Calculation of Electric Polarization with Berry Phase

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What you learn here

- **Polarization strongly depends on the detailed atomic coordinates.**
  - **Structure optimization is mandatory.**

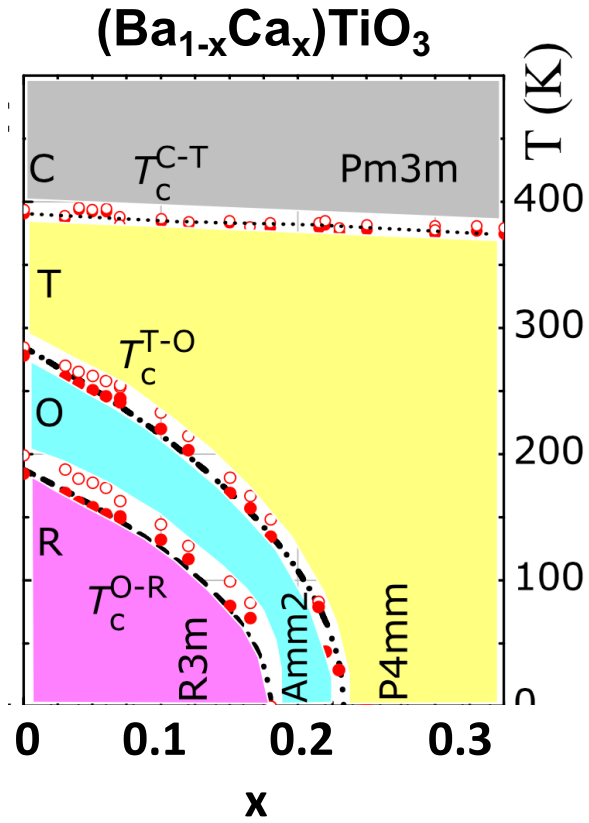
$$\boldsymbol{P} = \frac{e}{\Omega}\sum_n Z_n^* \boldsymbol{u}_n \qquad\qquad \frac{ea}{\Omega} \sim 1\mathrm{C/m}^2$$

- **Berry phase has 2π arbitrariness like ordinary phase.**
  - **Its variation along an adiabatic path possesses physical meaning.**

$$\Delta \boldsymbol{P} = \int_0^1 \left(\frac{\partial \boldsymbol{P}}{\partial \lambda}\right) d\lambda = \boldsymbol{P}^{(1)} - \boldsymbol{P}^{(0)}$$

$BaTiO_3$

- **Typical Ferroelectric Material**
- **Successive Phase Transitions (R < O < T < C)**
- **Competing Soft Modes**



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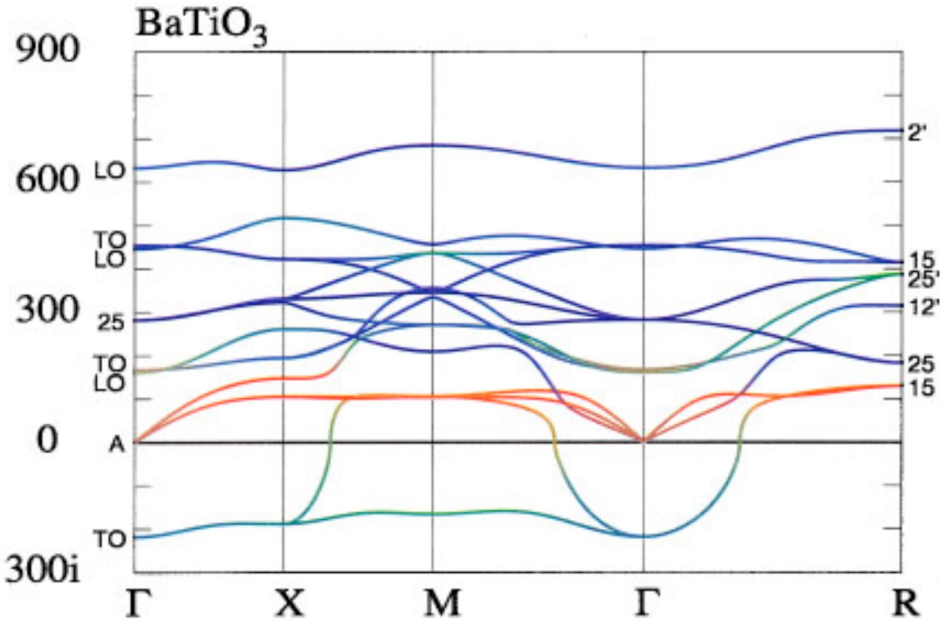


PRB 60, 836 (1999)

$BaTiO_3$

Crystal system	Space group	Lattice constants	Atom site fraction (para-phase)	Crystallography Open Database
tetragonal	P4mm (#99)	a=3.9905Å c=4.0412Å	z(Ti)=0.476 (0.5) z(O1)=0.043 (0) z(O2)=0.533 (0.5)	1513252
orthorhombic	Amm2 (#38)	a=3.9806Å b=5.6710Å c=5.6904Å	z(Ti)=0.5143 (0.5) z(O1)=0.489 (0.5) y(O2)=0.2561 z(O2)=0.24833	9014627
rhombohedral	R3m (#160)	a=4.0036Å α=89.84°	x(Ti)=0.488 (0.5) x(O)=0.5116 (0.5) z(O)=0.0195 (0.0)	9014230

http://www.crystallography.net/cod/

$BaTiO_3$

$$E(a,b,c,\alpha,\beta,\gamma,\{R_n\})$$

system=(BaTiO3_P4mm BaTiO3_Amm2 BaTiO3_R3m)

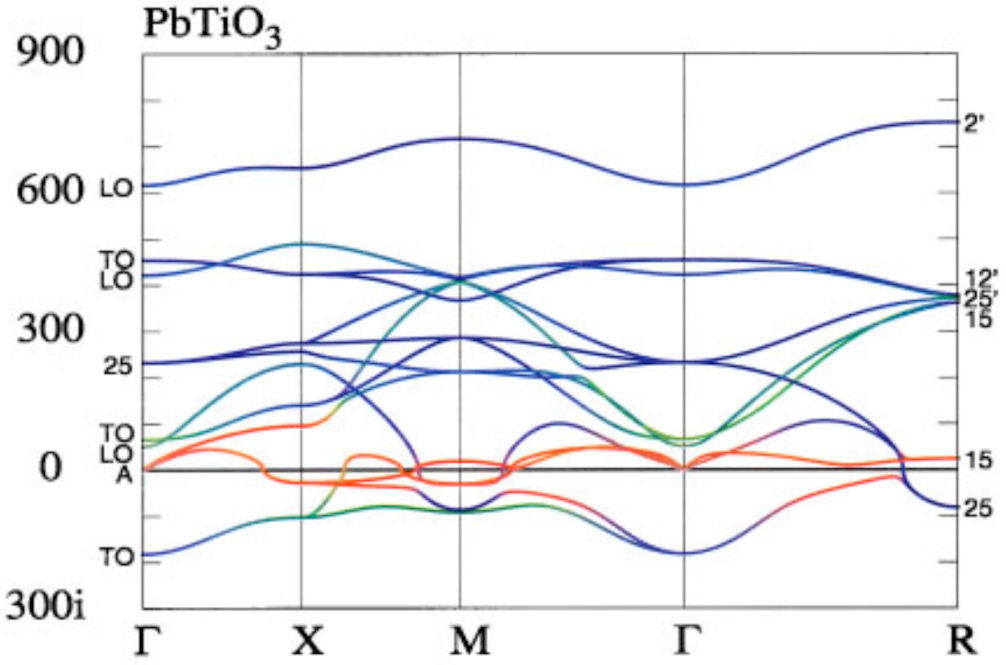
SCF → Polarization
Optimization → Polarization

Crystal system	Space group	Polarization		
		unrelaxed	relaxed	Experiment*
tetragonal	P4mm (#99)	-0.50 C/m²	-0.34 C/m²	0.27 C/m²
orthorhombic	Amm2 (#38)	+0.23 C/m²	+0.37 C/m²	0.36 C/m²
rhombohedral	R3m (#160)	-0.41 C/m²	-0.40 C/m²	0.33 C/m²

*: Landolt-Bornstein Numerical Data and Functional Relationships in Science and Technology (Springer-Verlag, 1981) NS, III/16.

$PbTiO_3$ → piezo $Pb(Zr_{1/2}Ti_{1/2})O_3$

- **Typical Ferroelectric Material**
- **Phase Transition between Tetragonal ⇄ Cubic**
- **Larger Displacement than $BaTiO_3$ → Role of Pb**

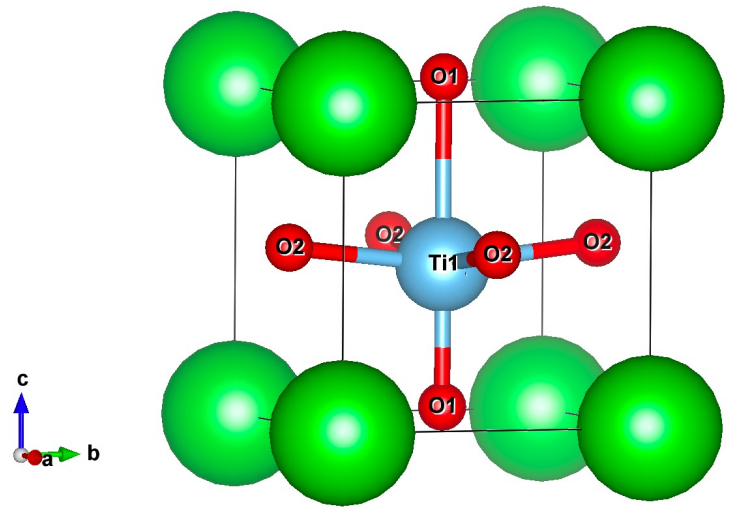


PRB 60, 836 (1999)

Tetragonal $PbTiO_3$ and $BaTiO_3$

System	Lattice constants	Atom site fraction	Bond length
$BaTiO_3$ (COD:1513252)	a= 3.9905Å c= 4.0412Å c/a= 1.0127	z(Ti) = 0.476 -> 0.4857 z(O1)= 0.043 -> 0.0306 z(O2)= 0.533 -> 0.5179	Ti-O1=1.750Å Ti-O2=2.009Å Ba-O2=2.746Å Ba-O1=2.827Å
$PbTiO_3$ (COD:1525905)	a= 3.90044Å c= 4.15115Å c/a= 1.06428	z(Ti) = 0.5370 -> 0.5472 z(O1)= 0.1088 -> 0.1194 z(O2)= 0.6123 -> 0.6257	Ti-O1=1.764Å Ti-O2=1.977Å Pb-O2=2.529Å Pb-O1=2.795Å

P=-0.90 -> -0.94
relaxed

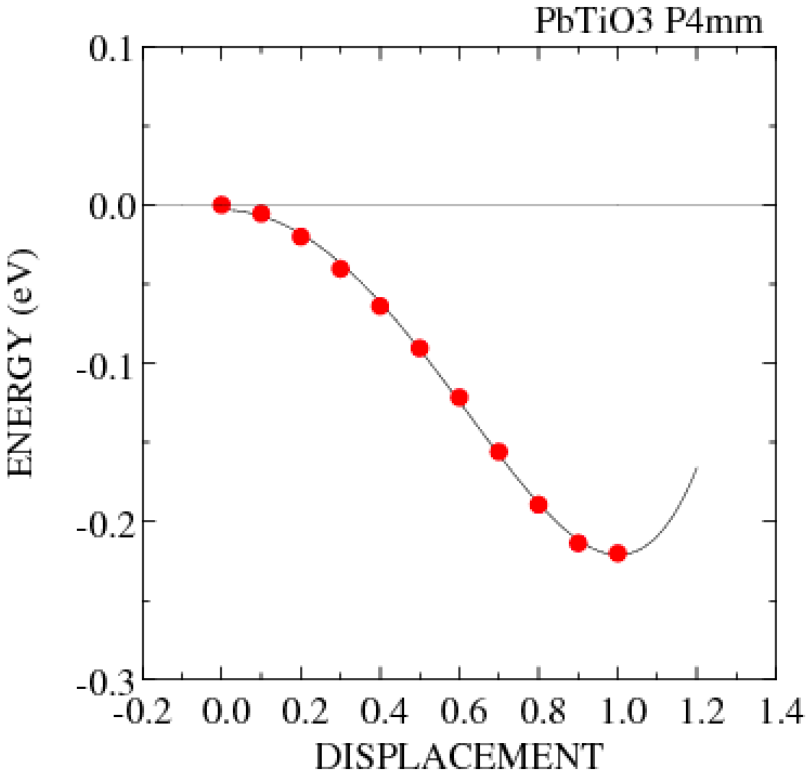


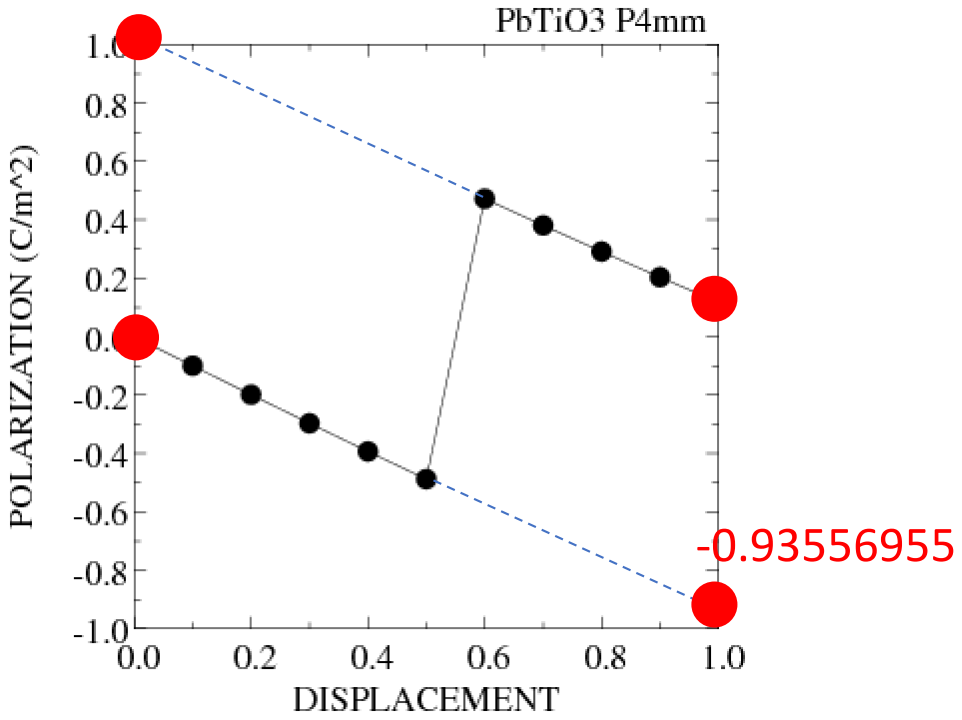
Ba, Pb:	0,	0,	0
Ti:	1/2,	1/2,	z
O1:	1/2,	1/2,	z
O2:	0,	1/2,	z

$PbTiO_3$

- **Adiabatic Path with Gap Open**

Paraelectric Phase • • • • • Ferroelectric Phase





Polarization Calculations

```
# cd
# tar zxvf ~teac03/hilapw_Ferroelectrics.tar.gz
# cd hilapw_Ferroelectrics
# cd BaTiO3_P4mm
# qsub JOB.sh
# cd ../BaTiO3_Amm2
# qsub JOB.sh
# cd ../BaTiO3_R3m
# qsub JOB.sh
```

Polarization Calculations

~/hilapw_Ferroelectrics/PbTiO3_P4mm
[STEP1]
qsub JOB.sh ← for SCF & optimization of the ferroelectric phase

[STEP2]
Check a file list_newtau
xlist_newtau < list_newtau

[STEP3]
in JOB.sh file
./JOB-ALL ← comment
./JOB-LIST ← comment out
qsub JOB.sh

[STEP4]
./GET-POL > polarization_all
PSP < psp_POL > POL.ps

[STEP5]
./GET-TEN > TEN_P2
cat efitn_n.in TEN_P2 | xefitn_n > fit_TEN_P2
tail -123 fit_TEN_P2 > TEN2_P2
PSP < psp_TEN > TEN.ps

Additional Calculations

FINDSYM

```
# cd
# cp ~teac03/iso.zip .
# unzip iso.zip
```

Look at the findsym site (https://stokes.byu.edu/iso/isolinux.php) for configuration

cif conversion tool

```
# cd
# tar zxvf ~teac03/cif2esc.tar.gz
# cd cif2esc
# ./configure.sh
# source ~/.bash_profile
```