Epitaxial strain tunes polarization and band gap in $SnTiO_3$

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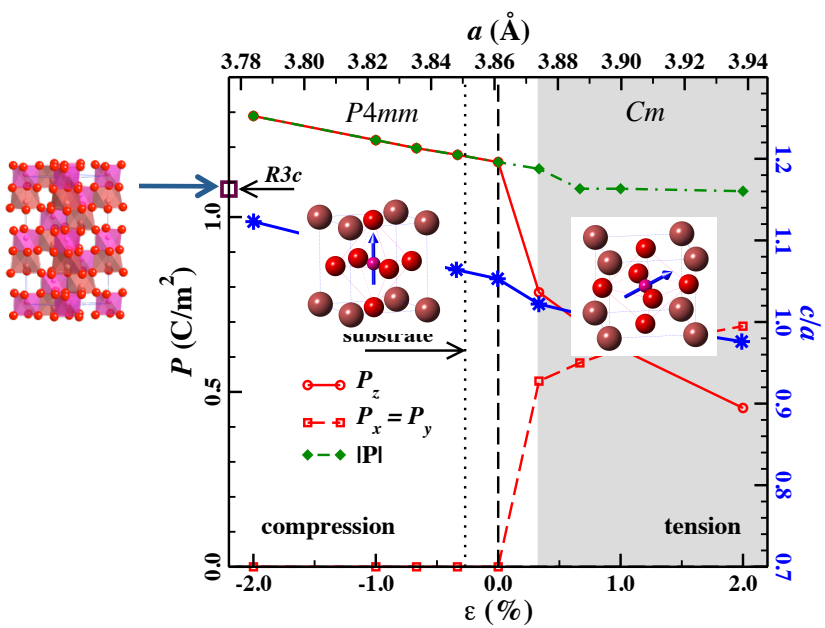
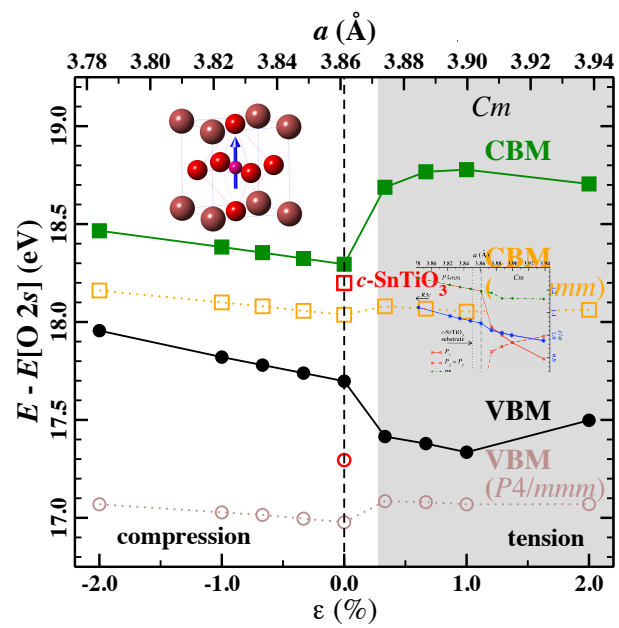
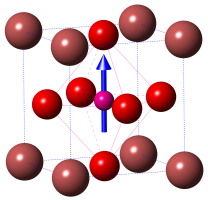




Why $SnTiO_3$?

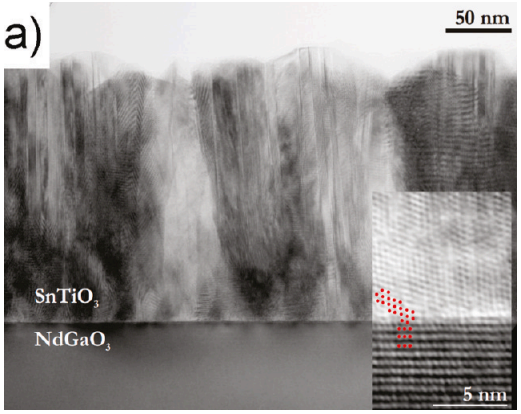
- Sn lacks Pb's toxicity and would be a welcome replacement where it can reproduce Pb's behavior



- Tetragonal perovskite (*P4mm)* $SnTiO_3$ is predicted to have higher polarization than $PbTiO_3$ but no evidence that it is stable

- Electron lone pair drives polar distortion in $PbTiO_3$. Sn also exhibits lone pair activity but is more difficult to stabilize in 2+ oxidation state.

- Perovskite $SnTiO_3$ has been challenging to make (two attempts reported: one bulk, one thin film)



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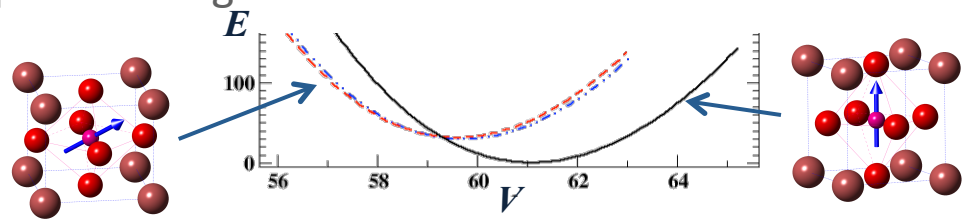
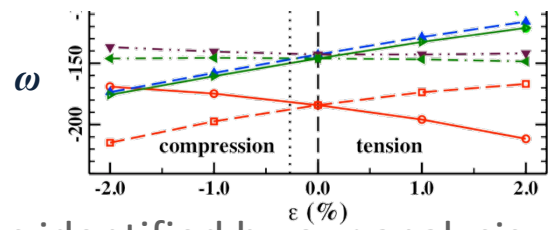
Our plan to examine $SnTiO_3$:

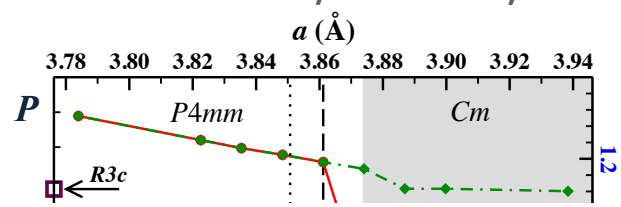
- Compare energies of $SnTiO_3$ polymorphs to find ground state



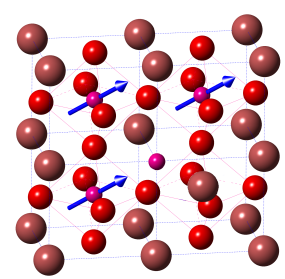
- Analyze stability of structures compatible with square-lattice epitaxy



- Study polar properties for interesting structures identified by our analysis



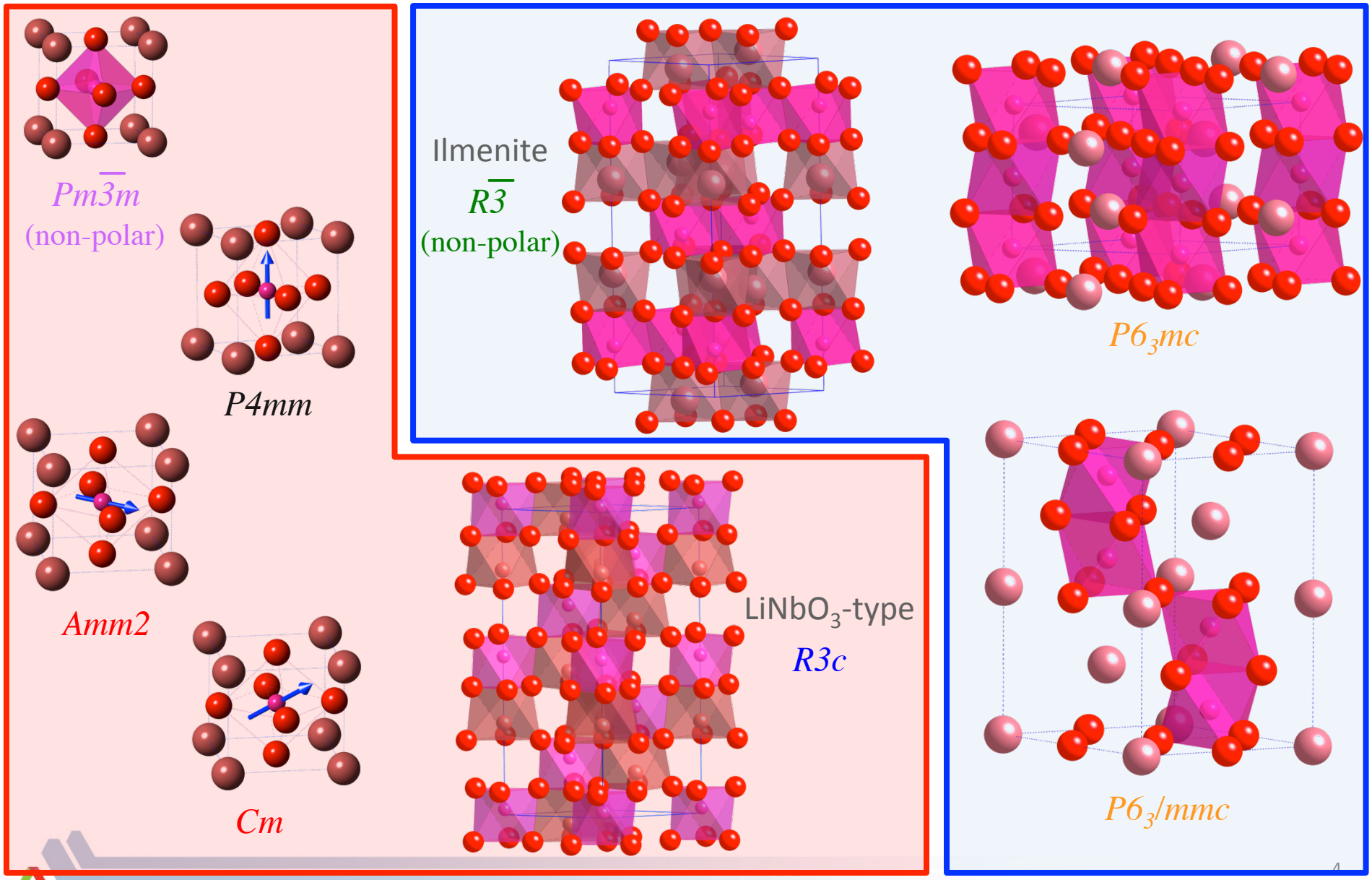
- Investigate effect of Sn^{4+} substitutional defects on B-site



Polymorph grouping by TiO_6 octahedron orientation

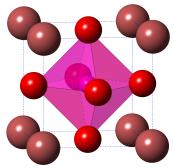
Corner-sharing TiO_6

Edge- or face-sharing TiO_6

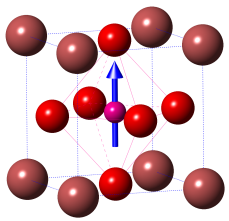


Energy ordering of polymorphs at T=0

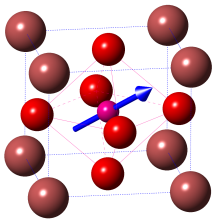
Perovskites:



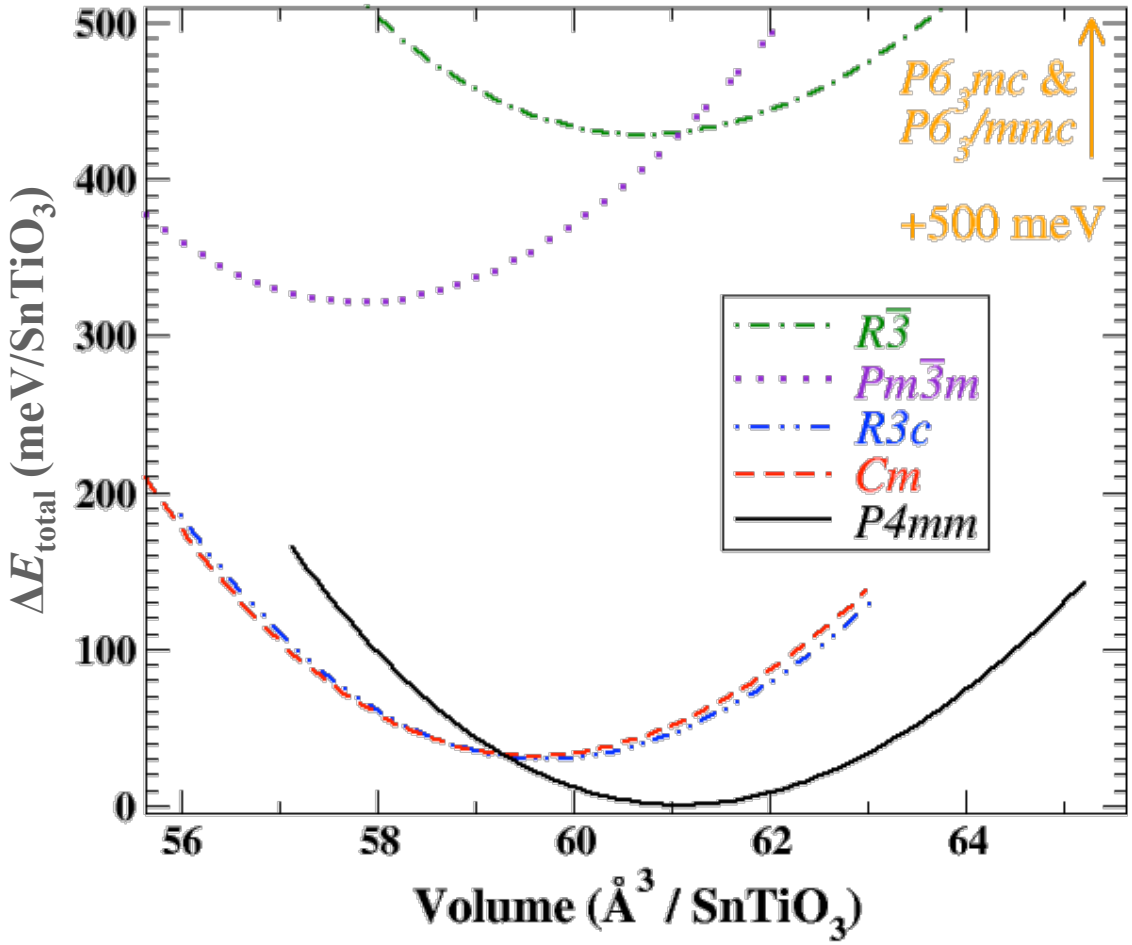
$Pm\bar{3}m$
(non-polar)



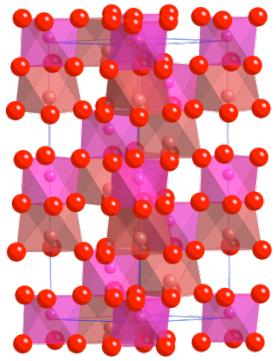
$P4mm$



Cm

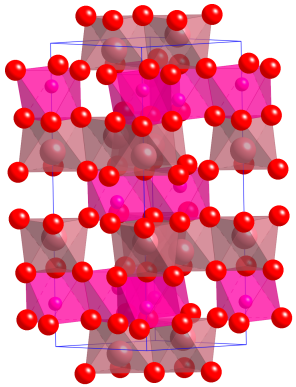


LiNbO$_3$-type



$R3c$

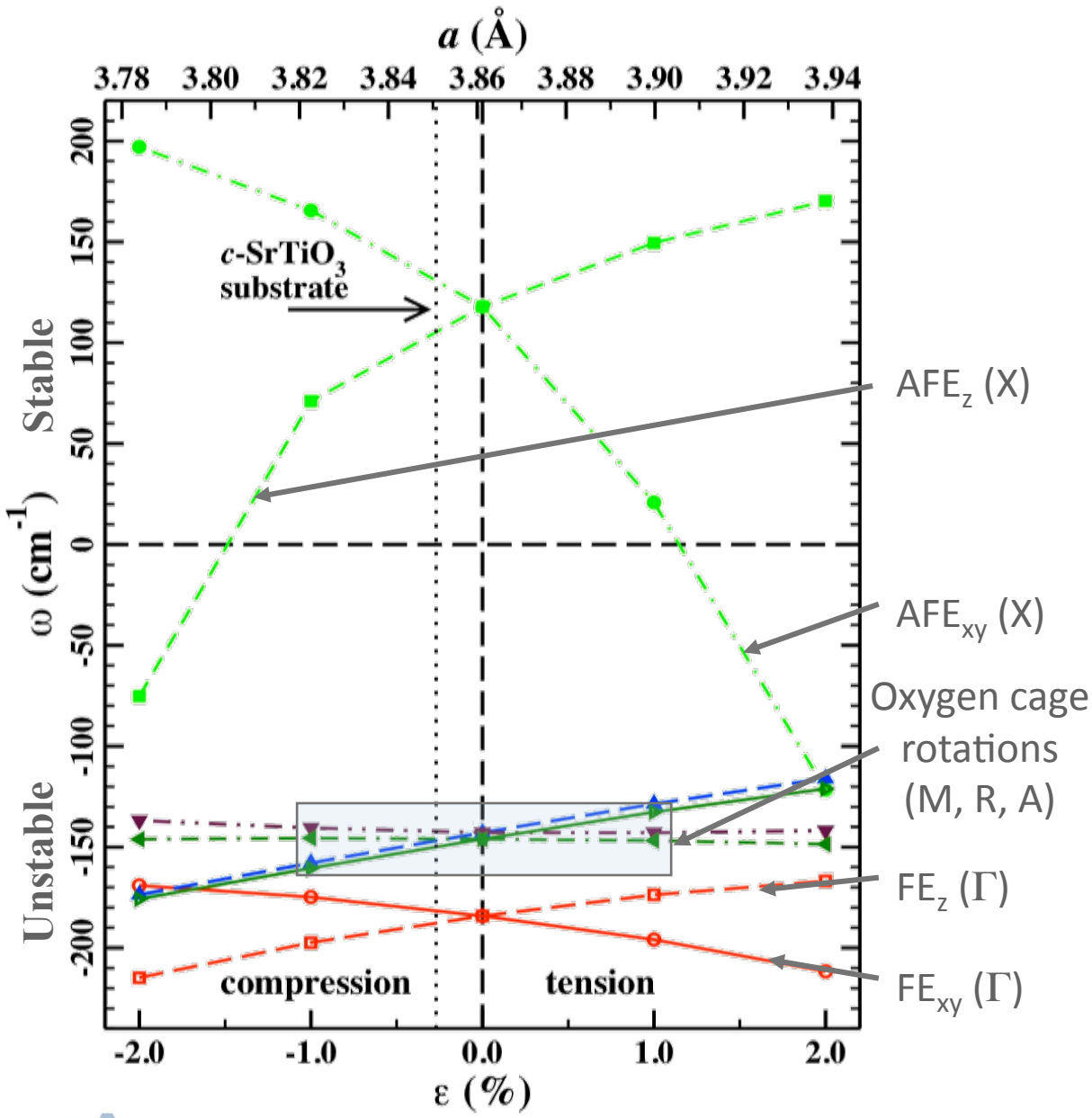
Ilmenite



$R\bar{3}$
(non-polar)

- Tetragonally distorted perovskite ($P4mm$) SnTiO$_3$ lies lowest in energy.
- Cm and $R3c$ polar phases are nearly degenerate in energy (local structure similar).
- Energies of corner-sharing structures are lower than edge- or face-sharing ones.

Structural instability analysis at varying strain

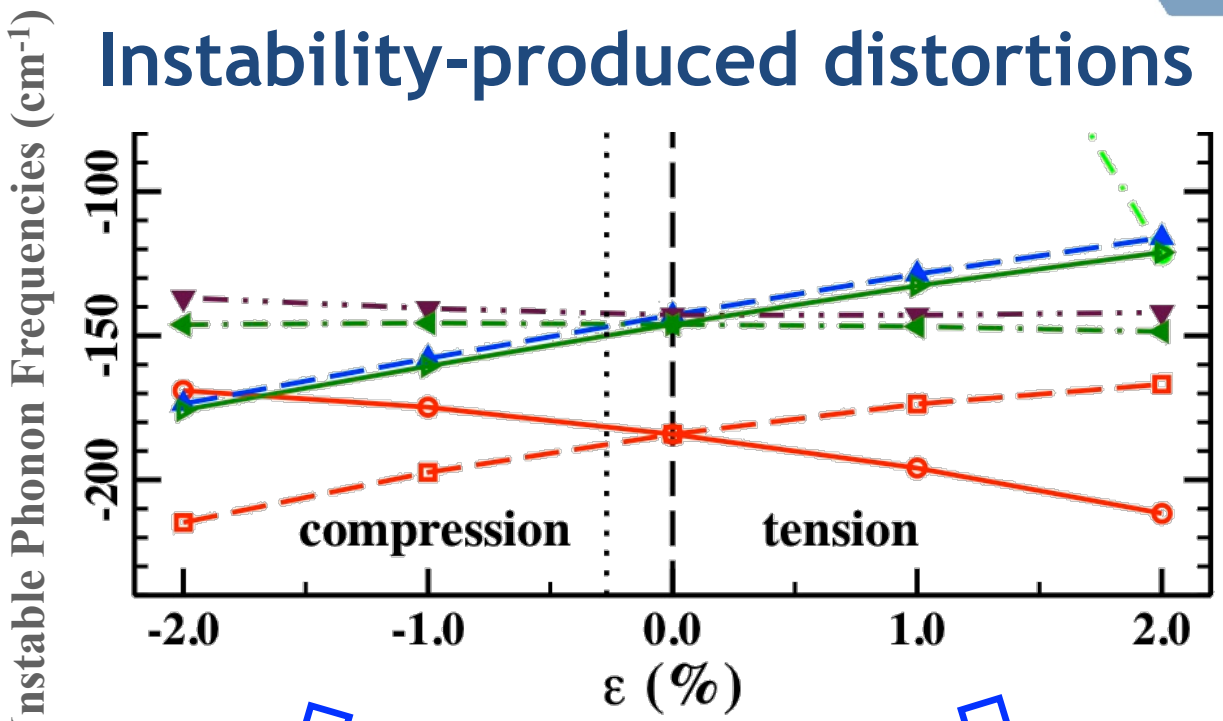


- Negative phonon frequencies indicate instabilities
- Biaxial ($a = b$) strain simulated by allowing cell relaxation only along growth axis c at fixed, variable a
- Relaxed cubic ($Pm\overline{3}m$) perovskite lattice parameter a_0 sets zero strain

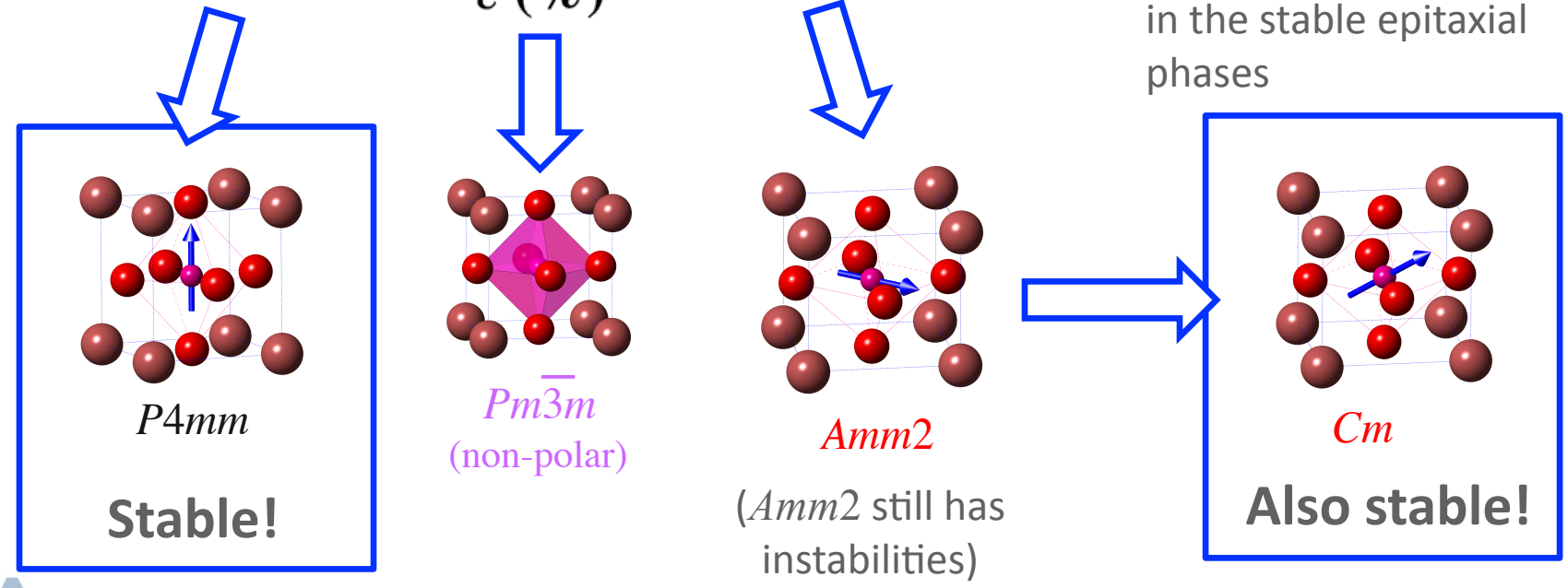
$$\varepsilon = (a/a_0) - 1$$

- Freezing instabilities into ionic displacements and relaxing electronic forces on ions and cell pressure will produce stable structures

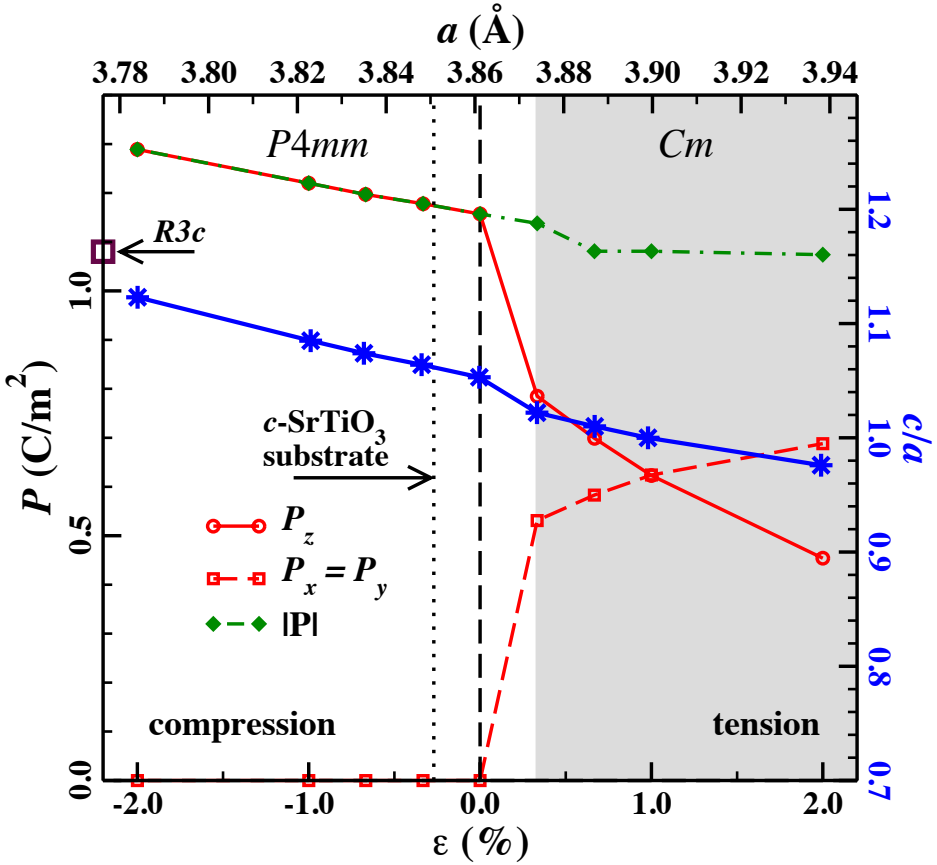
Instability-produced distortions



- The Cm phase is stabilized by tension ≥ 0.333%: $P_x = P_y \neq 0, P_z \neq 0$
- The $P4mm$ phase is stabilized by compression: $P_x = P_y = 0, P_z \neq 0$
- Antiferrodistortive rotations are not present in the stable epitaxial phases

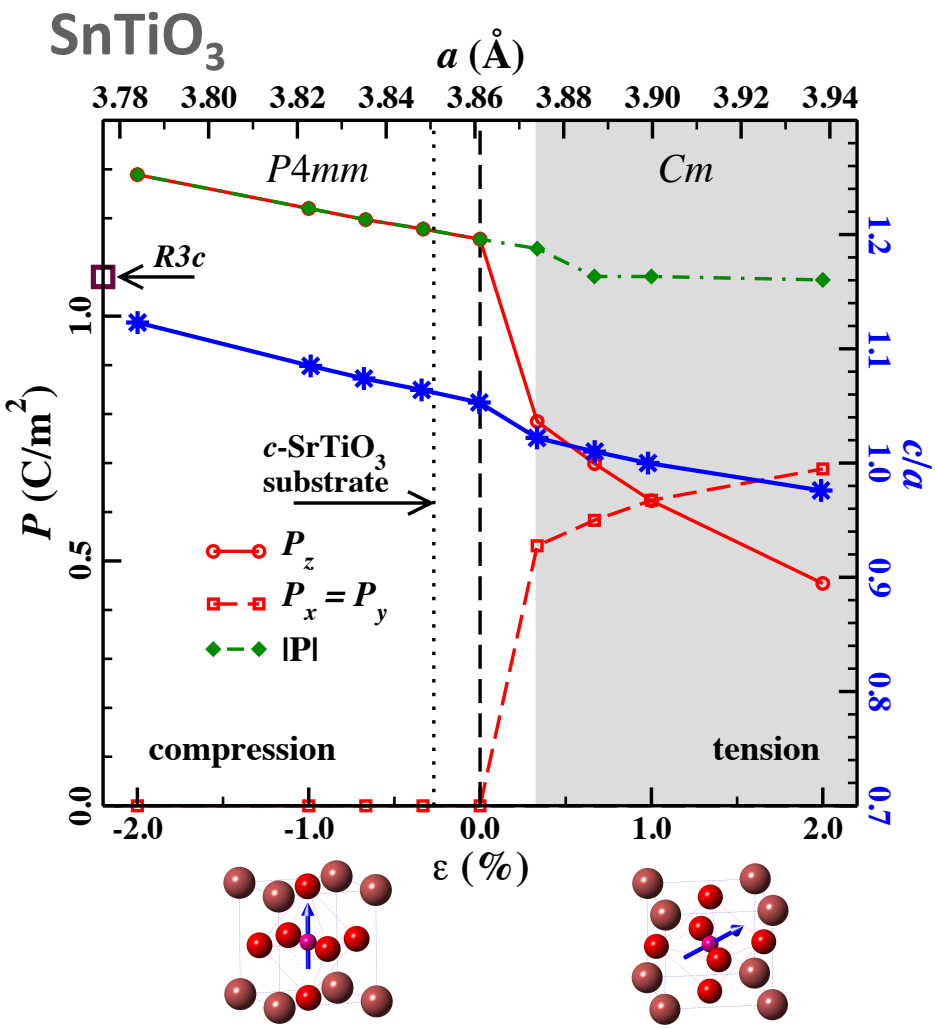


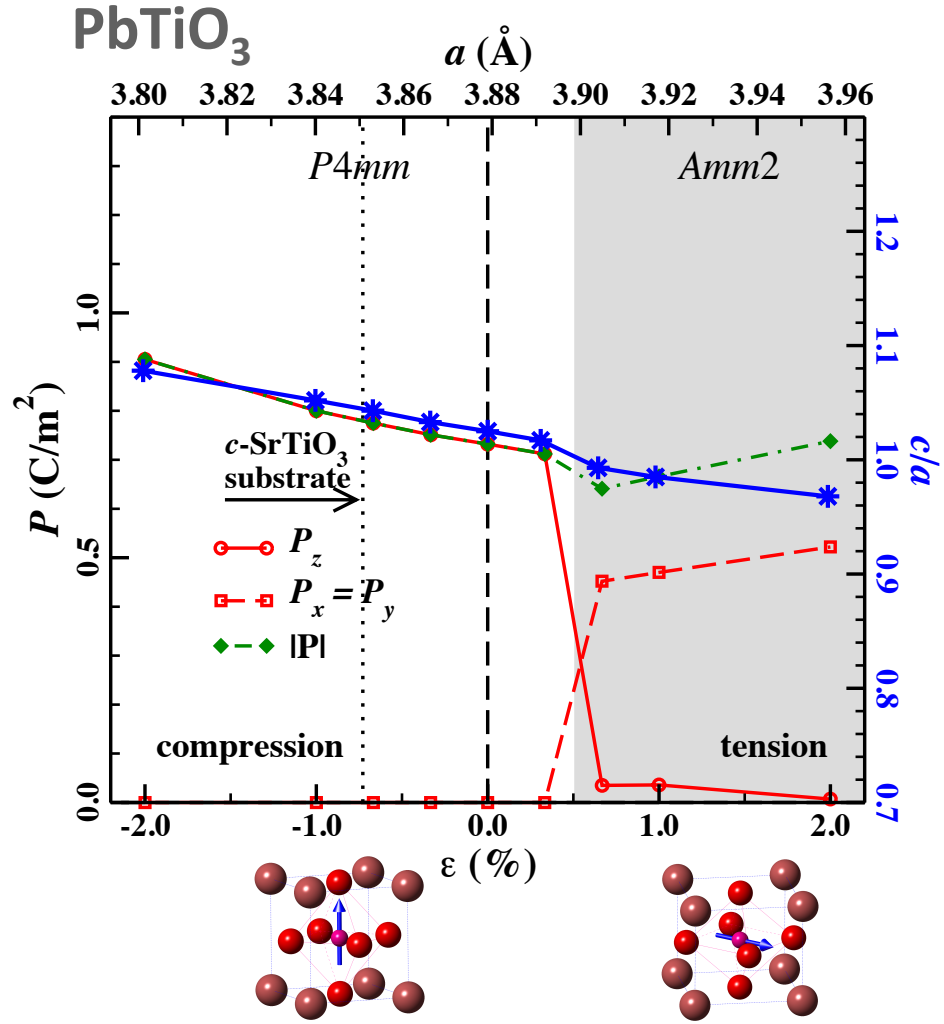
Epitaxial strain-tuned polar distortion



- Total polarization remains above 1 C/m^2 at all strains calculated
- Tetragonality follows polarization in $P4mm$
- Polarization direction shifts off growth axis under $P4mm$ to Cm transition
- Ferroelectricity remains robust under varying strain in $SnTiO_3$

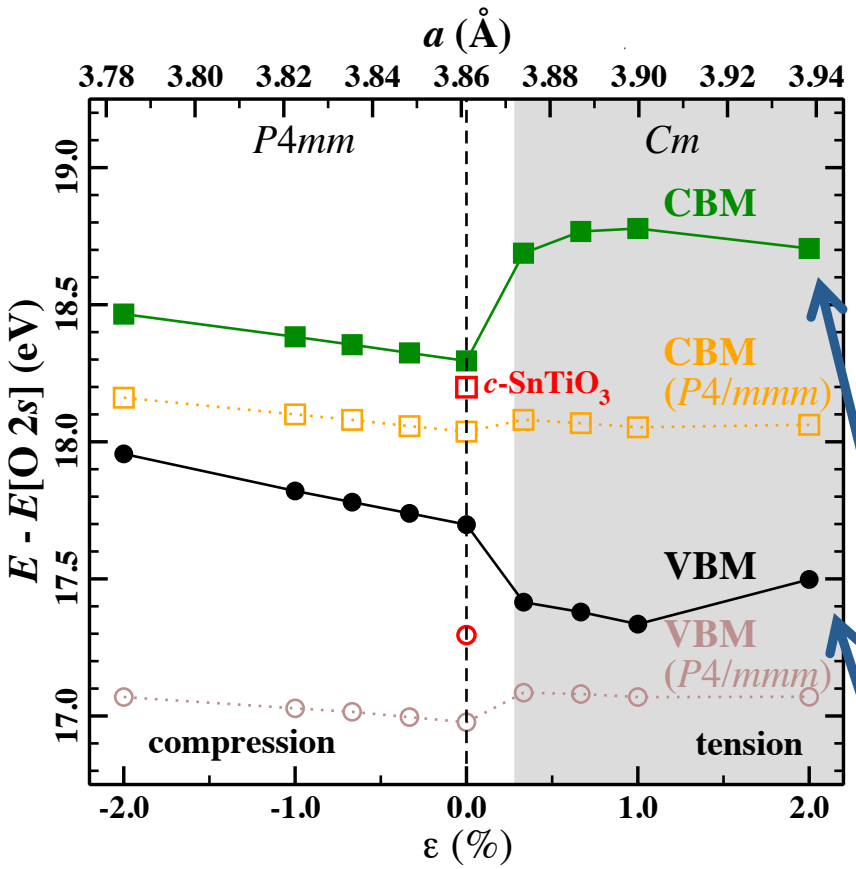
Strain-tuned polar distortion: Sn vs. Pb





- $SnTiO_3$ has 30-60% larger polarization than $PbTiO_3$ though tetragonality is comparable
- $SnTiO_3$ retains some polarization along growth axis under tension; $PbTiO_3$ does not

Epitaxial strain-tuned band gap



E_{gap} ~ 0.6 eV → 1.4 eV

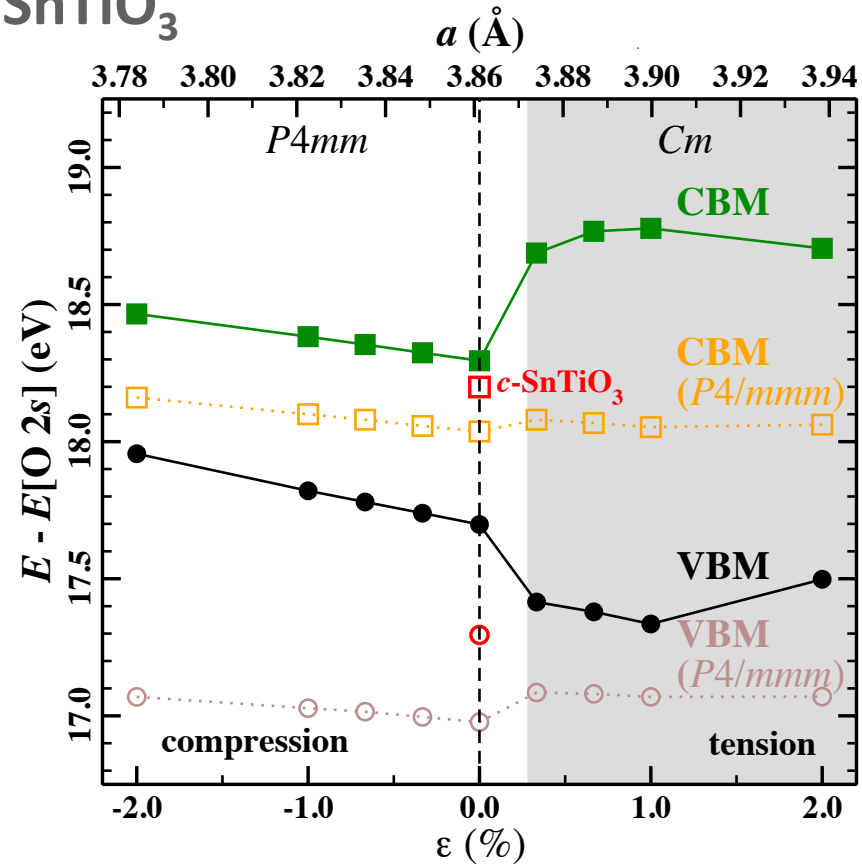
- Band gap widens from 0.6 eV to 1.4 eV under $P4mm$ to Cm transition
- Ionic-distortion-free $P4/mmm$ structures show no gap change as tetragonality decreases under tension
- Choice of substrate can significantly tune the electronic properties of $SnTiO_3$
- Potential for dynamic tuning of structure grown near transition

Conduction band minimum

Valence band maximum

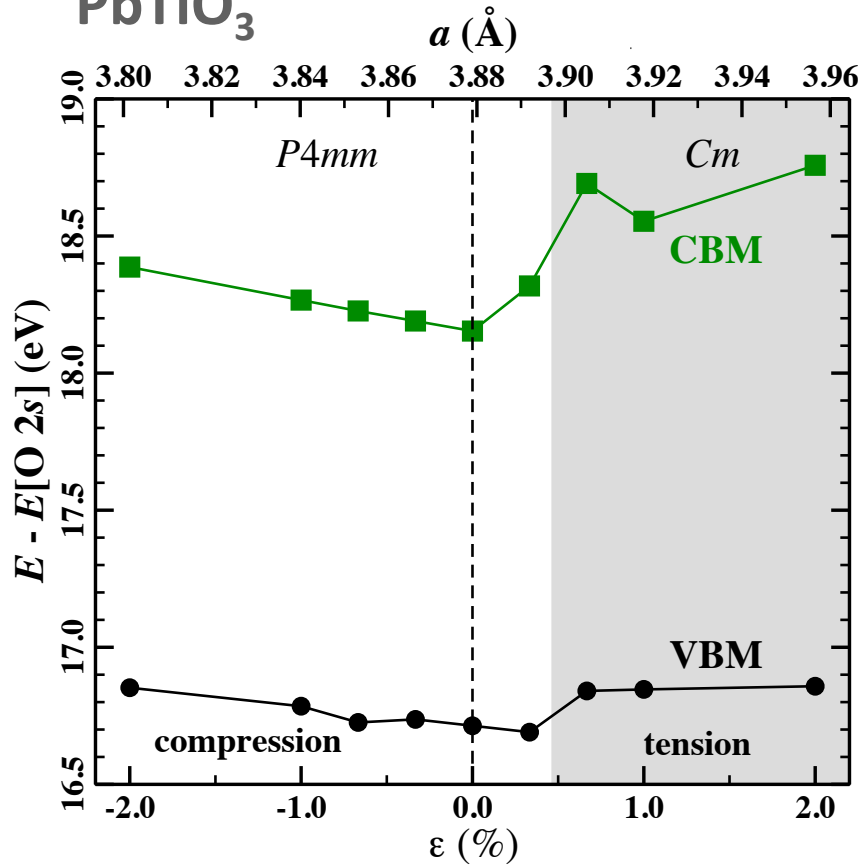
Strain-tuned band gap: Sn vs. Pb

$SnTiO_3$



E_{gap} ~ 0.6 eV → 1.4 eV

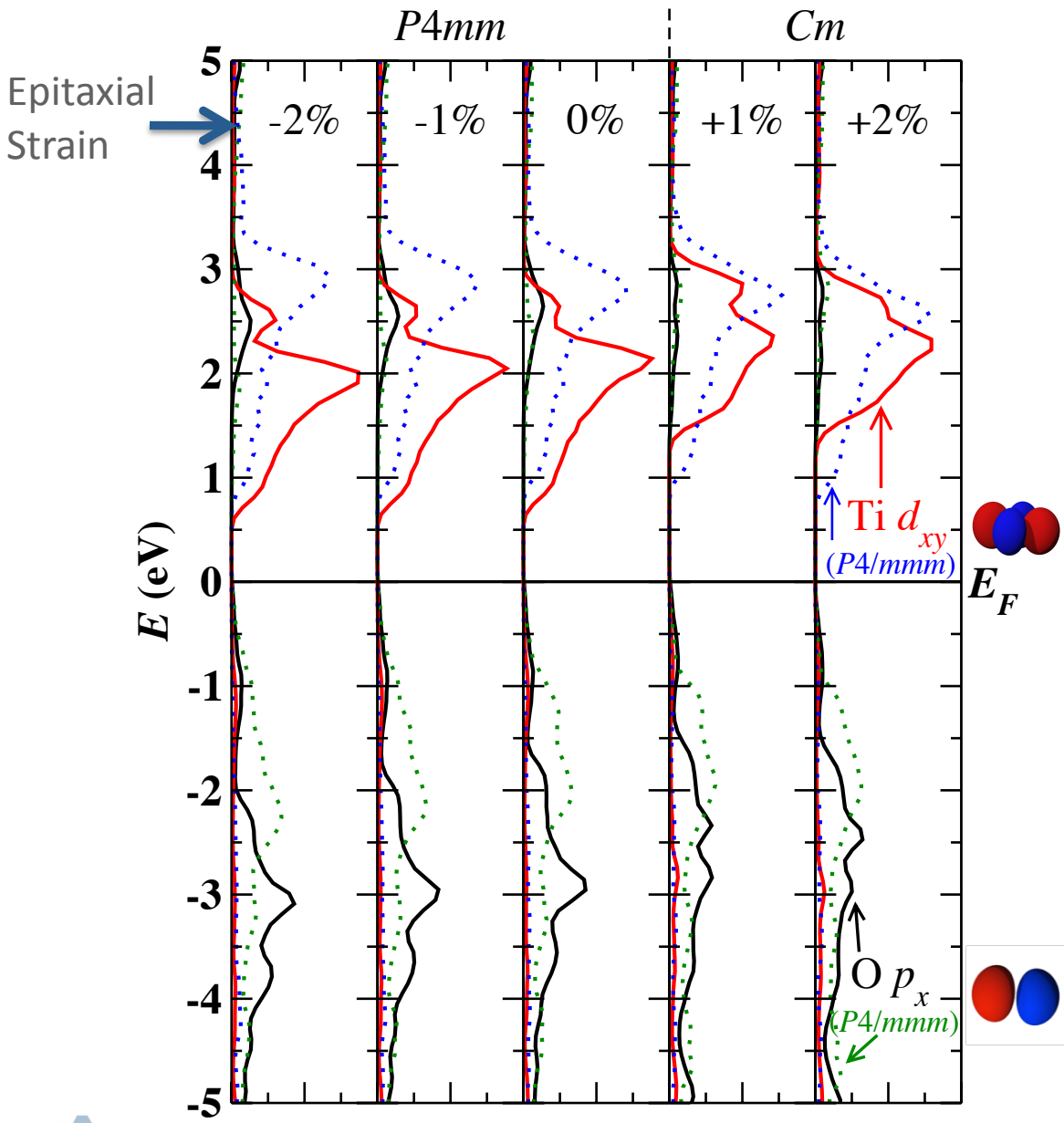
$PbTiO_3$



E_{gap} ~ 1.5 eV → 1.8 eV

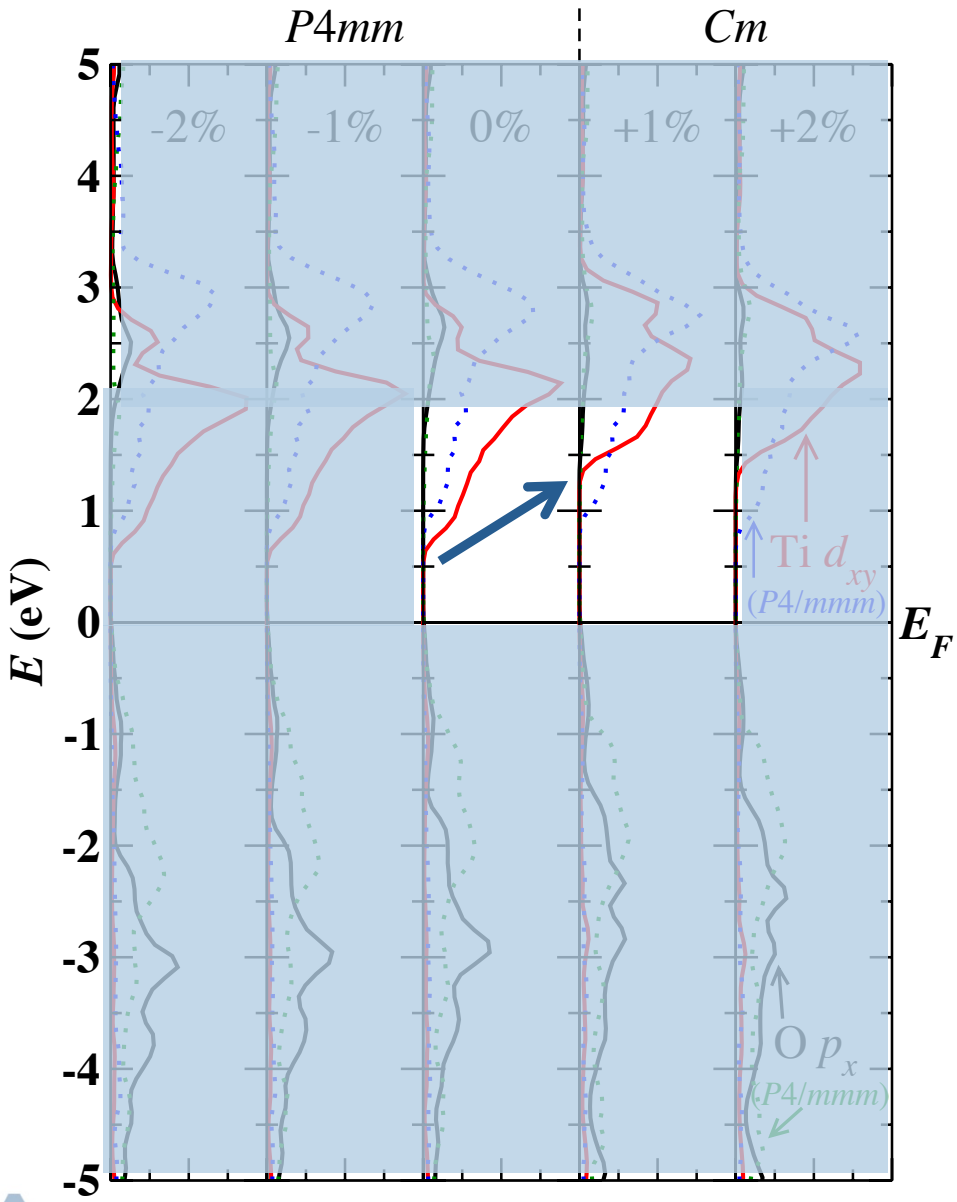
- $SnTiO_3$ band gap widens under strain-induced transition while $PbTiO_3$ gap changes little

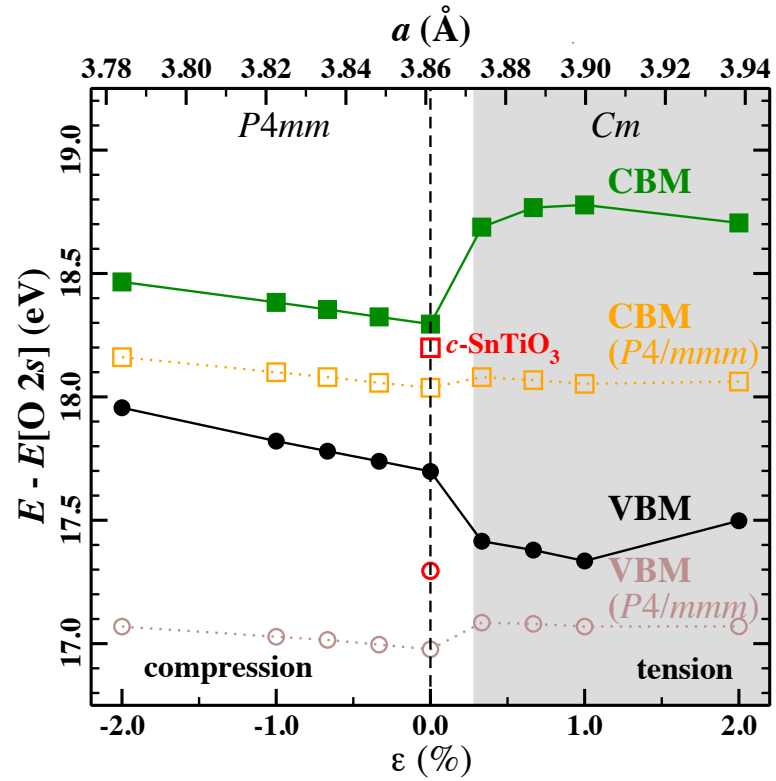
Strain-tuned electronic states



- Projected density of states (PDOS) relates occupied bands to atomic orbital contributions
- Ionic-distortion-free $P4/mmm$ structures show little change in PDOS as tetragonality decreases under tension
- Ti d_{xy} dominates conduction band minimum in $P4mm$

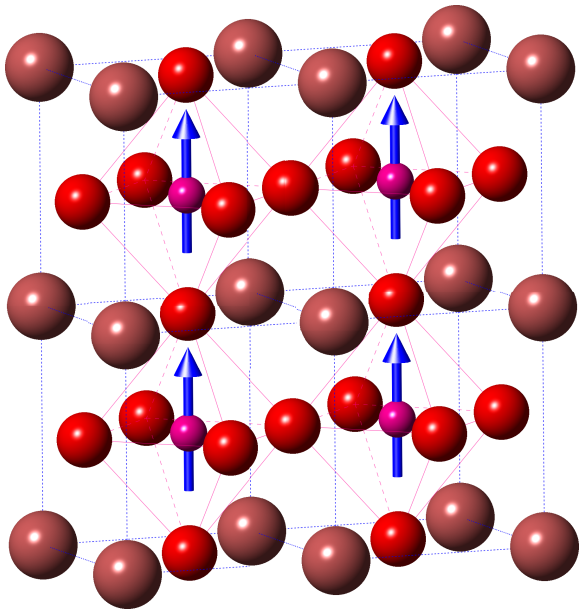
Broken-symmetry-induced gap widening





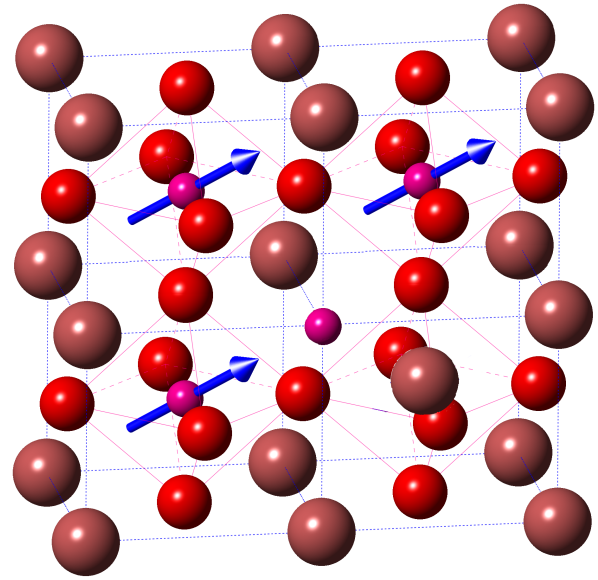
Ti d_{xy} orbital hybridizes with O p_x at Γ when four-fold symmetry is broken from *P4mm* to *Cm*

Sn^{4+} substitution on B-site effects



Switch 1:8 Sn-Ti pairs in $P4mm$

(12.5% defect concentration)

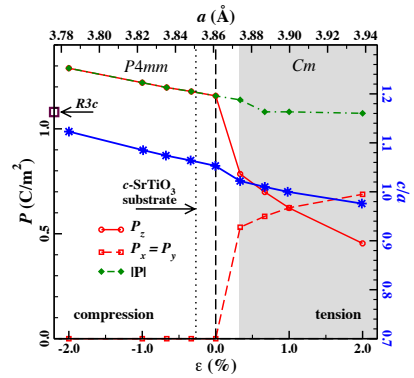


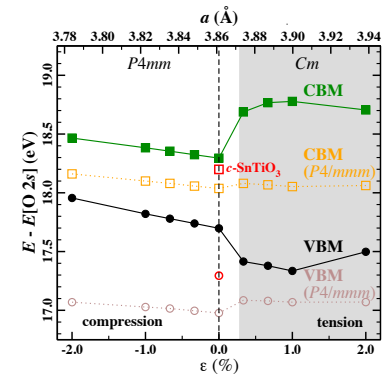
$P4mm$ → Symmetry reduces → Cm

$\boldsymbol{P}$ = 1.2 C/m^2 → Polarization reduces → 0.8 C/m^2 (estimated from ionic distortion)

Epitaxial strain tunes polarization and band gap in $SnTiO_3$

- Tetragonally distorted polar perovskite lies lowest in energy of all $SnTiO_3$ phases (polar and non-polar)
- Square-epitaxial strain favors the tetragonal perovskite under compression and monoclinic perovskite under tension (triangular substrate could favor low-energy polar $LiNbO_3$-type structure)
- Epitaxially-stabilized perovskite phases have significant (> 1 C/m^2) polarization, which shifts away from the growth axis under tension (larger than PTO, which loses growth axis component)
- Off-axis polar distortion breaks rotational symmetry and allows certain electronic states to mix, widening the electronic band gap (potential for dynamic tuning)
- Substitutional defects of Sn^{4+} on a Ti site reduce overall polar distortion and symmetry but do not eliminate polar distortion





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Backup Slides

Computational details

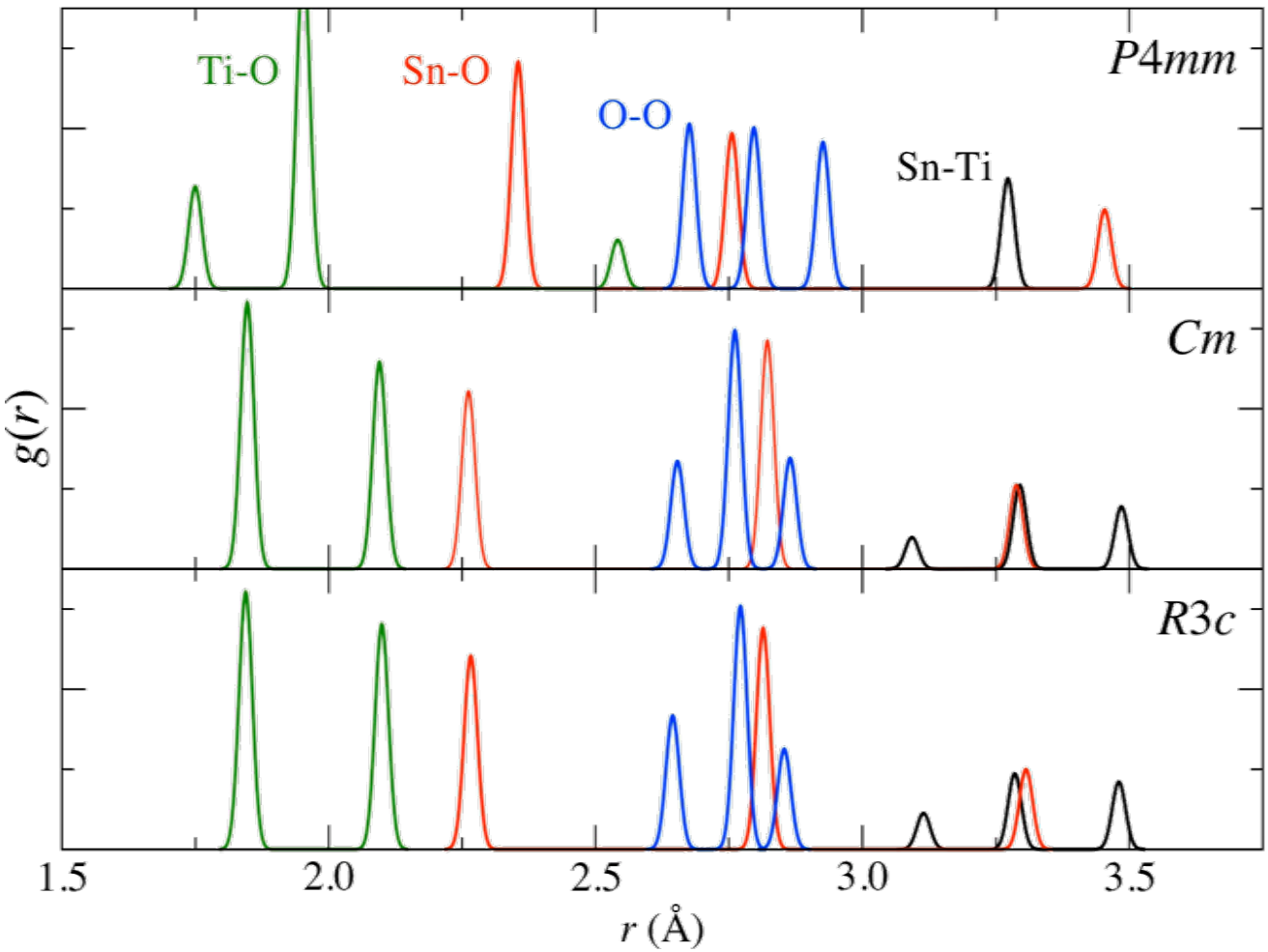
- Density functional theory with the local density approximation (LDA) using ultrasoft pseudopotentials for total energies and forces on ions using the QUANTUM ESPRESSO package (http://www.quantum-espresso.org/)
  - Plane wave basis cutoff at 30 Ry to converge total energy differences to within 10 meV
  - Brillouin zone sampled with 8x8x8 mesh centered at zone corner to converge total energy to within 1 meV
  - Ionic force components relaxed to below 10^{-4} Ry/Bohr
- Wentzcovitch symmetry-preserving algorithm relaxed cell stresses to below 1 kbar
- Density functional perturbation theory to calculate phonon frequencies
- Berry phase calculation of polarization

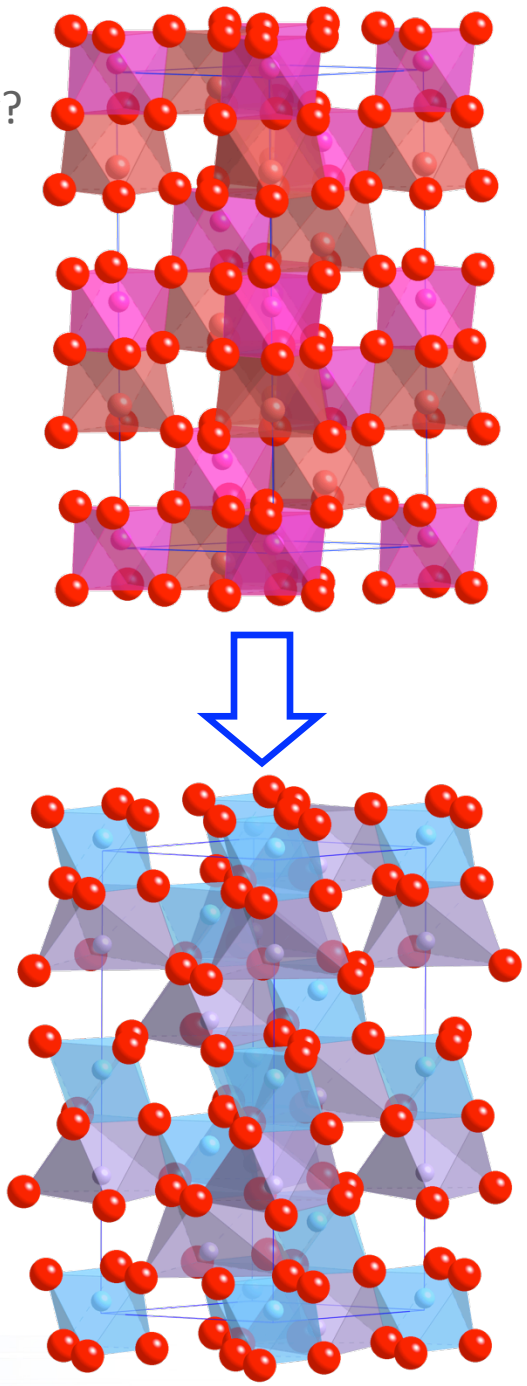
GGA (PW91) orders phases the same as LDA

	E – E[*P4mm*] (eV)	
	LDA	GGA (PW91)
*R*3*c*	0.031	0.157
Cm	0.032	0.168
R-3	0.428	0.548
$P6_3mc$	2.000	1.914

Polymorph comparison: Structure

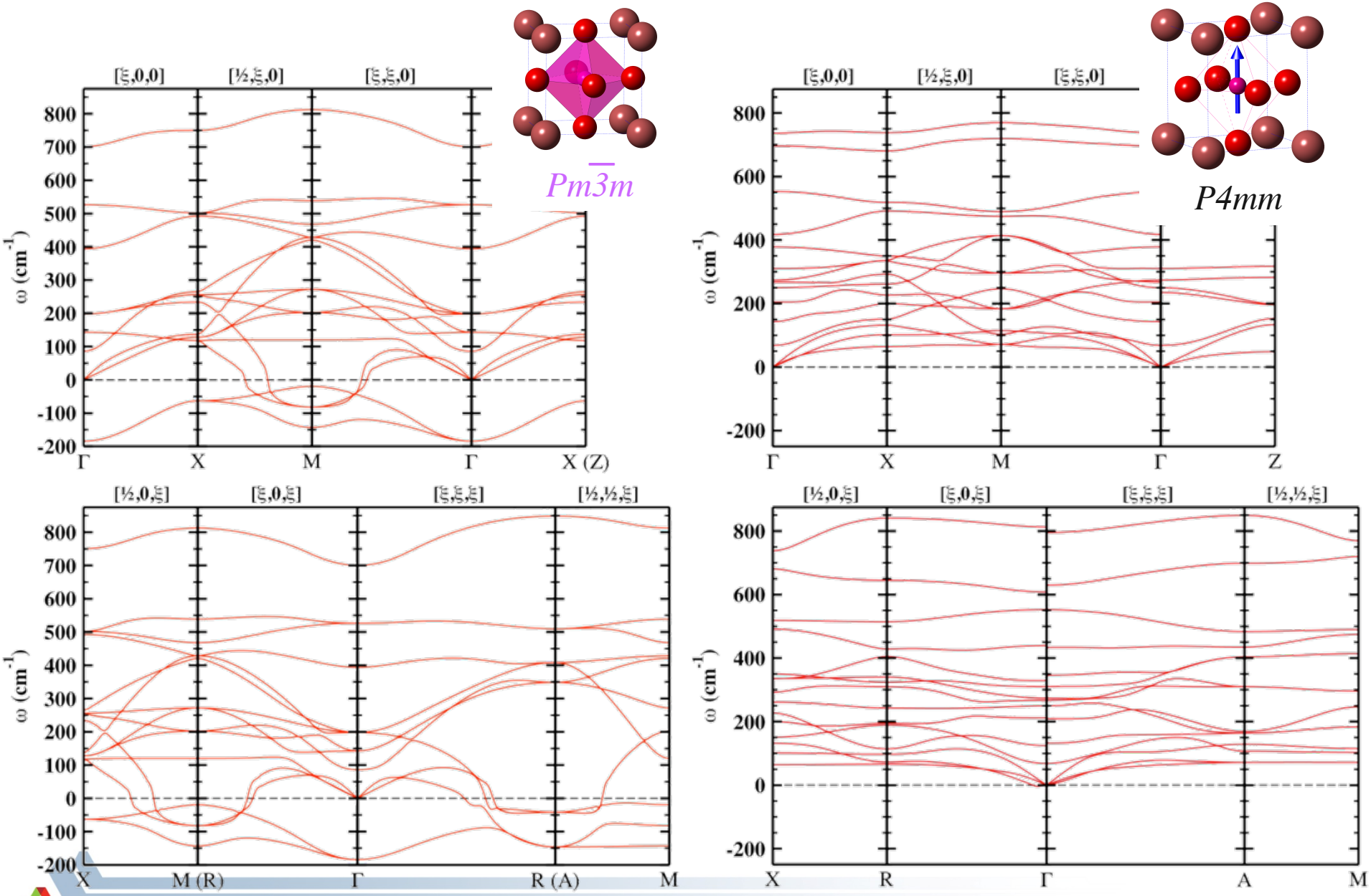
- Why are the *Cm* and *R3c* polar phases almost degenerate in energy?
- That is because structurally they look very similar





- Can we stabilize the phase we want by an appropriate choice of epitaxy?

Epitaxial perovskite phases: structural instability analysis



Bader charge estimates in $SnTiO_3$

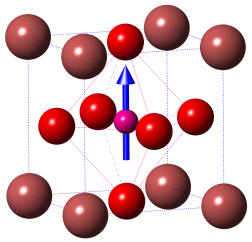
Fully-relaxed structures

Space group	Sn	Ti	O	O	O
P4mm	+1.422	+2.032	-1.193	-1.193	-1.067
Cm	+1.412	+2.121	-1.175	-1.177	-1.182
$R\bar{3}c$	+1.411(2)	+2.15(1)	-1.186(4)	-1.186(4)	-1.186(4)
$Pm\bar{3}m$	+1.445	+2.146	-1.197	-1.197	-1.197
*R*3	+1.405(2)	+2.114(2)	-1.173(1)	-1.173(2)	-1.173(2)
$P6_3/mmc$	+1.7(4)	+1.68(4)	-1.112(5)	-1.118(9)	-1.126(2)
$P6_3mc$	+1.430	+1.998	-1.142	-1.143(5)	-1.143(5)

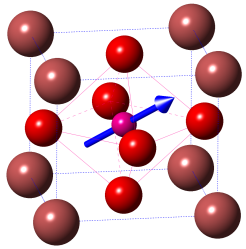
Epitaxially-strained structures

ε	Sn	Ti	O	O	O
-2%	+1.425	+2.019	-1.192	-1.192	-1.061
-1%	+1.417	+2.028	-1.192	-1.192	-1.061
0%	+1.418	+2.125	-1.191	-1.191	-1.161
+1%	+1.413	+2.125	-1.175	-1.177	-1.182
+2%	+1.417	+2.132	-1.180	-1.180	-1.188

Electronic structure properties in epitaxial perovskite $SnTiO_3$

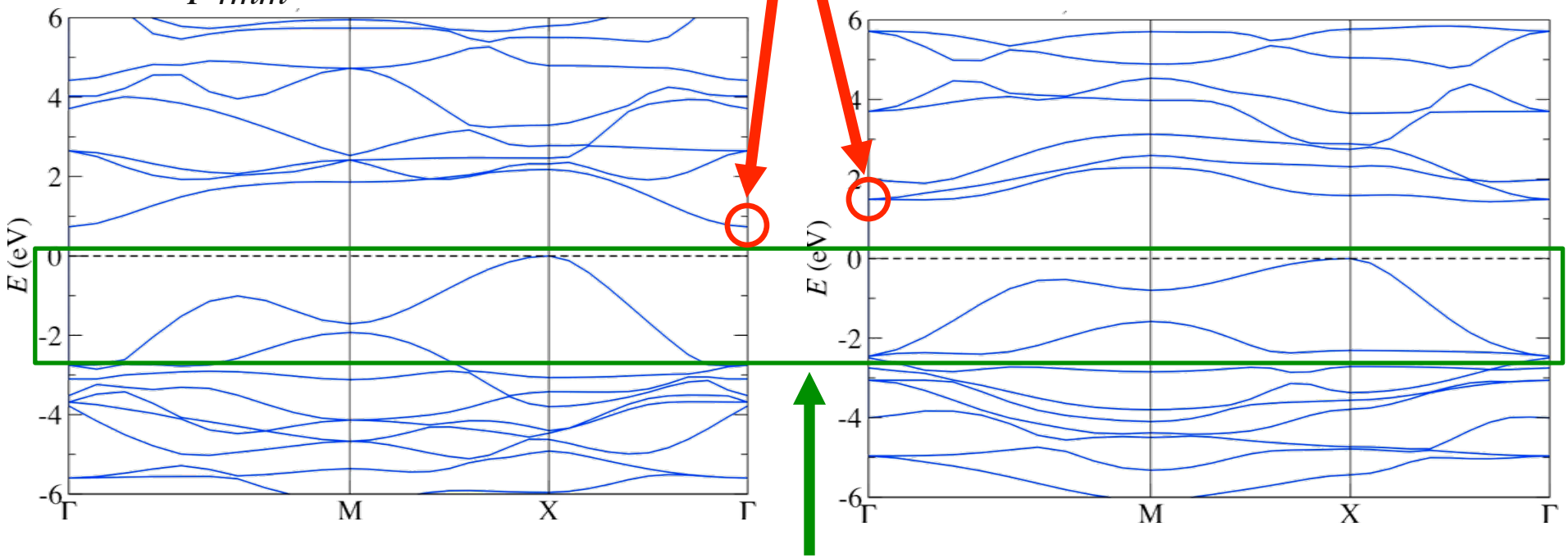


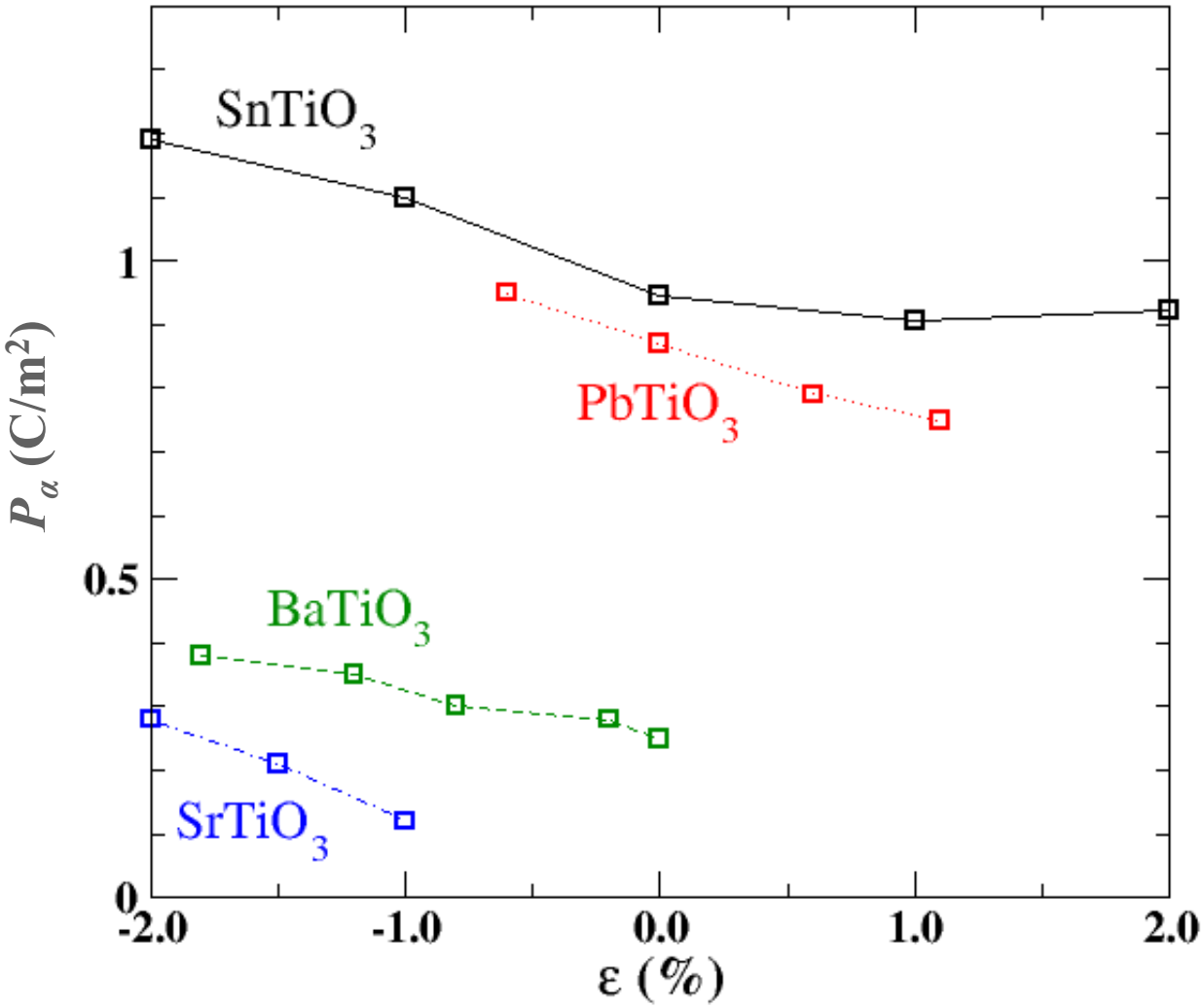
P4mm



Cm

Large shift of LUMO around Γ



HOMO bands look similar

$SnTiO_3$ has large polarization compared to other perovskite ferroelectrics