Testing Newly Developed Functionals on Typical Ferroelectric Materials

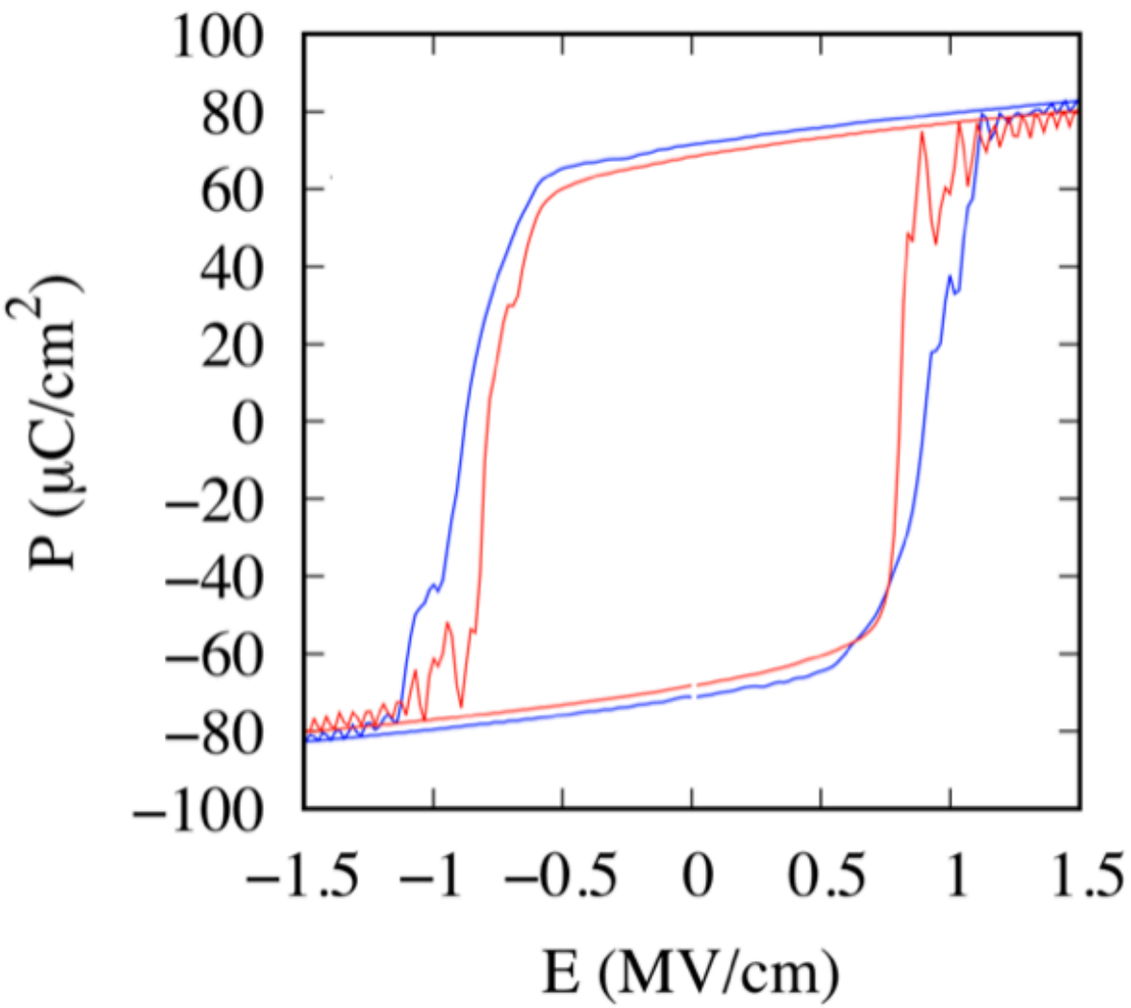
Maggie Kingsland[1,2], Inna Ponomareva[1], Xiao He[2]

[1]Department of Physics, University of South Florida, Tampa, FL 33620, USA
[2]School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200062, China

Ferroelectrics

- Materials that become spontaneously polarized under the application of an electric field
- Polarization is switchable under the application of an electric field
- Exhibit a hysteresis loop P(E)
- Used in capacitors, RAM, RFID cards, solid-state refrigeration, etc.

Hysteresis loop for $PbTiO_3$



K. Rabe, C. H. Ahn, J.-M. Triscone (Eds.): Physics of Ferroelectrics: A Modern Perspective, Topics Appl. Physics 105, 1–30 (2007)

Density Functional Theory

- A method for finding an approximate solution to the Schrödinger equation for a many-body system

- All ground-state properties are determined by the electron density of the system

- Hamiltonian is constructed from
    - ion-electron, ion-ion, and electron-electron potential energies
    - Kinetic energy
    - Exchange-correlation energy

http://newton.ex.ac.uk/research/qsystems/people/coomer/dft_intro.html

Common Functionals

- Local density approximation (LDA)
    - Assumes that the exchange-correlation energy density at every position is the same
- Generalized Gradient approximation (GGA)
    - Improved accuracy than that of LDA
    - Energy density is a gradient at every position
- Meta-GGA
    - Includes kinetic energy density in addition

http://newton.ex.ac.uk/research/qsystems/people/coomer/dft_intro.html

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Motivation

- Commonly used functionals (LDA and GGA) under- or overestimate the curie temperature in ferroelectrics, respectively

- Generally common functionals are not good at estimating band gap energies

Goals

- Test and find which (if any) functionals match experimental results best for $PbTiO_3$ (PTO) and $BaTiO_3$ (BTO)

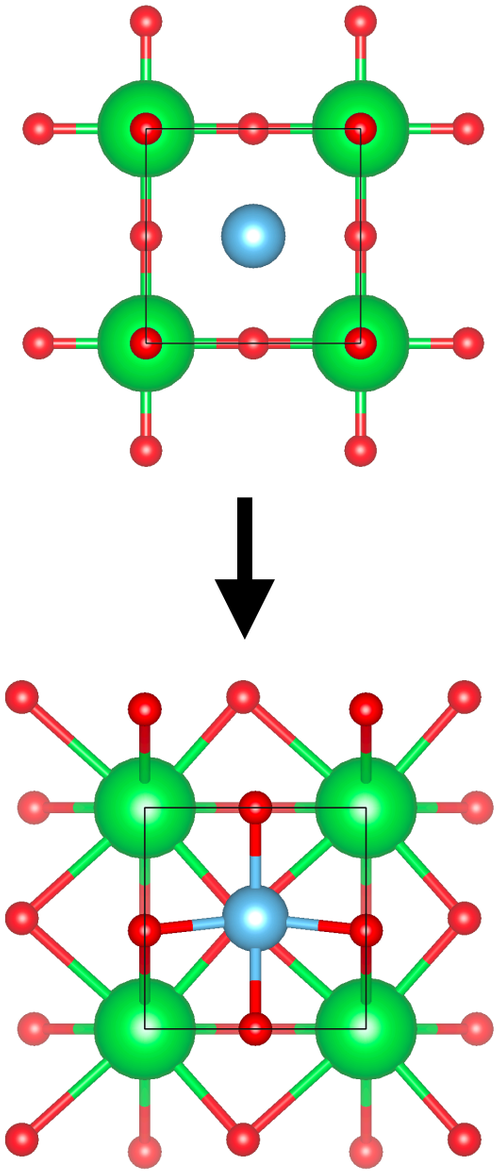
- Compare change in energy from non-polar to polar structure, polarization, and band gap energy

Test Preparation

- Obtain relaxed structures for $BaTiO_3$ (BTO) and $PbTiO_3$ (PTO) for cubic and tetragonal phases using PBE

- Use ISOTROPY to generated a distortion path from cubic parent structure (non-polar) to tetragonal distorted structure (polar)

- Same distortion path used for all functionals (structures not allowed to relax for each functional)



Cubic

Tetragonal

BTO Results

Method	$\|\mathbf{P}\|$ ($\mu C/cm^2$) Tetragonal State	$\mathbf{\Delta E}$ (meV/atom) E_{cubic}-$E_{tetragonal}$	$\mathbf{E_g}$ (eV) Tetragonal State	Total CPU time used (sec)
LDA	38.72	7.55	1.599	42.826
PBE	43.08	7.6	1.602	47.722
SCAN	33.34	3.09	1.98	202.057
GAM	40.12	25.66*	1.658	63.507
HLE17	41.23	19.76	1.608	257.106
Experiment [1]	26	34 (393 K)	3.27-3.38	—

[1] *Phys. Rev. B* **96**, 035143 (2017).

BTO Results (cont.)

Method	$\|\mathbf{P}\|$ ($\mu C/cm^2$) Tetragonal State	$\mathbf{\Delta E}$ (meV/atom) E_{cubic}-$E_{tetragonal}$	$\mathbf{E_g}$ (eV) Tetragonal State	Total CPU time used (sec)
MN12-L	42.32	112.3	2.0253	242.157
N12	39.87	8.11	1.402	69.300
SOGGA	38.74	7.44	1.516	59.934
SOGGA11	38.9	4.83	1.537	66.843
Experiment [1]	26	34 (393 K)	3.27-3.38	—

[1] *Phys. Rev. B* **96**, 035143 (2017).

BTO Conclusion

- No functional best at estimating spontaneous polarization

- GAM functional is computationally cheap and describes energy difference best

- MN12-L functional cheaply calculates a band gap energy with results comparable to the SCAN functional

- Didn't find a functional that was better for estimating all investigated properties

PTO Results

Method	|**P**| (μC/cm^2) Tetragonal State	**ΔE** (meV/atom) E_{cubic}-$E_{tetragonal}$	$\mathbf{E_g}$ (eV) Tetragonal State	Total CPU time used (sec)
LDA	93.15	19.5	1.392	108.498
PBE	93.09	19.3	1.508	75.191
SCAN	93.33	22.9	1.788	234.808
GAM	92.22	38.9	1.537	77.752
HLE17	85.21	52.7	1.746	307.029
Experiment[1]	57-100	67 (760 K)	3.6	—

[1] *Phys. Rev. B* **96**, 035143 (2017).

PTO Results (cont.)

Method	$\|\mathbf{P}\|$ ($\mu C/cm^2$) Tetragonal State	$\mathbf{\Delta E}$ (meV/atom) E_{cubic}-$E_{tetragonal}$	$\mathbf{E_g}$ (eV) Tetragonal State	Total CPU time used (sec)
MN12-L	104.43	394.5	3.006	287.552
N12	92.56	31.7	1.751	66.715
SOGGA	92.98	14.8	1.761	61.755
SOGGA11	93.28	17.9	1.75	63.211
Experiment[1]	57-100	67 (760 K)	3.6	—

[1] *Phys. Rev. B* **96**, 035143 (2017).

PTO Conclusion

- No functional best at estimating spontaneous polarization
- HLE17 functional describes energy difference best
- MN12-L functional cheaply calculates a band gap energy with results comparable to the HSE functional
- Didn't find a functional that was better for estimating all investigated properties

Future Plans

- Run the MN15-L, revM06-L, N12-SX, SOGGA11-X, and HSE06 functionals for BTO and PTO

- Find properties of fully relaxed structures for BTO and PTO for all functionals tested

- Possibly obtain individual distortion path for each functional

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