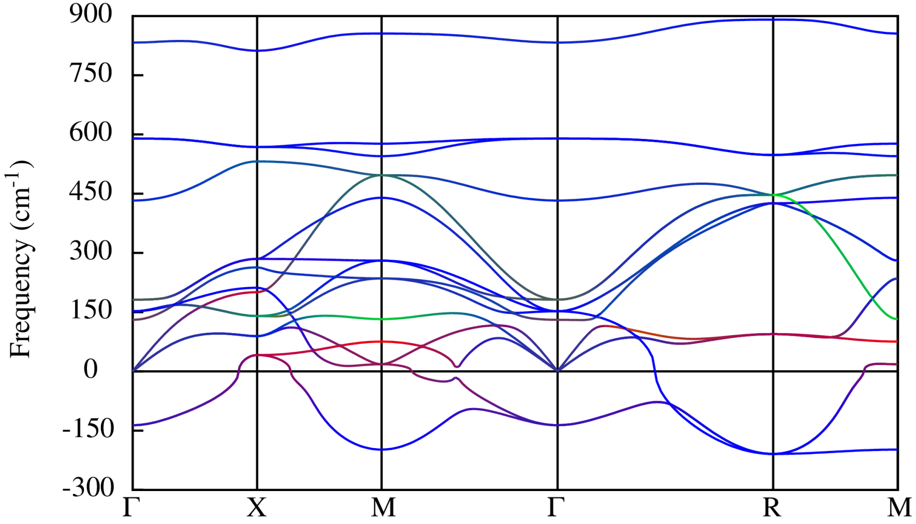
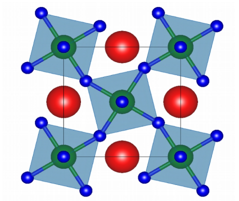
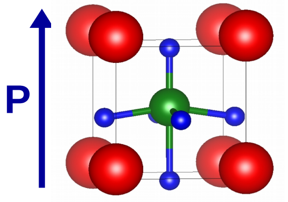
$CaTiO_3$ (a_c = 3.840 Å , *t* = 0.97)

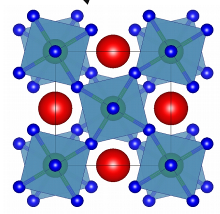




In-phase (+)
O-rotations



Polar distortion
(Ca,O)-dominated

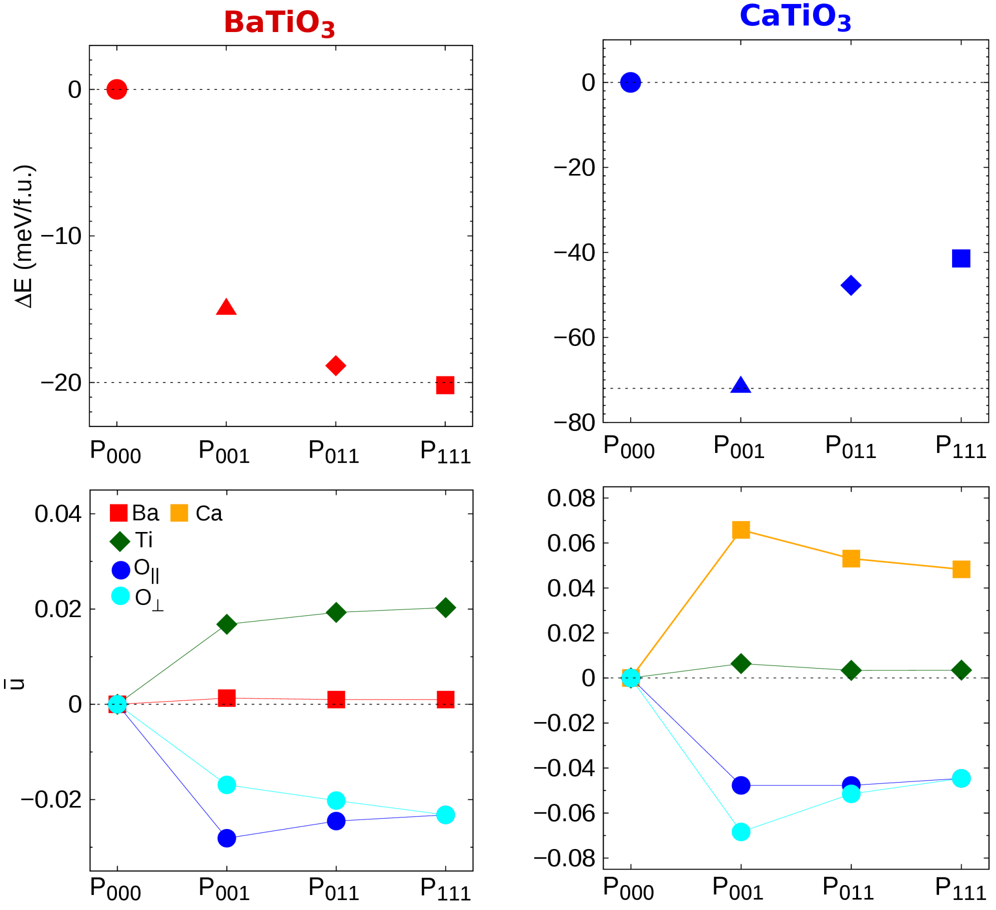


Out-of-phase (-)
O-rotations

Solid Solution : $BaTiO_3$-doping with $CaTiO_3$

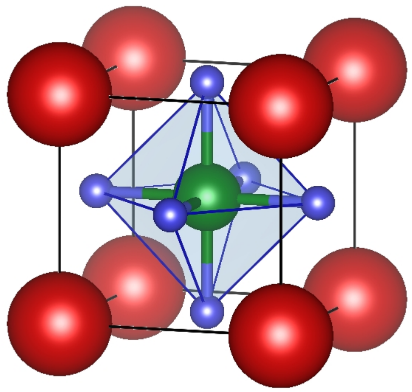
Two key mechanisms characterize **$(Ba,Ca)TiO_3$**

1) Ti-driven distortion + Ca-driven distortion



2) Steric effect

$r_{Ba} > r_{Ca} \leftrightarrow t^{BTO} > 1 , t^{CTO} < 1$

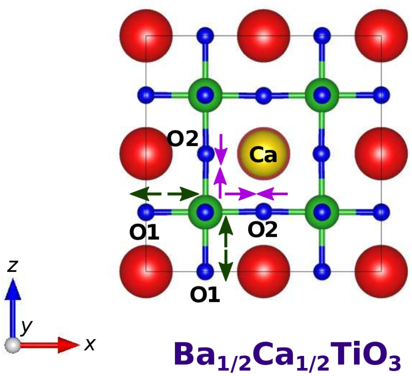


$V_{BTO} > V_{CTO} \leftrightarrow d^{BTO}_{Ti-O} > d^{CTO}_{Ti-O}$

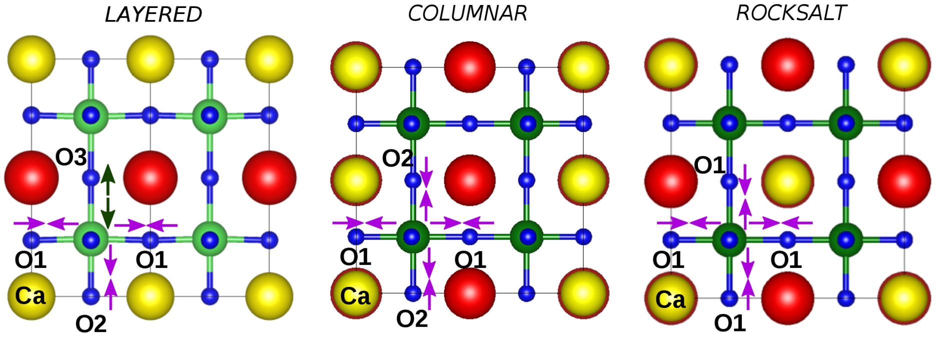
Solid Solution : $BaTiO_3$-doping with $CaTiO_3$

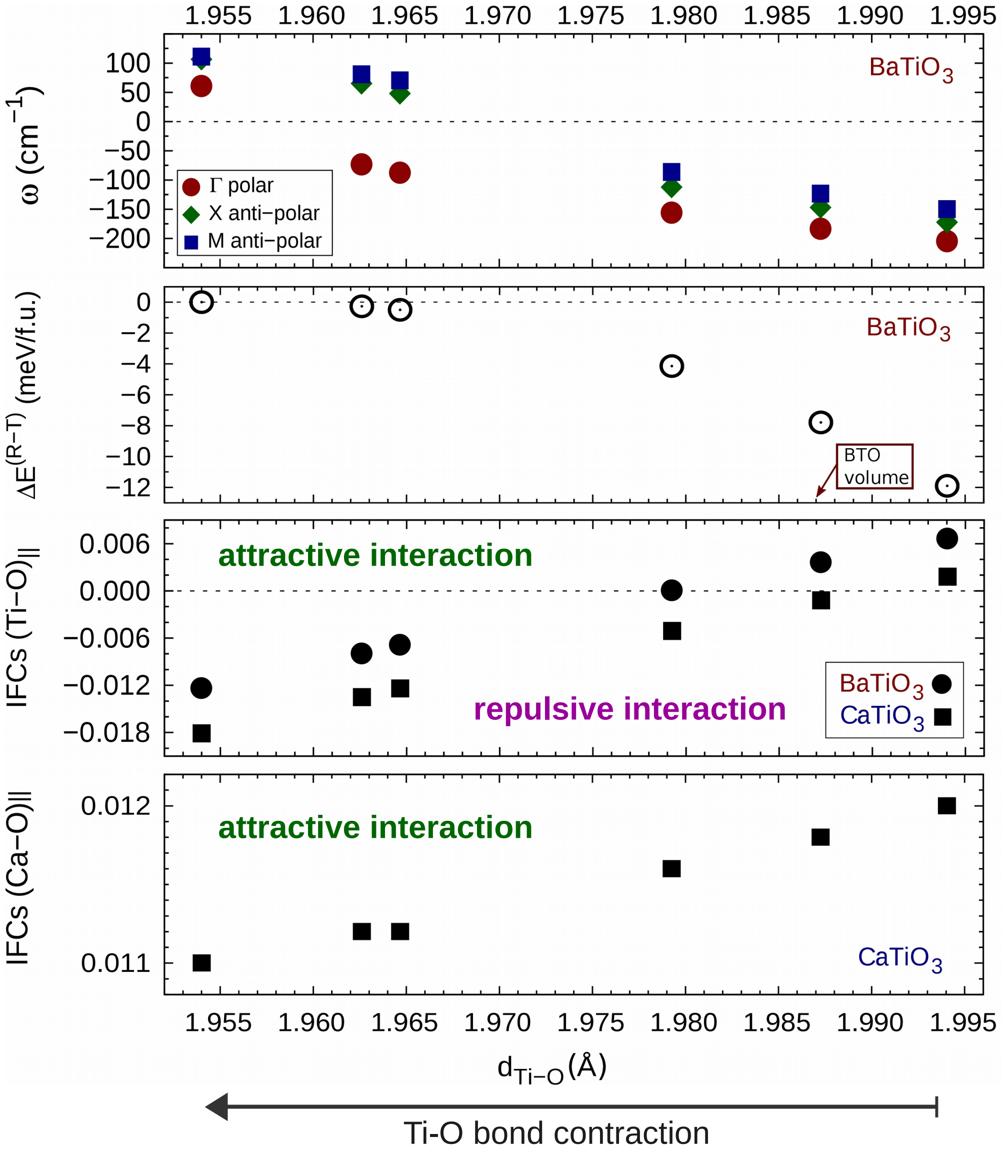
Ca-doping produces
shortening of surrounding Ti-O bonds
weakening Ti-driven distortion
while
Ca-driven distortion remains **unaffected**

$Ba_{7/8}Ca_{1/8}TiO_3$

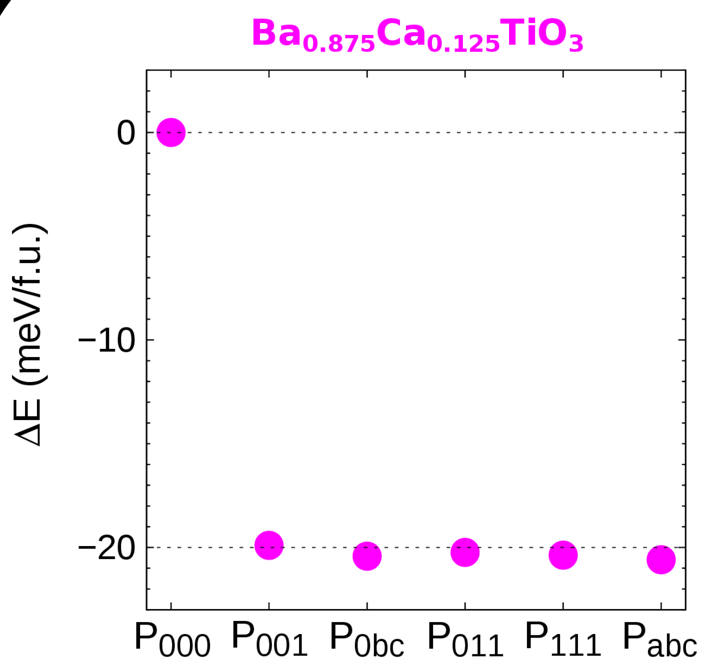


$Ba_{1/2}Ca_{1/2}TiO_3$





Solid Solution : $(Ba,Ca)TiO_3$



$Ba_{0.875}Ca_{0.125}TiO_3$

low Ca-concentration

alternating short/long Ti-O bonds

↓

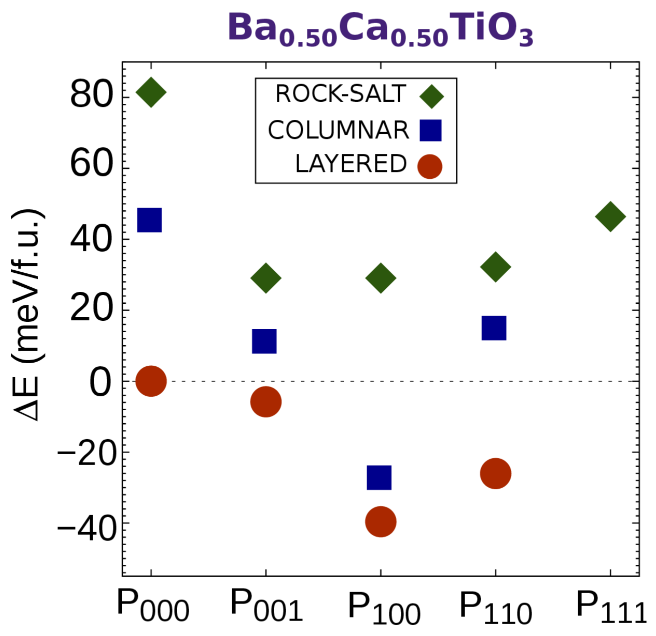
Competition
attractive/repulsive Ti-O forces

↓

Competitive Ca / Ti driven
mechanisms

↓

Competition of various polar states



$Ba_{0.50}Ca_{0.50}TiO_3$

higher Ca-concentration

overall compressed Ti-O bonds

↓

repulsive Ti-O forces

↓

Dominant Ca-driven mechanisms

↓

Spread energetics
with favored *T*-like states

Solid Solution : $(Ba,Ca)TiO_3$

low Ca-concentration

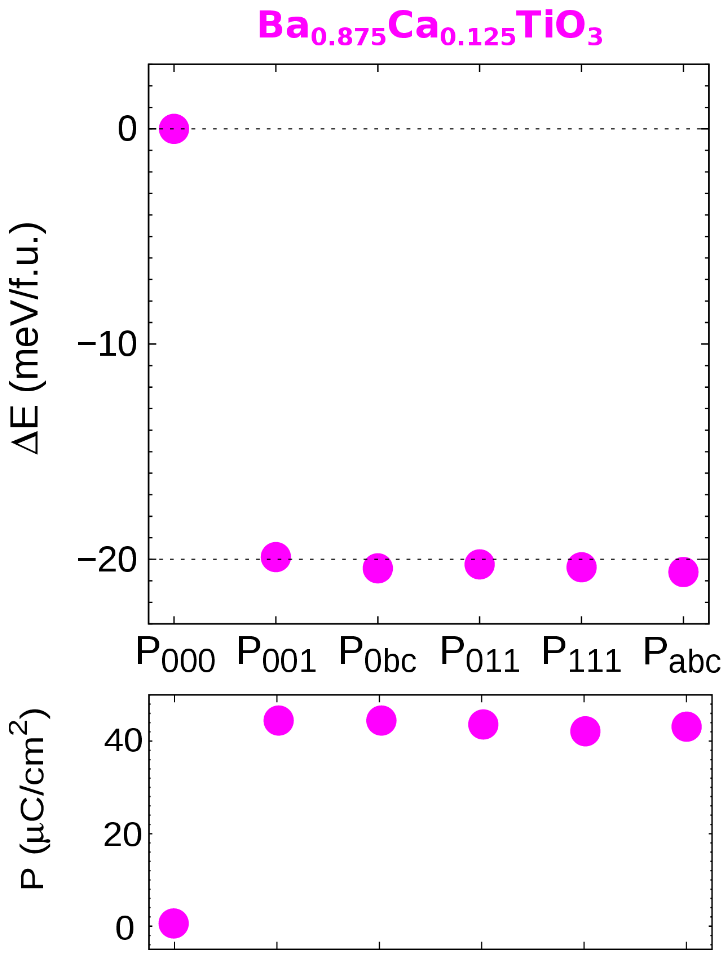
Degeneracy of polar phases

=

Isotropy of energy landscape

- Emergence of monoclinic phases
- Same values of *P*
- Enhanced piezo-response

***R3m* phase**	**d_{33} (pC/N)**	**d_{22} (pC/N)**	**d_{15} (pC/N)**
$B_{7/8}C_{1/8}TO$	16	344	1455
BTO	15	76	270



Solid Solution : (Ba,Ca)TiO_3

$(1-x)BaTiO_3 + (x)CaTiO_3$

↓

Evolution with *x* from *B*-driven into *A*-driven ferroelectricity

↓

For low Ca-concentration the 2 mechanisms compete

↓

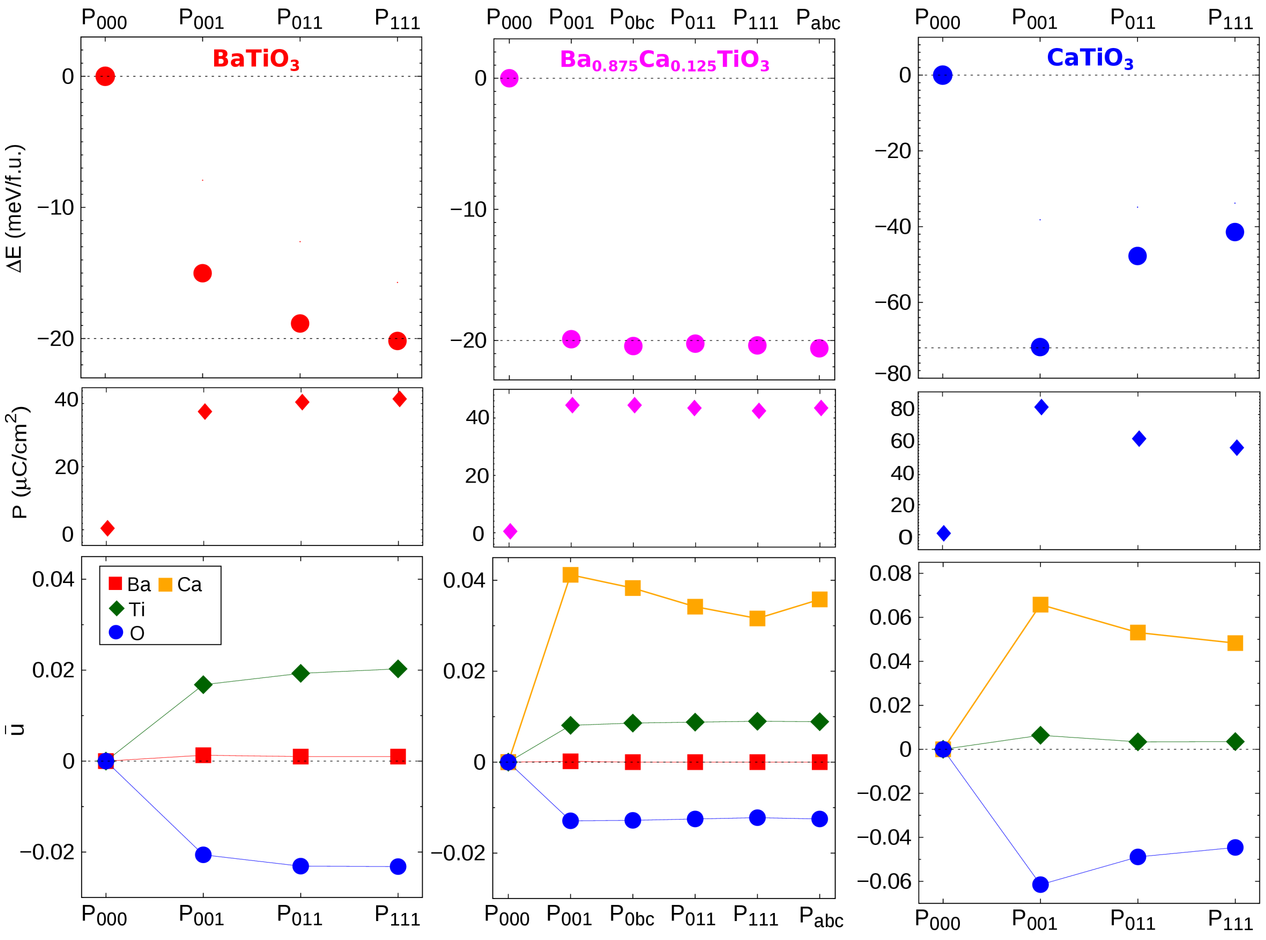
Vanishing energy barrier between different polar states

↓

Isotropic polarization

↓

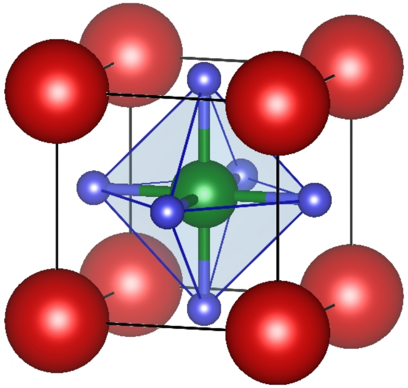
Enhanced piezoelectric response



- ArXiv.org > cond-mat > arXiv: 1801.08886

Parent Compounds : $BaZrO_3$

Two key factors characterize **$BaZrO_3$**

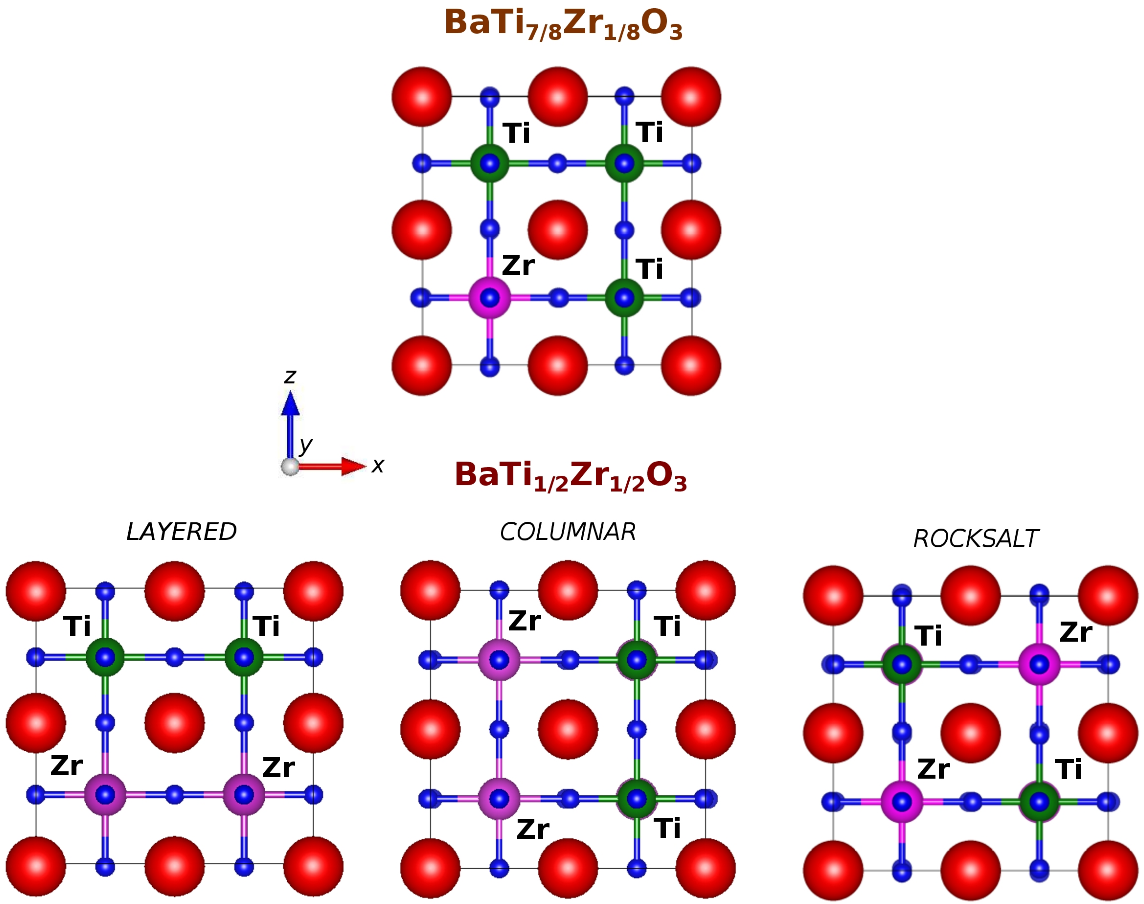


1) $t = \frac{(r_A + r_O)}{\sqrt{2}(r_B + r_O)} = 1 \longrightarrow$ ***A*** **and B fit ideal cubic perovskite**

2) Repulsive Zr-O interaction ↔ Zr polar inactive

Solid Solution : $BaTiO_3$-doping with $BaZrO_3$

Zr introduces **local break** of correlated **Ti-O-Ti-O chains sustaining $BaTiO_3$-polar distortion**



$BaTi_{7/8}Zr_{1/8}O_3$

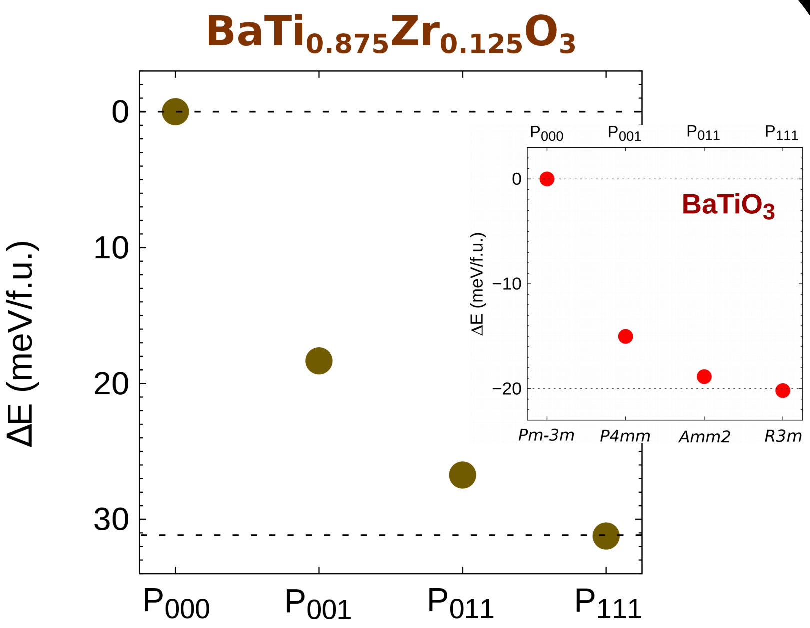
$BaTi_{1/2}Zr_{1/2}O_3$

LAYERED

COLUMNAR

ROCKSALT

Solid Solution : $Ba(Ti,Zr)O_3$



low Zr-concentration

Local Zr-O-Ti-O chains

↓

Prevention
local polar distortion

↓

reduction
total polarization

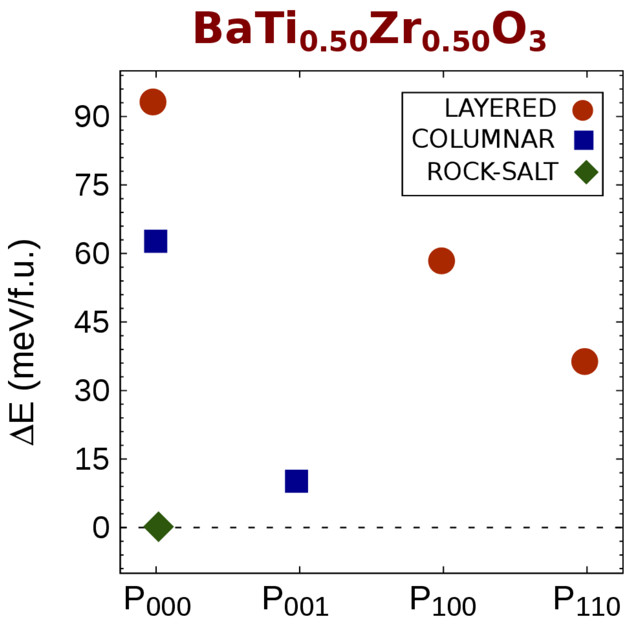
Bigger Zr size than Ti

↓

Volume increase

↓

Energetic favor
R3m-phase



higher Zr-concentration

Isotropic surrounding environment
rocksalt- like preferred

↓

No Ti-O-Ti-O chains in any
direction

↓

Paraelectric ground-state

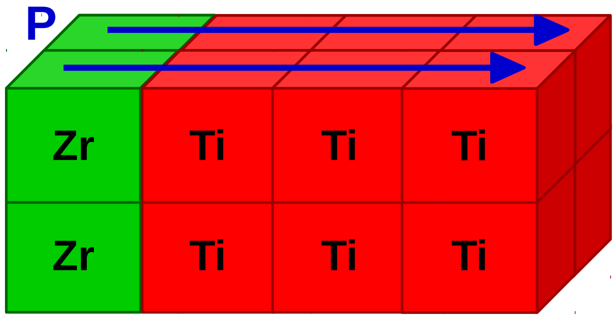
Solid Solution : $Ba(Ti,Zr)O_3$

$(1\text{-}y)BaTiO_3 + (y)BaZrO_3$

Zr-Ti correlation globally weakens $BaTiO_3$-like polar distortion with increasing *y . . .*

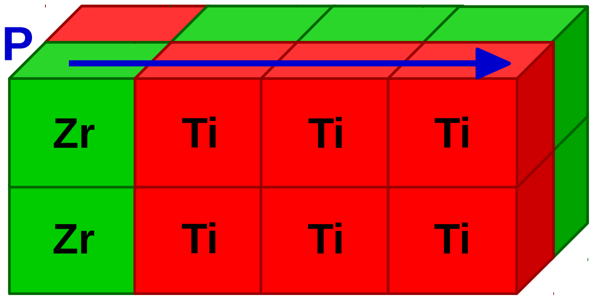
. . .But, *can the Zr-Ti correlation locally make Zr polar active?*

$BaZrO_3$/$m$$BaTiO_3$ system : Ti – Zr correlation

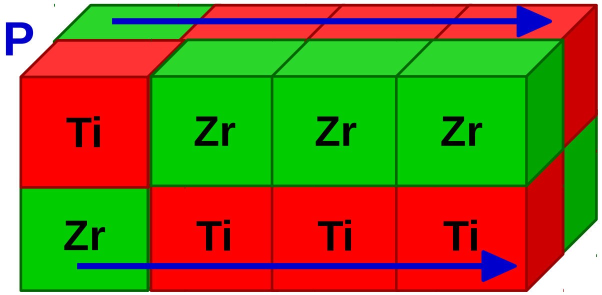


1x1xL

$L \geq 3$ ($m \geq 2$) homogeneous
P along **Zr-O-Ti-O-Ti-O**
↓
Polar activation of Zr



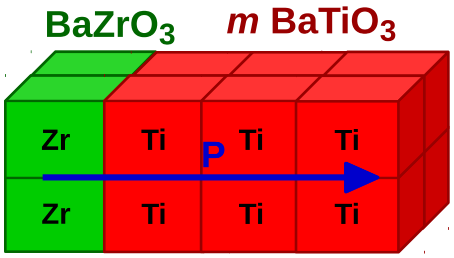
1x2xL

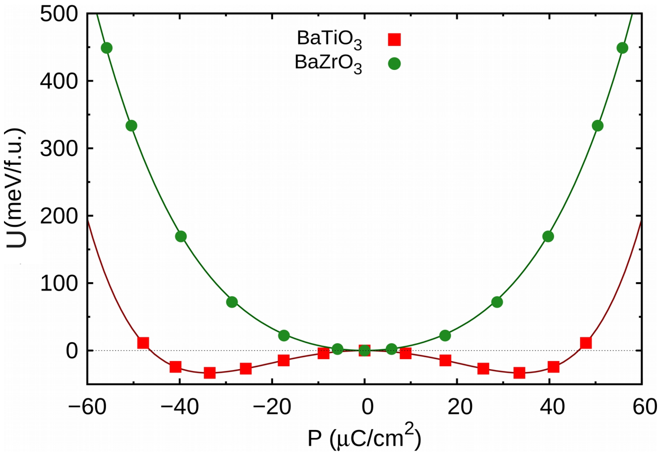


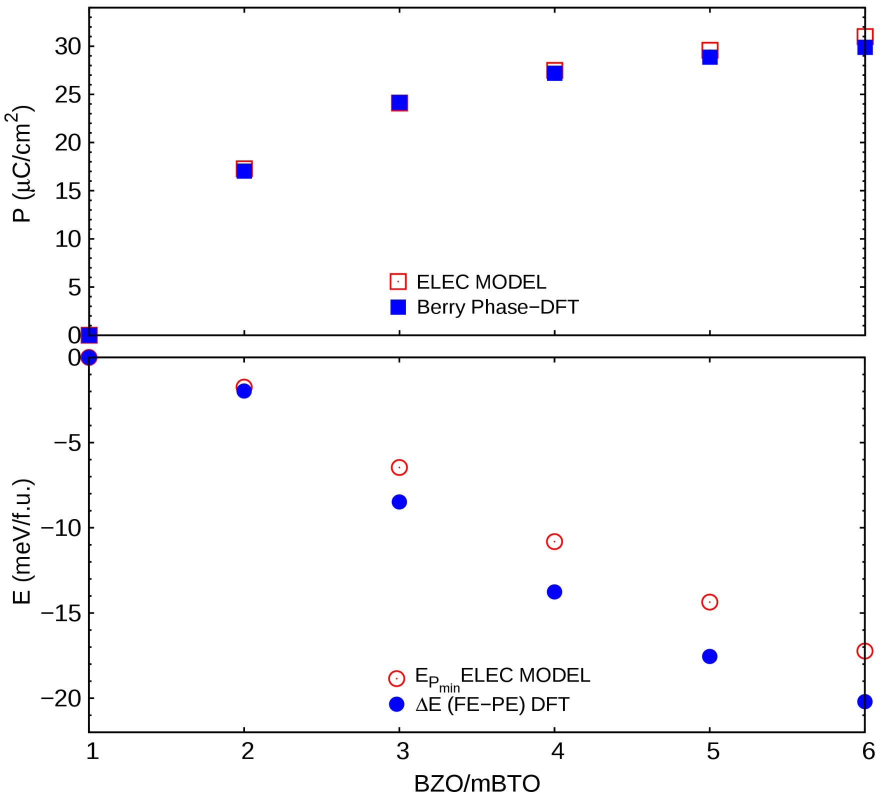
2x2xL

$BaZrO_3/mBaTiO_3$ system : Ti – Zr correlation

Electrostatic Zr-Ti coupling
forces Zr-polar activation to sustain uniform P







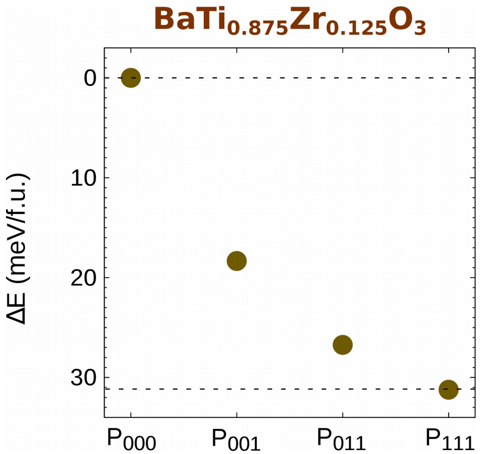
$$E(P;m) \approx U_{BZO}(P) + mU_{BTO}(P)$$

$$\equiv$$

$P_{BZO} = P_{BTO}$ → zero electrostatic energy cost

Solid Solution : $Ba(Ti,Zr)O_3$

$(1-y)BaTiO_3 + (y)BaZrO_3$



Progressive weakening of ferroelectricity with increasing Zr-doping

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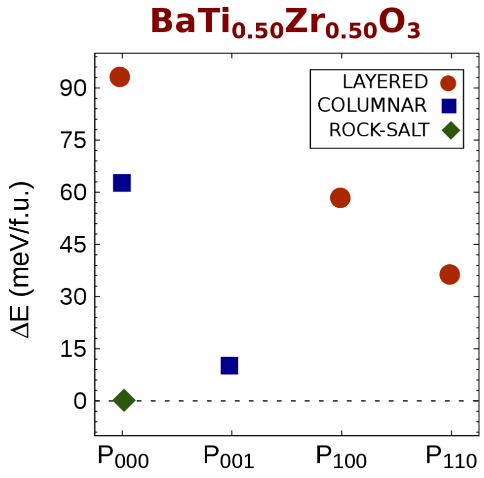
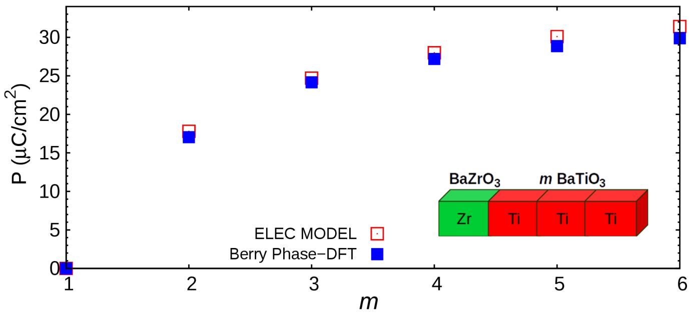
y≈0.30 limit for ferroelectric BTZ

HOWEVER

Ferroelectric domains locally preserved in Ti-rich region via Ti-O-Ti-O and Zr-O-Ti-O-Ti-O dipoles





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(Ba,Ca)TiO$_3$ & Ba(Ti,Zr)O$_3$ toward (Ba,Ca)(Ti,Zr)O$_3$

low Ca-concentration

Competition

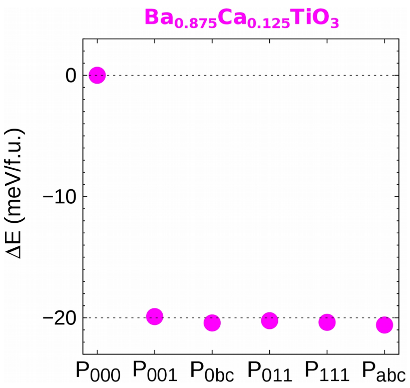
B- and *A*- type ferroelectricity

↓

Low energy barrier between polar phases

↓

Enhanced piezoelectric response



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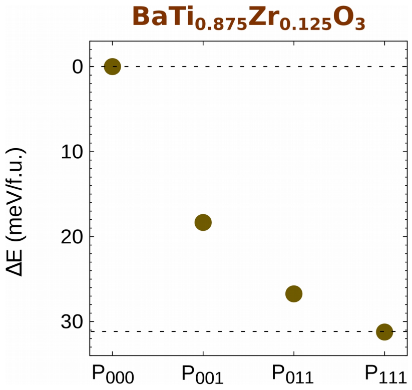

low Zr-concentration

Strong preference

R3m-like phase

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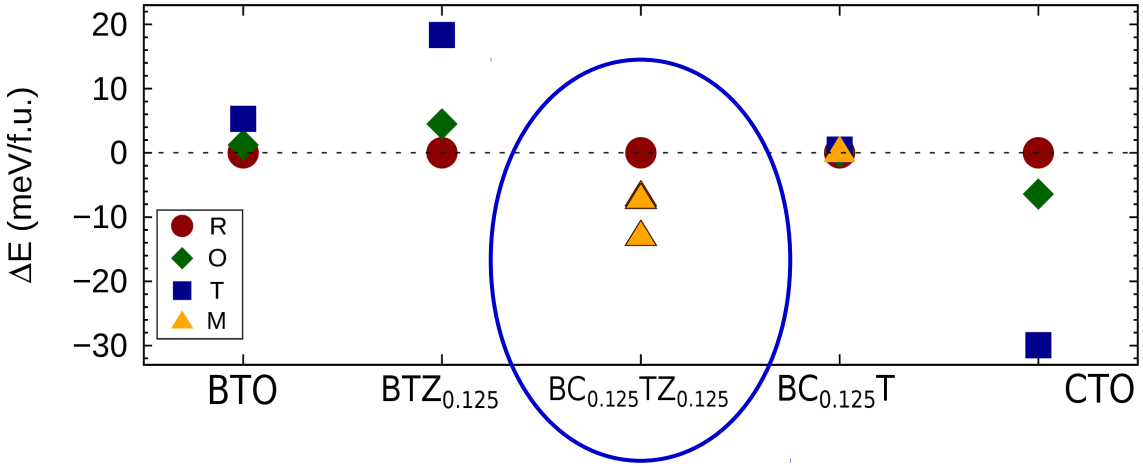
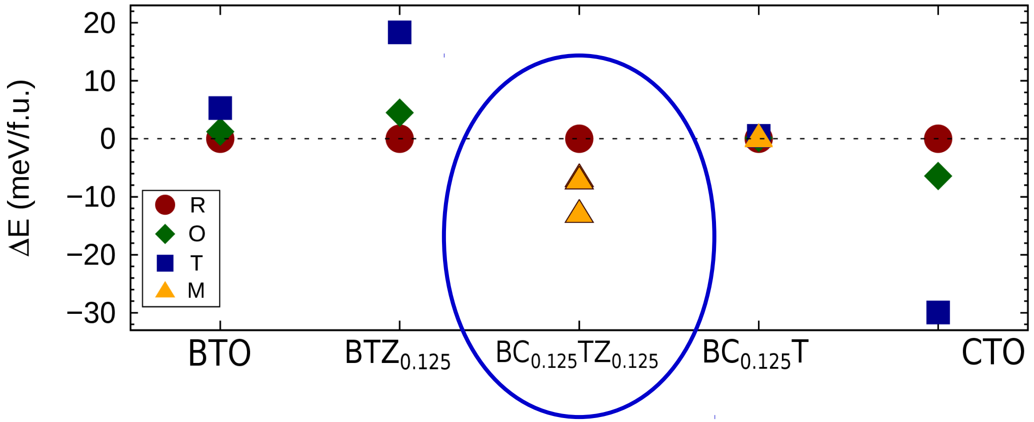


Appearance of different monoclinic phases *Cm*-like close in energy

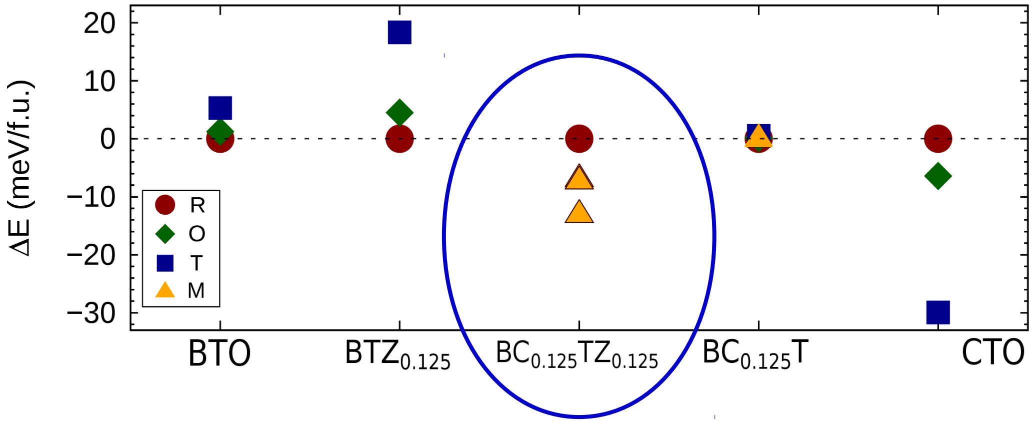
Outlook: $(Ba,Ca)(Ti,Zr)O_3$



Can this landscape justify the enhanced piezoelectricity in BCTZ with low Ca- and Zr- concentration?

- Part 1 on ArXiv.org > cond-mat > arXiv: 1801.08886

Outlook: $(Ba,Ca)(Ti,Zr)O_3$



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Thank you
for your attention

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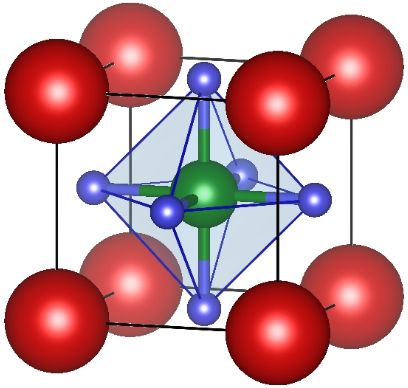
Two key factors characterize
$BaTiO_3$



1) $$t = \frac{(r_A+r_O)}{\sqrt{2}(r_B+r_O)} > 1 \longrightarrow$$ ***B*** **too small**

2) Destabilizing Ti-O interaction

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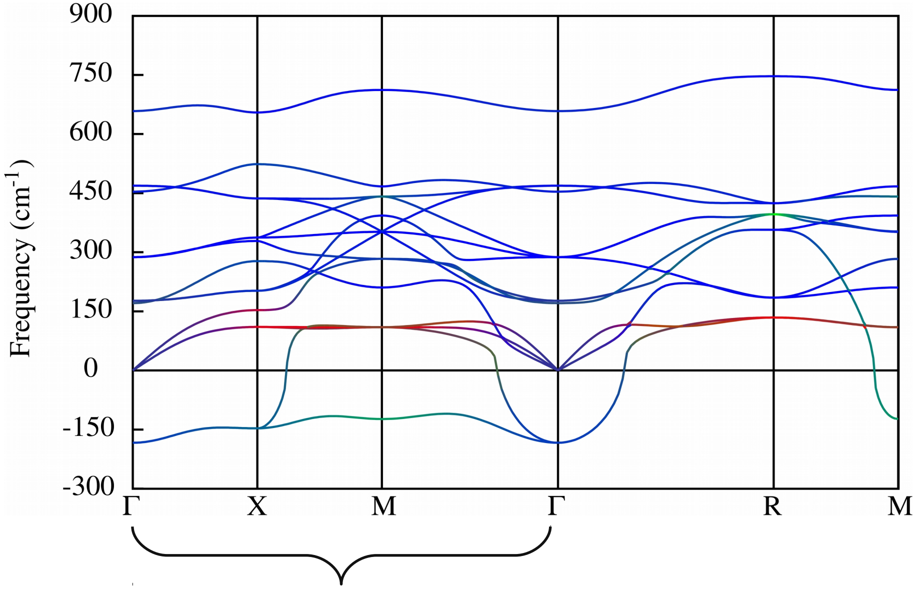
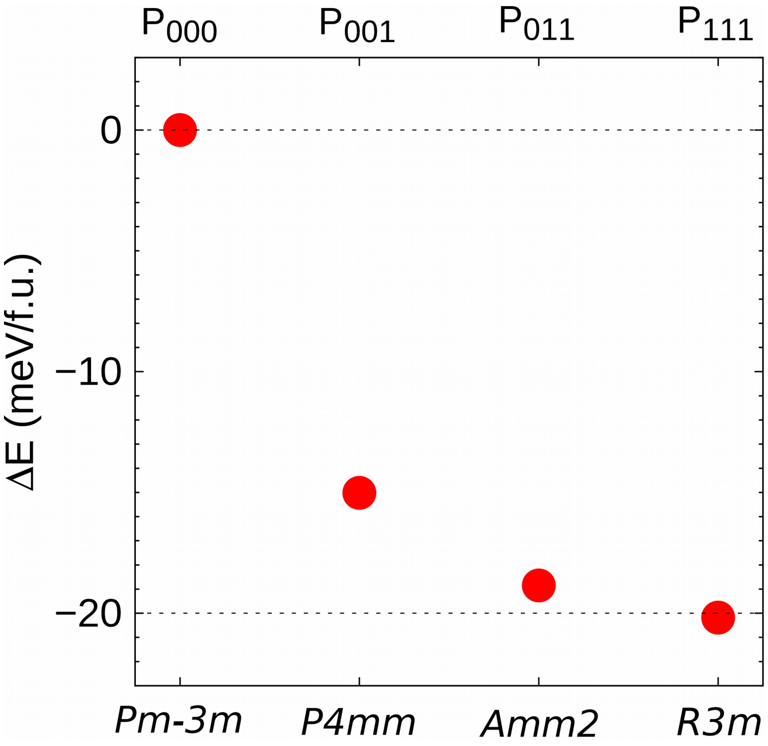


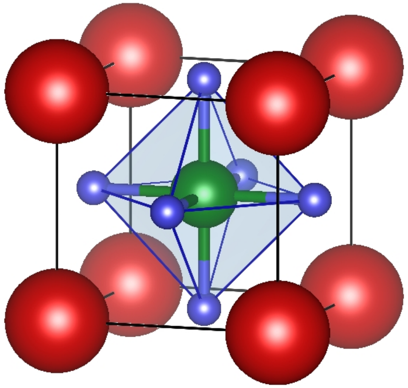
Polar-antipolar unstable branch
≡
chain-like instability in real space
↓
cooperative atomic motions
along correlated Ti-O-Ti-O chains
[Ph. Ghosez *et al.*, *Ferroelectrics*, **206**, 205 (1998)]

3 polar states in the phase diagram
with **stabilization** of the ***R3m*-phase**



Parent Compounds : $CaTiO_3$

Two key factors characterize
$CaTiO_3$

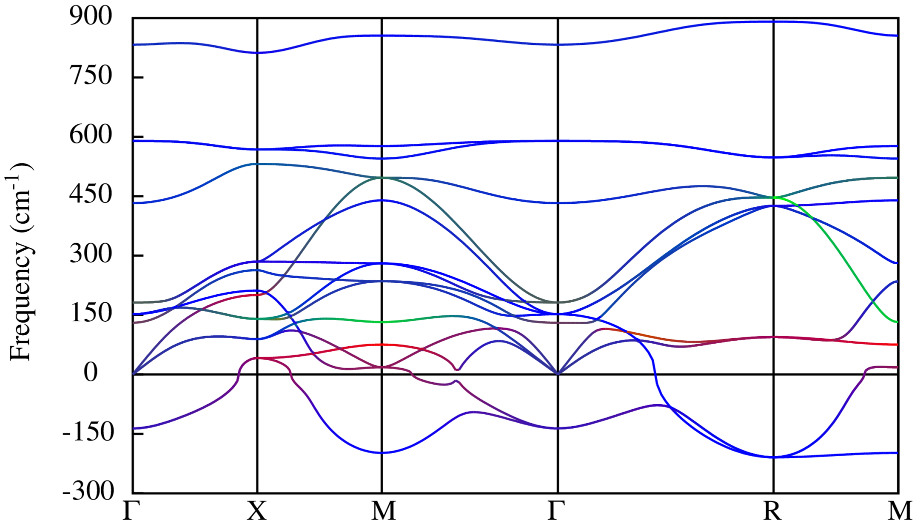


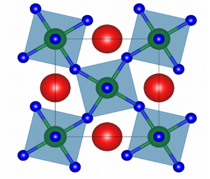
1) $t = \dfrac{(r_A+r_O)}{\sqrt{2}(r_B+r_O)} < 1 \longrightarrow$ ***A*** **too small**

2) Destabilizing Ca-O interaction

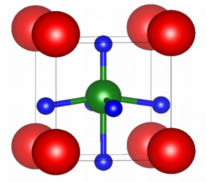
Parent Compounds : $CaTiO_3$

$CaTiO_3$ (a_c = 3.840 Å , t = 0.97)

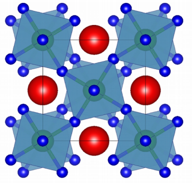




In-phase (+) rotations

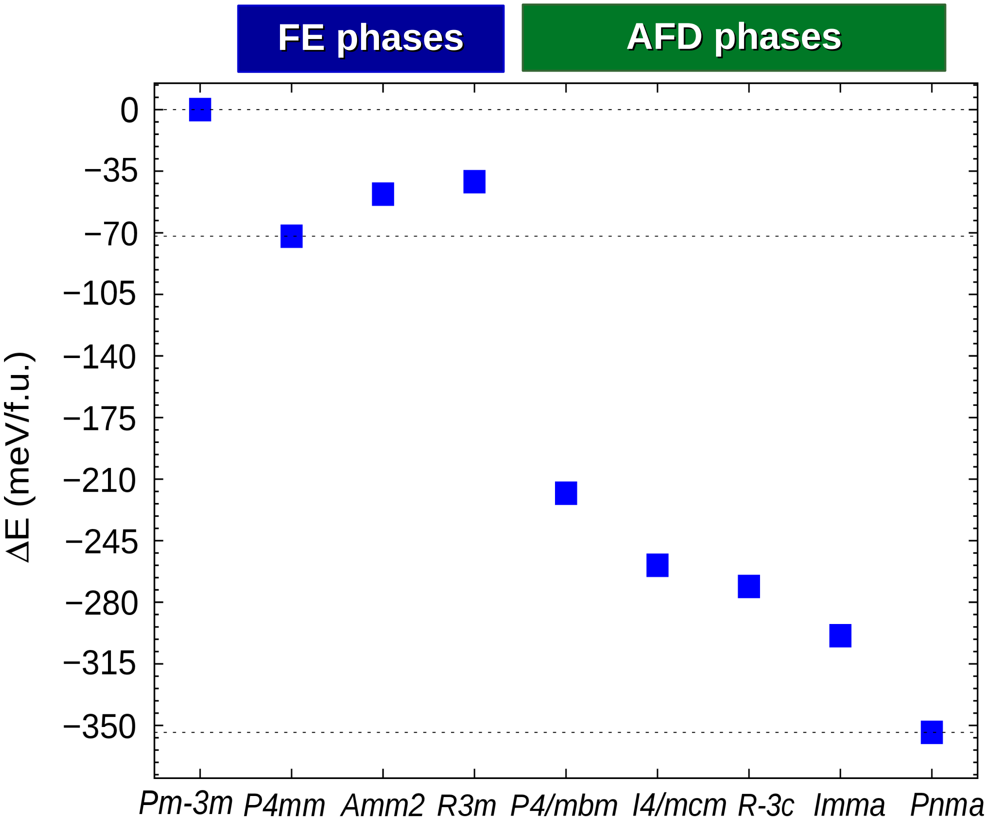


Polar distortion



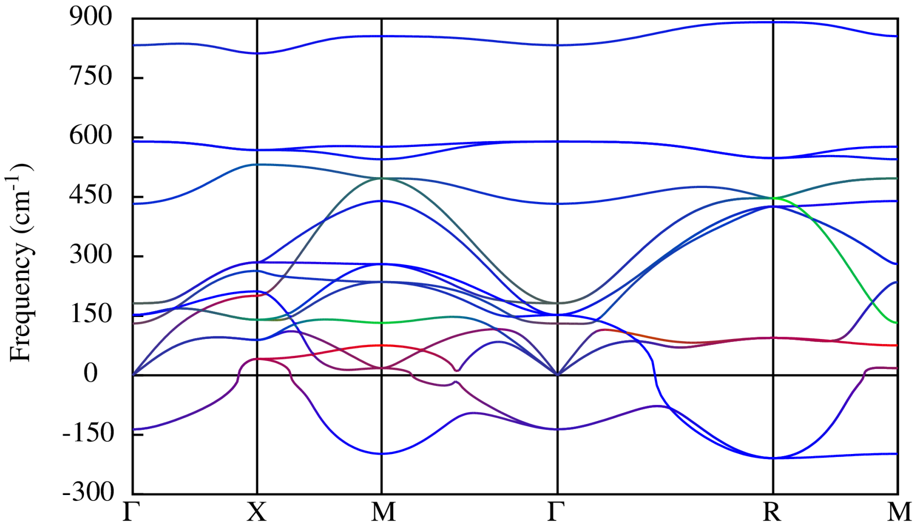
Out-of-phase (-) rotations

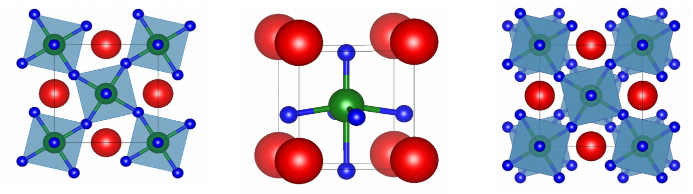
Spread energy landscape
with paraelectric *Pnma* ground-state



Parent Compounds : $CaTiO_3$

$CaTiO_3$ (a_c = 3.840 Å , *t* = 0.97)





In-phase (+) rotations

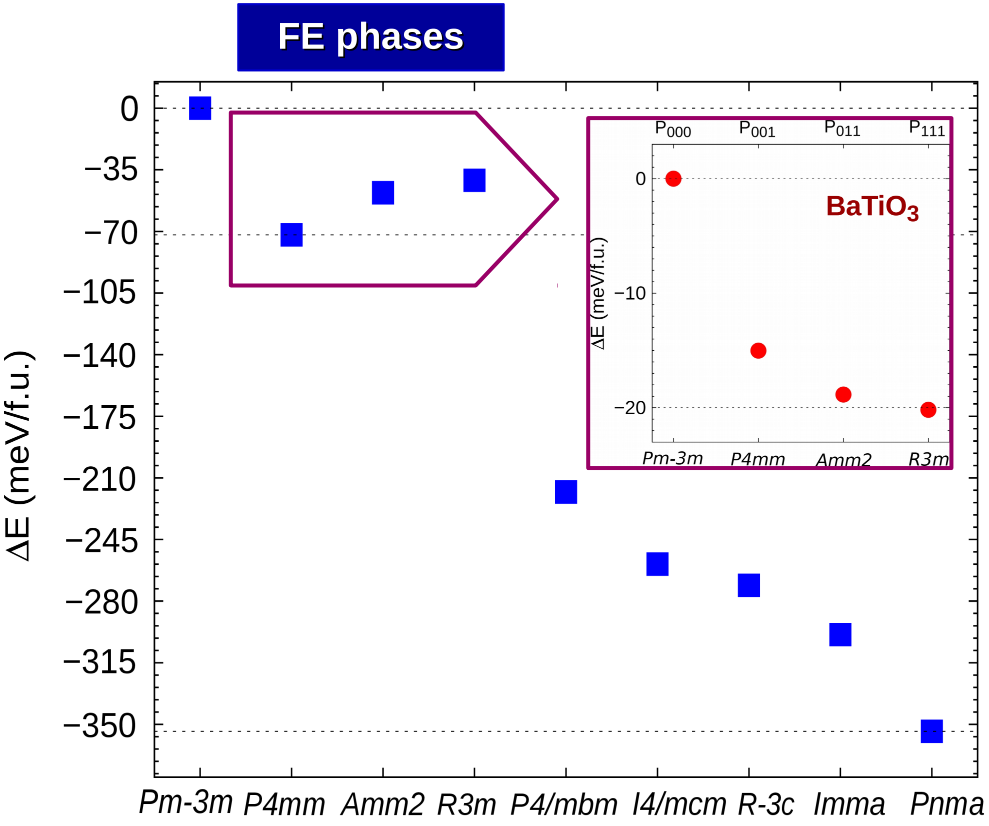
Polar distortion

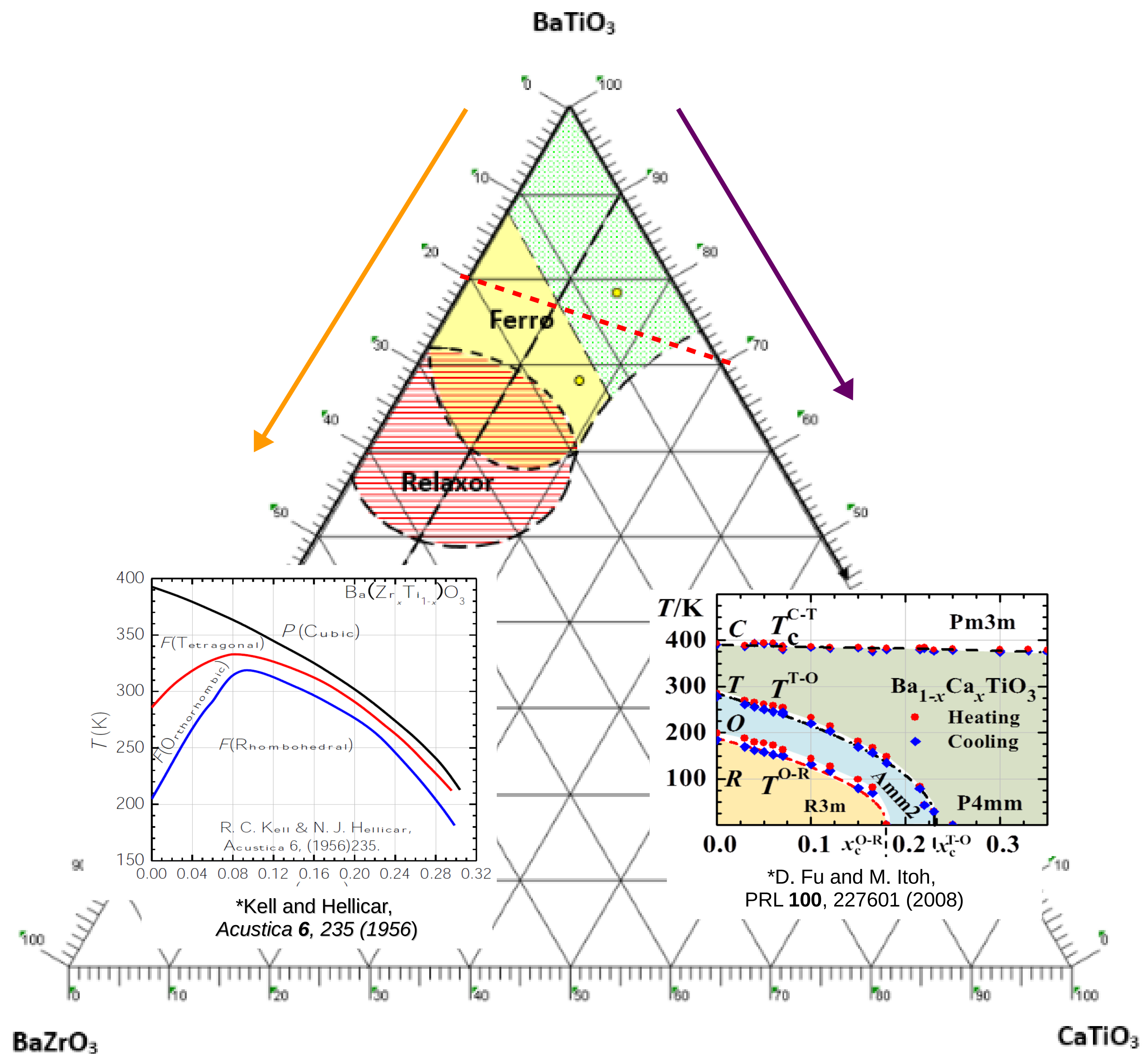
Out-of-phase (-) rotations

Inverted order of polar phases

&

increased energy gain with respect to $BaTiO_3$

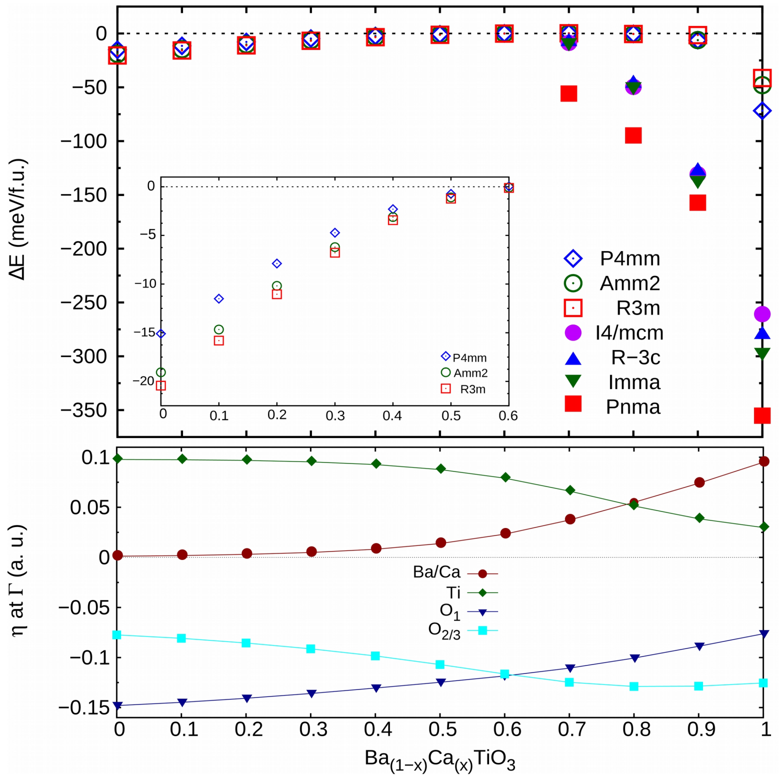


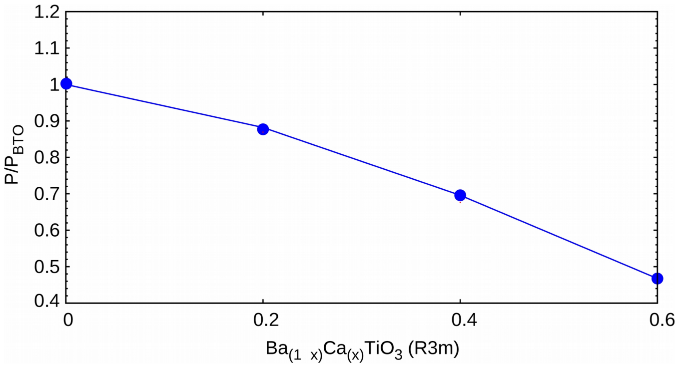


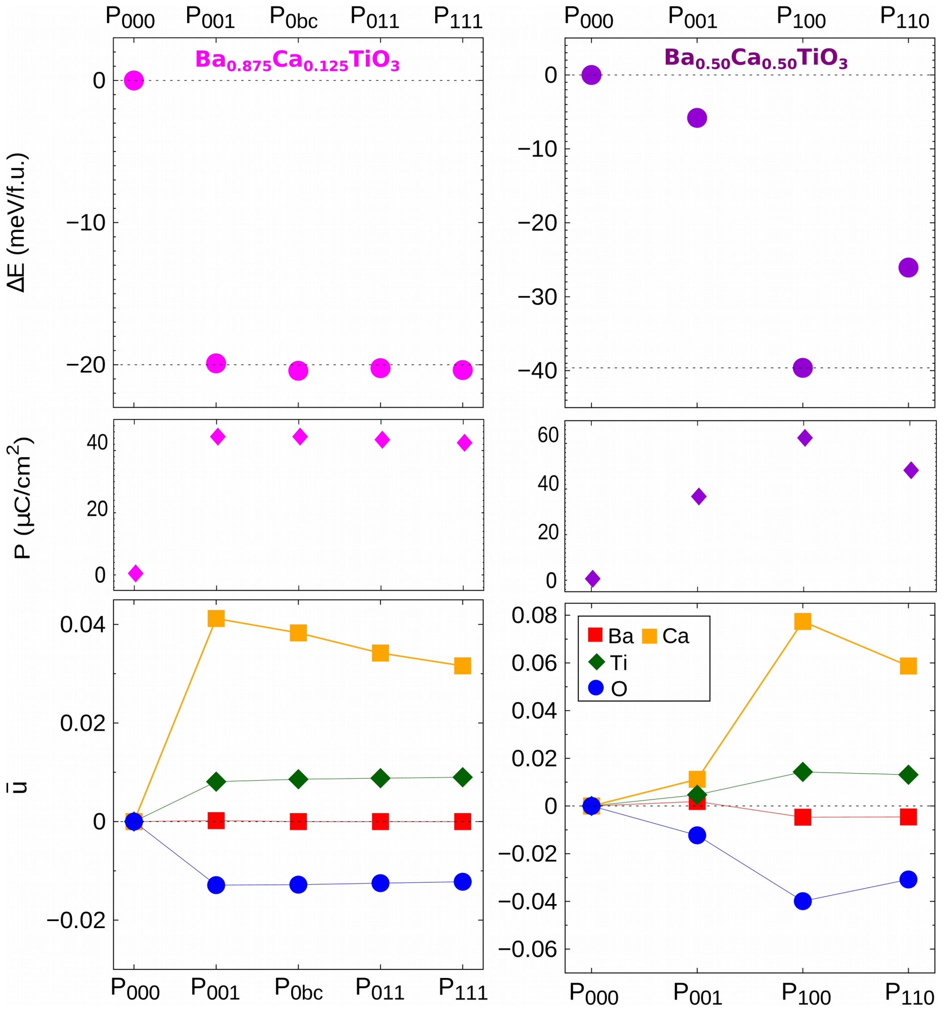
*Kell and Hellicar, *Acustica* ***6****, 235 (1956)*

*D. Fu and M. Itoh,
PRL **100**, 227601 (2008)

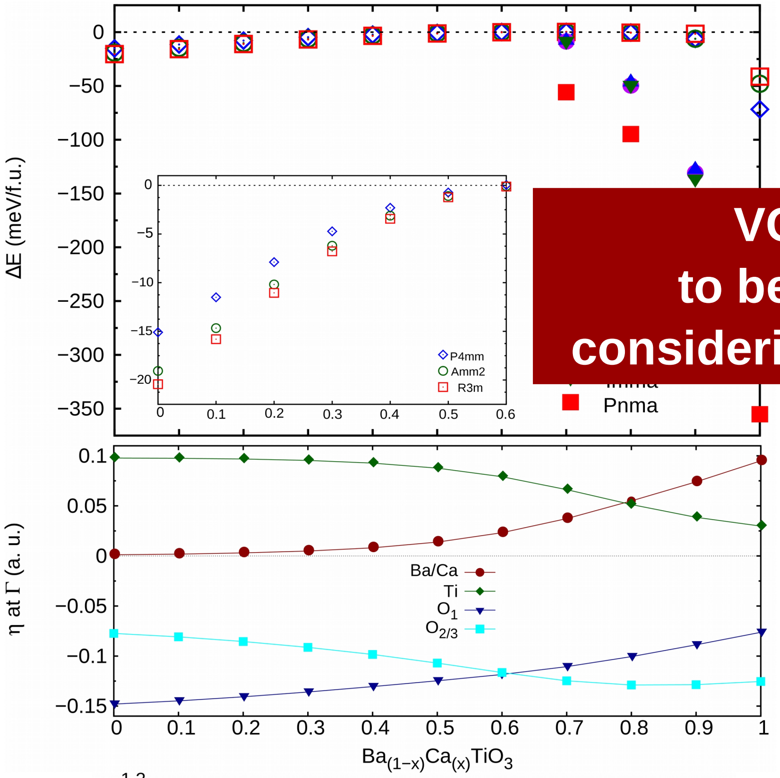
(Ba,Ca)TiO$_3$: VCA vs SUPERCELL

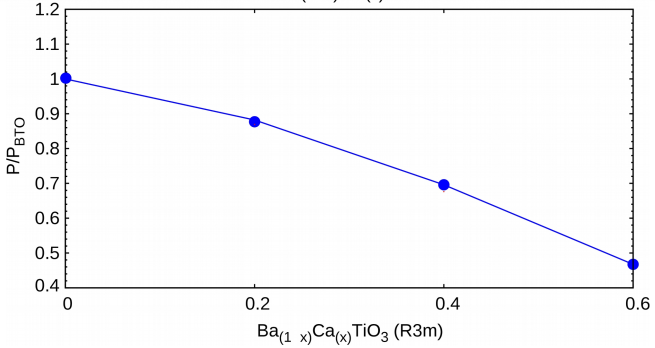


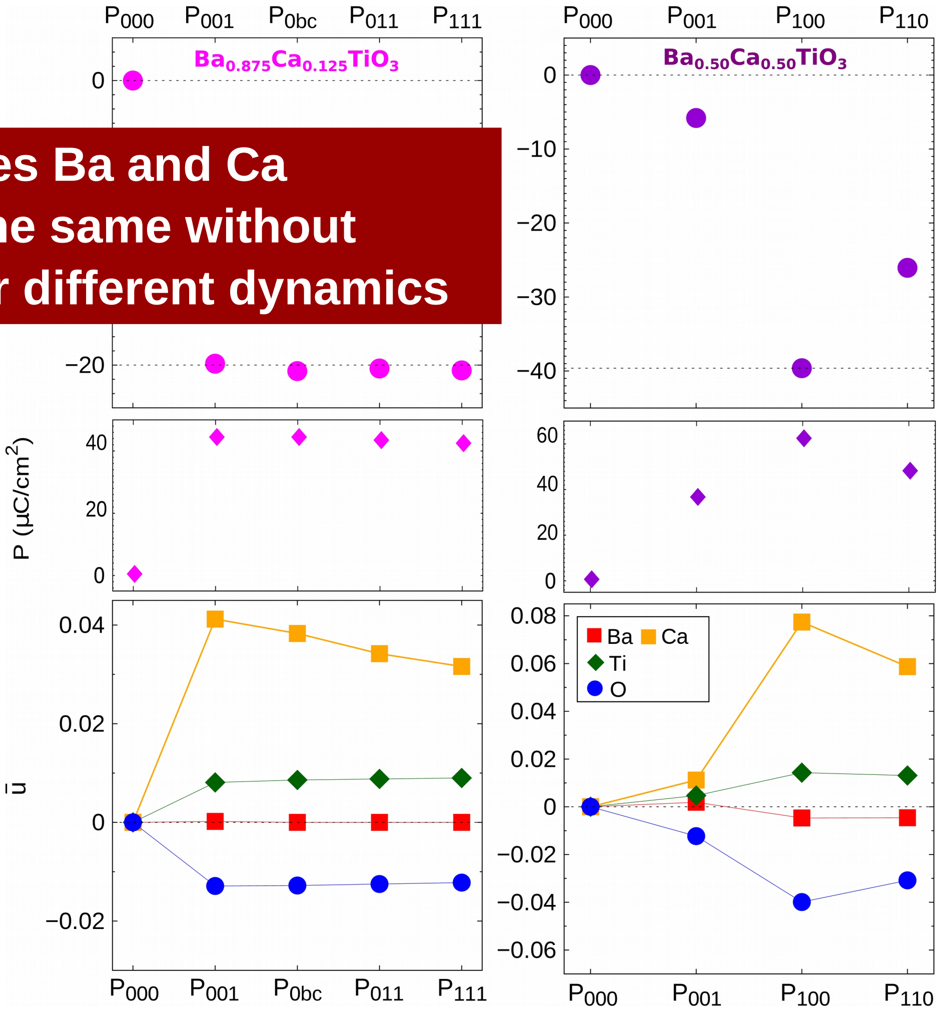




$(Ba,Ca)TiO_3$: VCA vs SUPERCELL

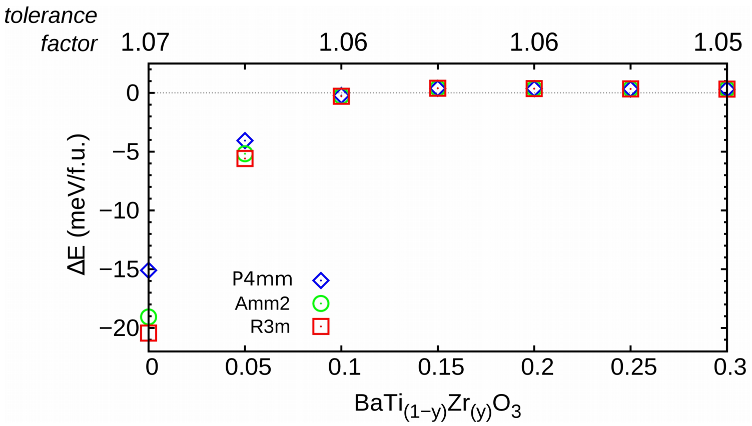




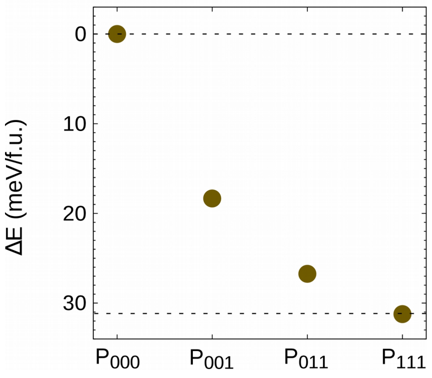


VCA forces Ba and Ca to behave the same without considering their different dynamics

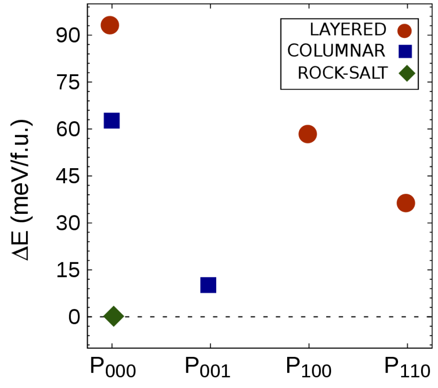
$Ba(Ti,Zr)O_3$: VCA vs SUPERCELL

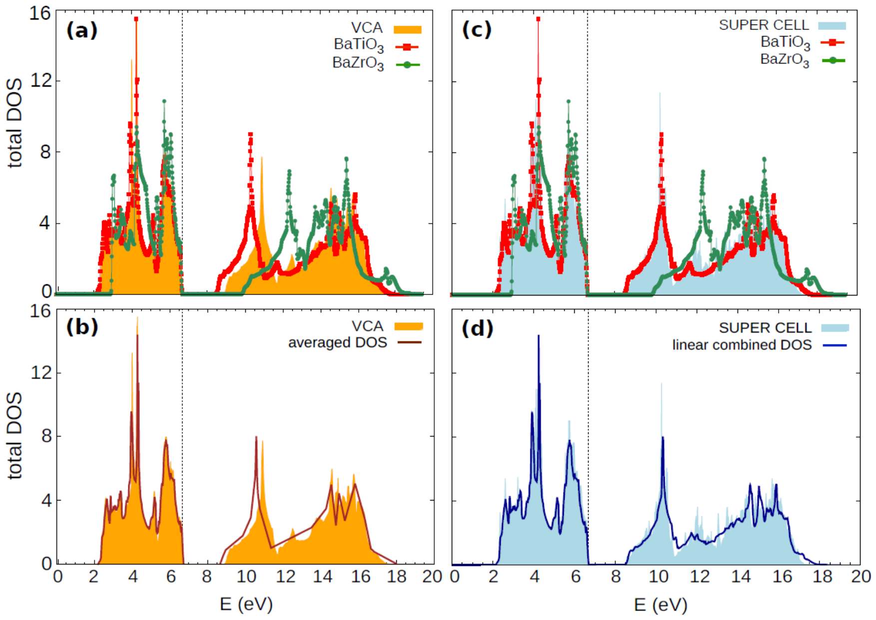


$BaTi_{0.875}Zr_{0.125}O_3$

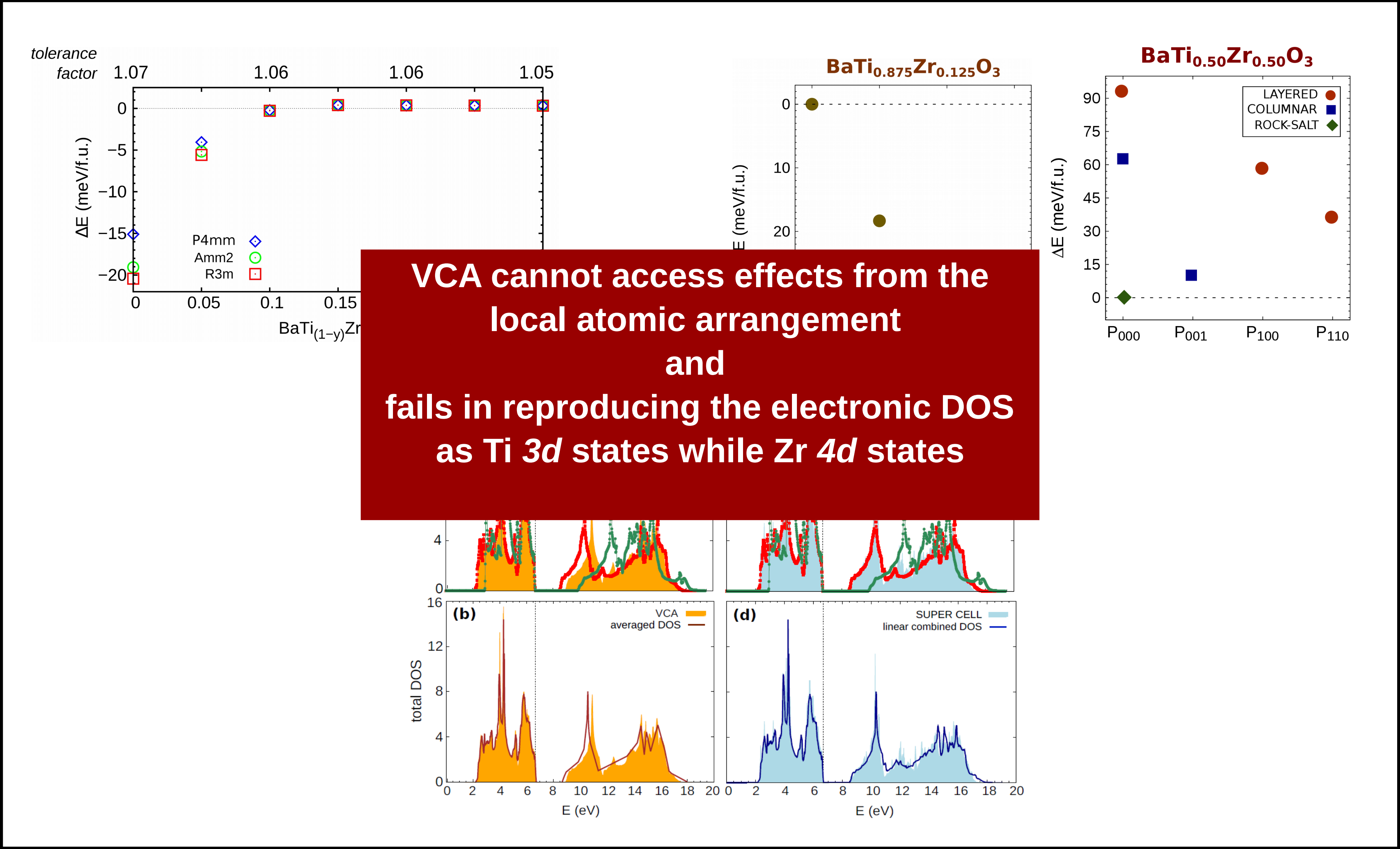


$BaTi_{0.50}Zr_{0.50}O_3$





Ba(Ti,Zr)O_3 : VCA vs SUPERCELL

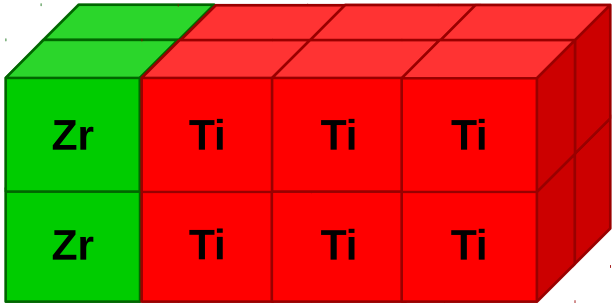


VCA cannot access effects from the local atomic arrangement

and

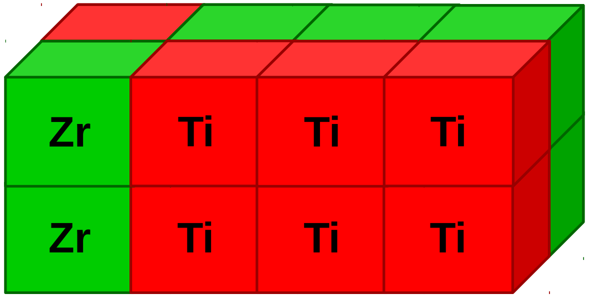
fails in reproducing the electronic DOS as Ti *3d* states while Zr *4d* states

$BaZrO_3$/*m*$BaTiO_3$ system : Ti – Zr correlation

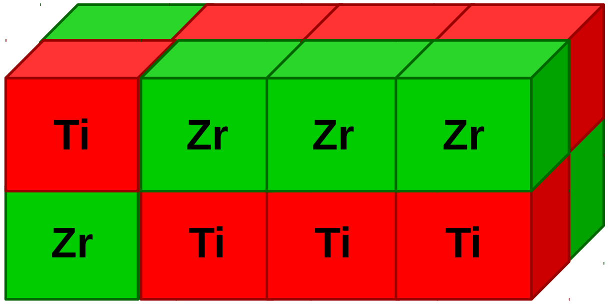


1x1xL

Decreasing Zr-concentration
50% → 17%



1x2xL



2x2xL

50% composition