

Metastable antiferroelectric phases of BiFeO₃ from first principles

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Motivation

- Sm-doped BiFeO₃ with unique electromechanical properties: high switchable polarization and high piezoelectric coefficient comparable to PZT thin films.¹
- Structural phase transition of Bi_{1-x}Sm_xFeO₃ at the morphotropic phase boundary (MPB) at x≈0.14: rhombohedral BiFeO₃ transforms to a pseudo-orthorhombic SmFeO₃ going through a triclinic phase of Bi_{0.86}Sm_{0.14}FeO₃.¹
- Ferroelectric (FE) to antiferroelectric (AFE) transition at the MPB:²
 - (i) Antiparallel cation displacements for 0.1<x<0.14 with onset of formation of AFE clusters in a FE matrix
 - (ii) Antiphase oxygen octahedra tilts for 0.14<x<0.2 inducing complete AFE
 - (iii) Non-polar phase at x=0.3.

Plan

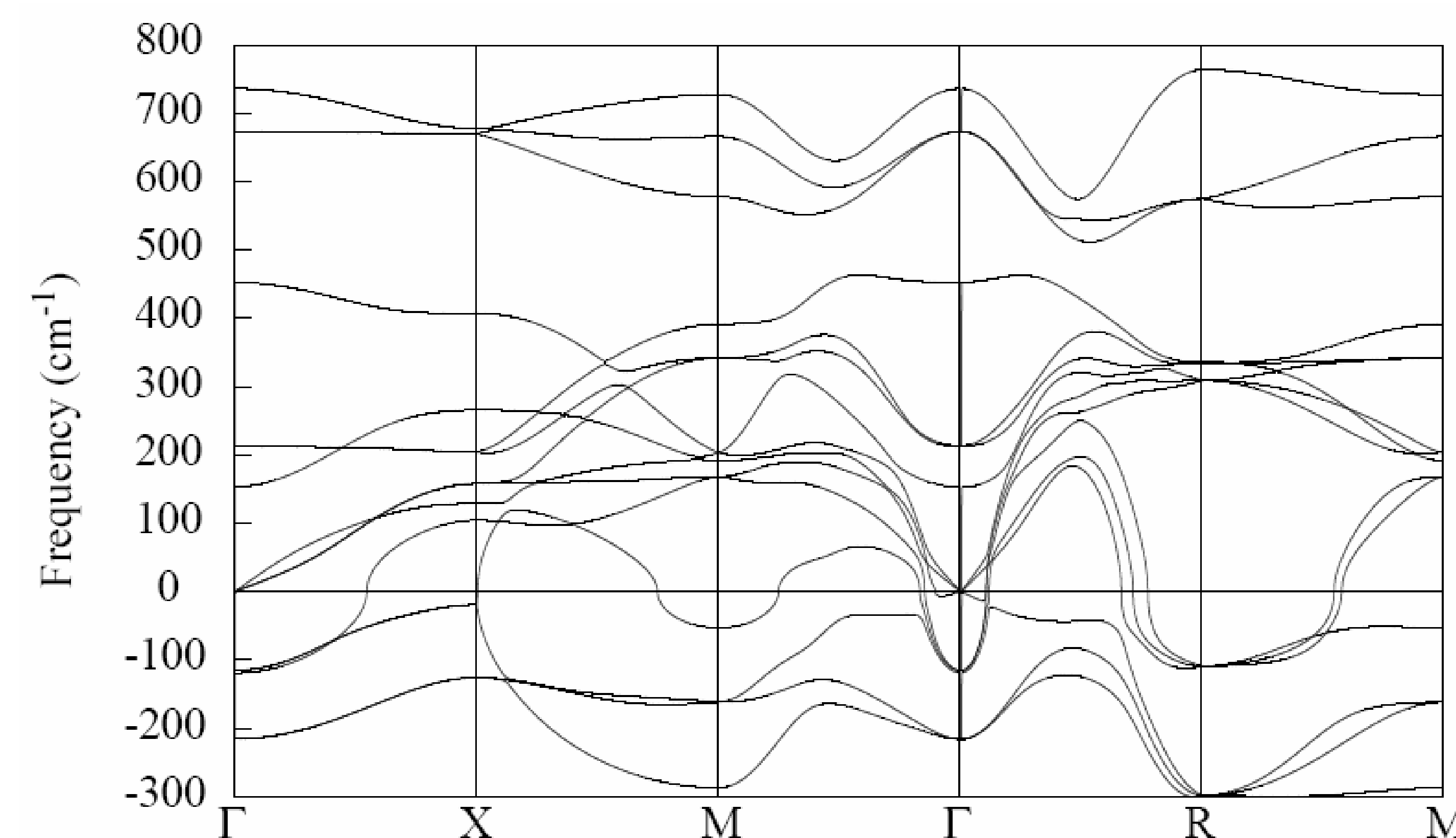
- We study oxygen octahedron tilts and antiparallel cation displacements of pure BiFeO₃, with the idea that the presence of such instabilities indicates the possibility of a corresponding low symmetry phase stabilized by low substitutional doping (Sm), or by some other perturbation.
- Pure BiFeO₃ is FE with T_c = 1100K and G-AFM with T_N = 640K.
- Our starting point : G-antiferromagnetic cubic perovskite BiFeO₃.

Method

- Density functional theory
- Local spin-density approximation +U
 - U = 5eV
 - J = 1eV
- Vienna *ab initio* simulation package (VASP)
- Projector augmented-wave potentials (PAW)
- Plane wave basis set with cutoff energy 800eV
- Monkhorst-pack k-point mesh
 - 6x6x4 (√2x√2x2 perovskite cell), 6x6x4 (Pnma), 6x6x6 (R3c cell), 4x2x3 (Pbam)
- Modern theory of polarization - Born eff. charges in cubic BiFeO₃:
 - q(Bi) = +6.2 |e|, q(Fe) = +3.9 |e|, q(O¹) = -3.4 |e|, q(O²) = -2.5 |e|
- Insulating gap of cubic BiFeO₃: 0.5 eV
- Anaddb package in ABINIT for phonon dispersion

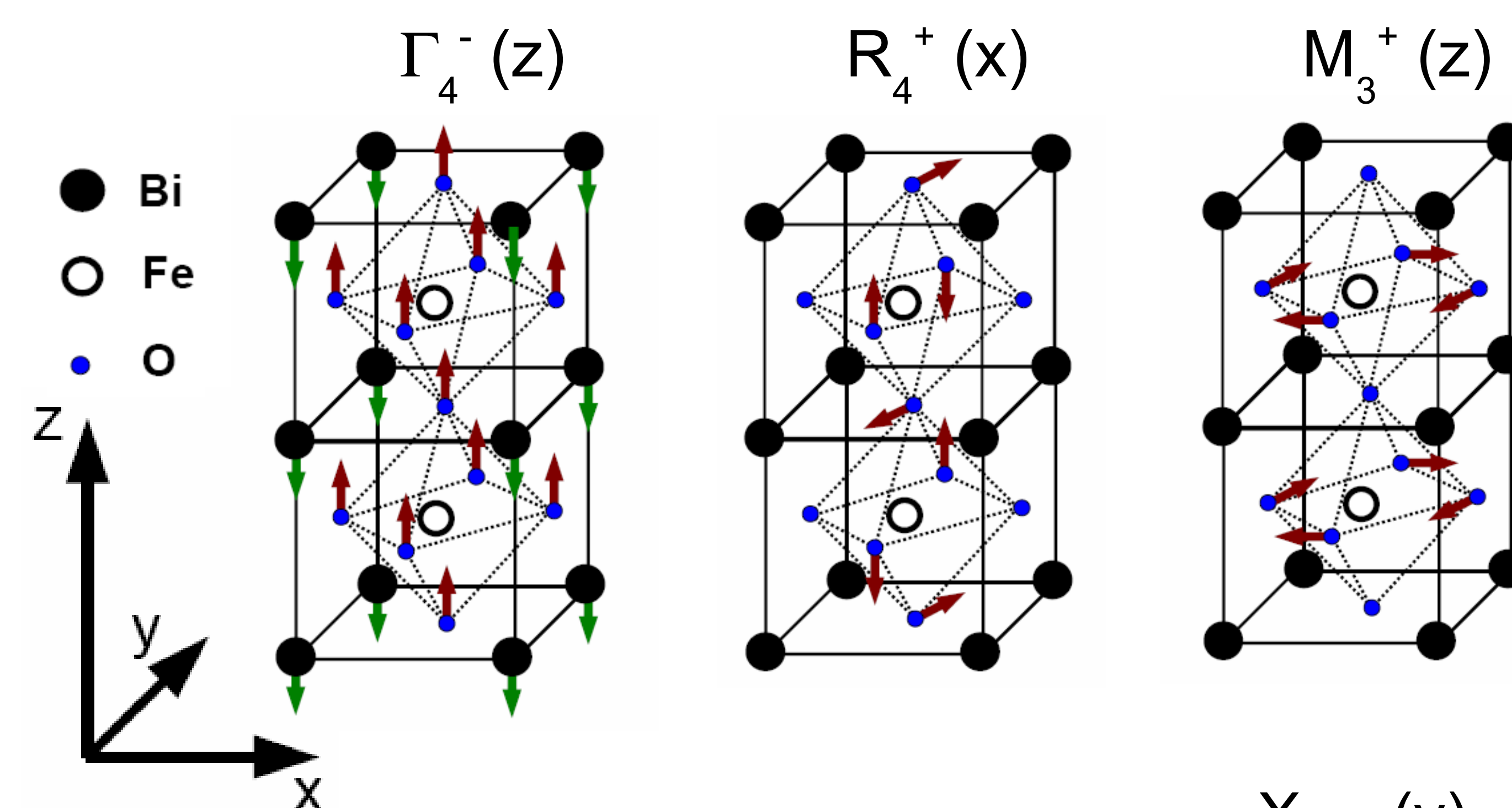
Phonon dispersion

of cubic G-AFM BiFeO₃

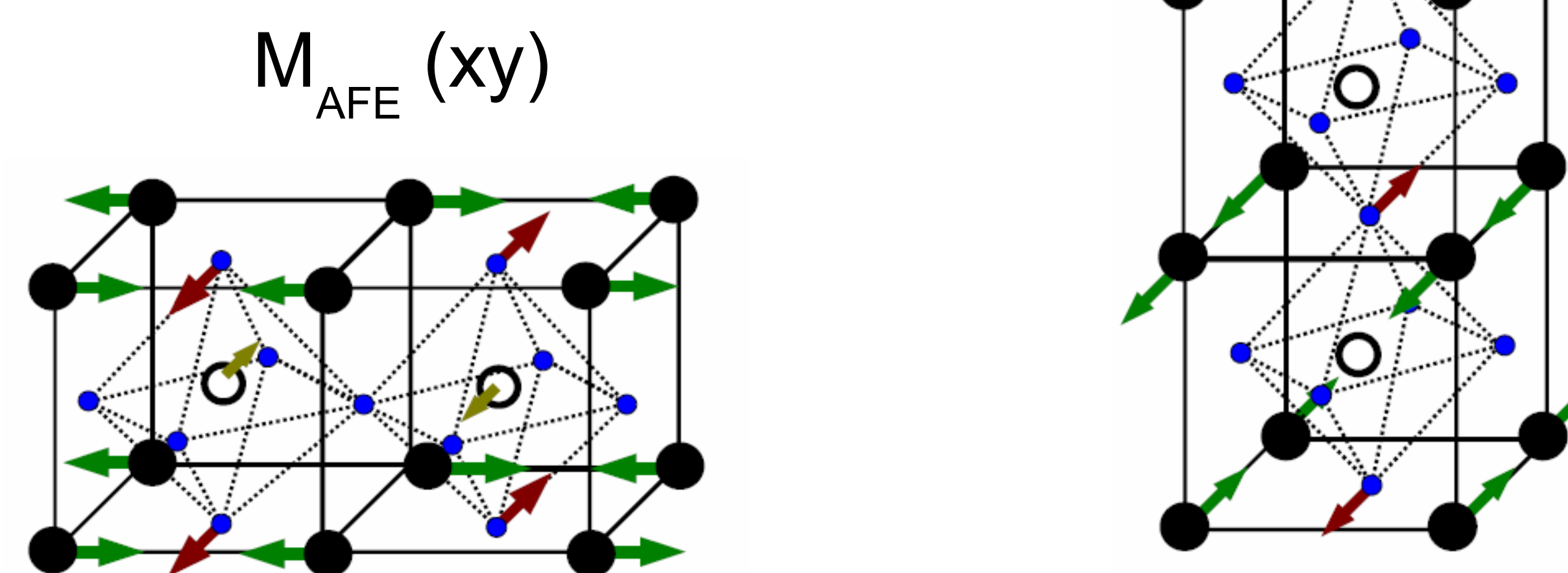


Most unstable zone-center and zone-boundary modes:

Ferroelectric zone-center Γ mode and two zone-boundary R and M rotational modes that lead to oxygen octahedron tilts:



Zone-boundary M and X modes that lead to antiparallel ionic distortions:

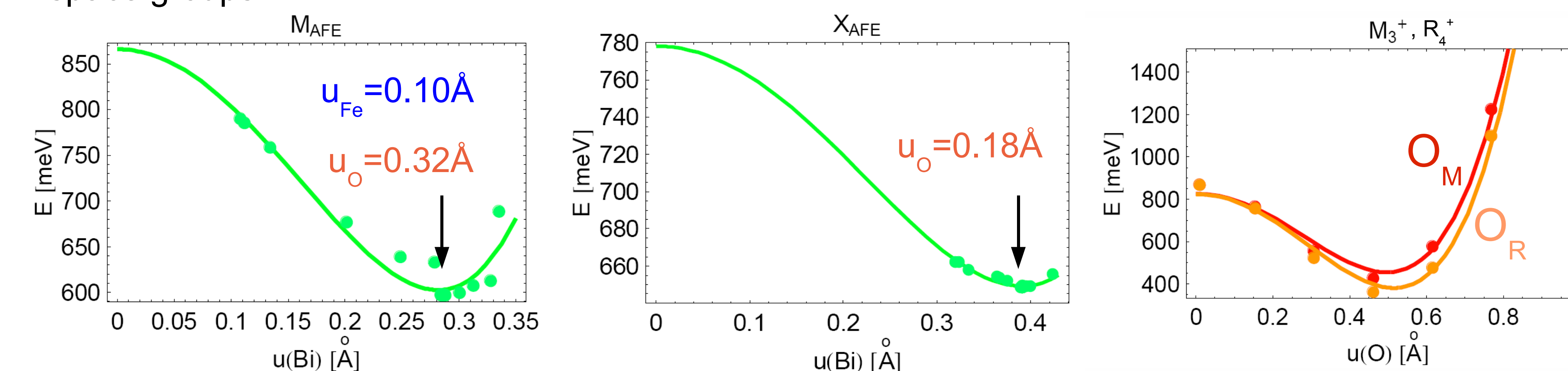


Rhombohedral FE ground state

- Non-polar R_4^+ [111] and polar Γ_4^- [111] modes in a linear combination lead to oxygen octahedron tilts and polar ionic distortions respectively in ferroelectric BiFeO₃ R3c ground state with spontaneous polarization 90 $\mu\text{C}/\text{cm}^2$.

AFE instability

- We freeze in the following modes, singly or in combination: antiferroelectric M_{AFE} and X_{AFE} and octahedron tilts modes R_4^+ and M_3^+ .
- We optimize atomic displacements (see Figures), and lattice parameters (see Table) in the resulting space groups.



Structure	Lattice (a,b,c) [Å]	Description	E diff. w.r.t. GS	
			Volume [Å ³]/f.u.	[meV]/f.u.
X_{AFE} (y)	(3.809,4.066,7.684)	optimized	59.40	573
M_{AFE} (xy)	(5.568,5.568,3.796)	optimized	58.85	538
M_3^+ (z)	3.847 cubic*	optimized	56.96	425
R_4^+ (x)	3.847 cubic*	optimized	56.96	354
M_3^+ (z) and R_4^+ (x)	3.847 cubic*	optimized	56.96	179
Pbam	(5.398,11.196,7.709) ¹	as in PbZrO ₃	58.24	354
Pbam	(5.490,11.160,7.675)	optimized	58.78	153
Pnma	(5.398,5.598,7.709) ¹	as in SrRuO ₃	58.24	244
Pnma	(5.398,5.598,7.709) ¹	optimized	58.24	17
R3c	(5.525,5.525,5.525)	optimized	59.31	0

* lattice parameters fixed

¹ exp. orthorhombic lattice parameters (ref¹)

- Pbam is the space group of AFE PbZrO₃. There is indication from experiment of "PbZrO₃" like AFE pockets emerging below Sm doping x≈0.14. Pbam consists of antiparallel ionic and polar oxygen displacements. It can be decomposed into $\Gamma_{25}^- R$, Γ_{15}^- , $(1/2 \ 1/2 \ 0)(\pi/a)\Sigma_3$, and $(110)(\pi/a)M_5'$ modes.
- Pnma represents a large family of perovskites (e.g. SrRuO₃, CaTiO₃). It can be decomposed into R_4^+ ([110]) and M_3^+ (z) modes.

Summary and Open Questions

- We have identified low energy phases generated by oxygen octahedron tilts and antiparallel ionic distortions.
- Low energy phases competitive with R3c ground state: nonpolar Pbam and Pnma, with different patterns of oxygen octahedron tilts than in R3c. Only 17-150 meV (unfinished optimization) energy difference.
- How does the Sm doping bring the alternative phase lower in energy?
- Sm doping = chemical pressure?
- A site doping favors the antiferroelectric BiFeO₃ phase, but B site doping does not. Why?
- Could we have predicted the AFE-FE phase boundary without knowing the experiment? Can we go beyond and predict new phase boundaries that have not yet been found experimentally?

¹S. Fujino, M. Murakami, A. Varatharajan, S.-H. Lim, V. Nagarajan, C. J. Fennie, M. Wuttig, L. Salamanca-Riba, and I. Takeuchi, Appl. Phys. Lett. **92**, 202904 (2008).

²C.-J. Cheng, S.H. Lim, S. Fujino, W. R. McKenzie, V. Nagarajan, P.R. Munroe, I. Takeuchi, L. Salamanca-Riba and I. B. Misirliglu, arXiv 0803.0777.