Calculation of Electric Polarization with Berry Phase

Tamio Oguchi

What you learn here

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

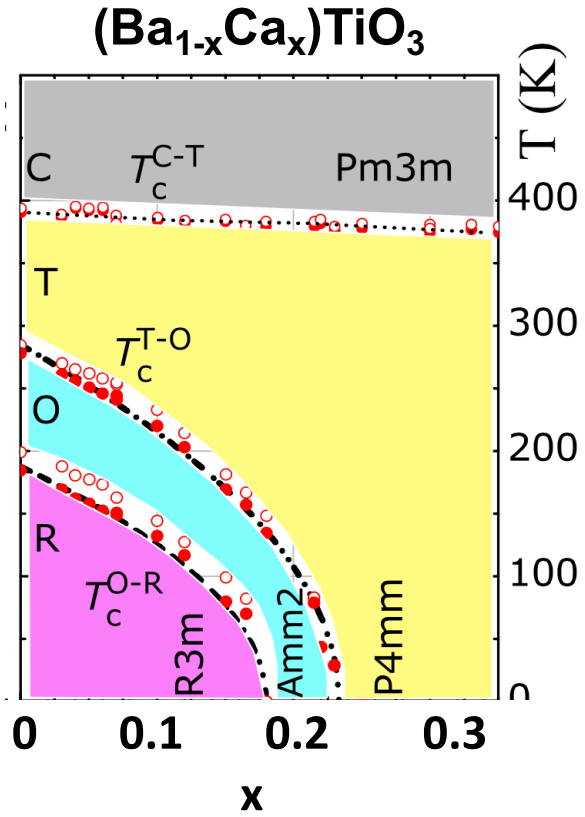
$$\boldsymbol{P} = \frac{e}{\Omega}\sum_n Z_n^* \boldsymbol{u}_n \qquad\qquad \frac{ea}{\Omega} \sim 1\mathrm{C/m}^2$$

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

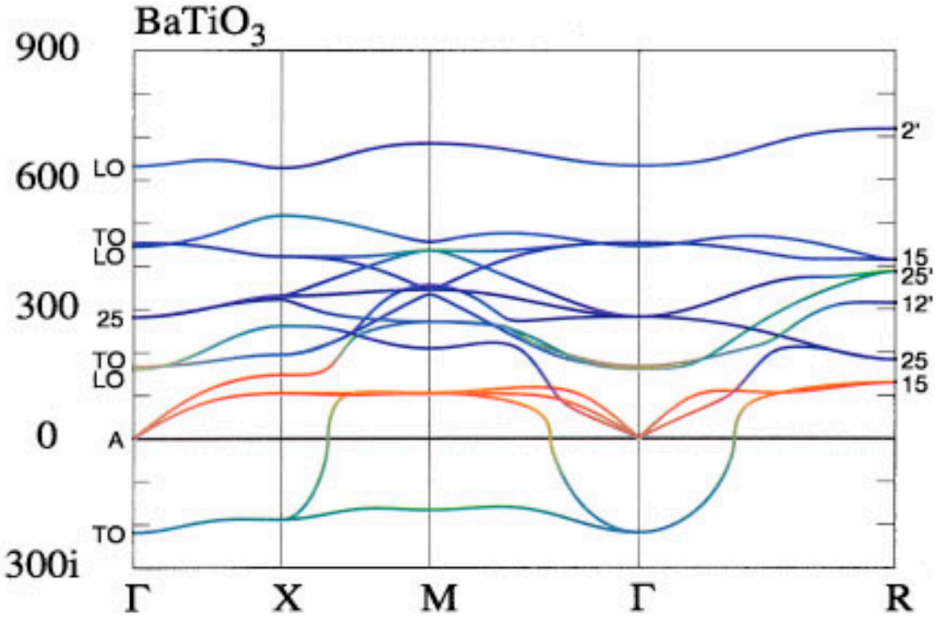
$$\Delta \boldsymbol{P} = \int_0^1 \left(\frac{\partial \boldsymbol{P}}{\partial \lambda}\right) d\lambda = \boldsymbol{P}^{(1)} - \boldsymbol{P}^{(0)}$$

$BaTiO_3$

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



PRL 100, 227601 (2008)



PRB 60, 836 (1999)

$BaTiO_3$

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

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

$BaTiO_3$

system=(BaTiO3_P4mm BaTiO3_Amm2 BaTiO3_R3m)

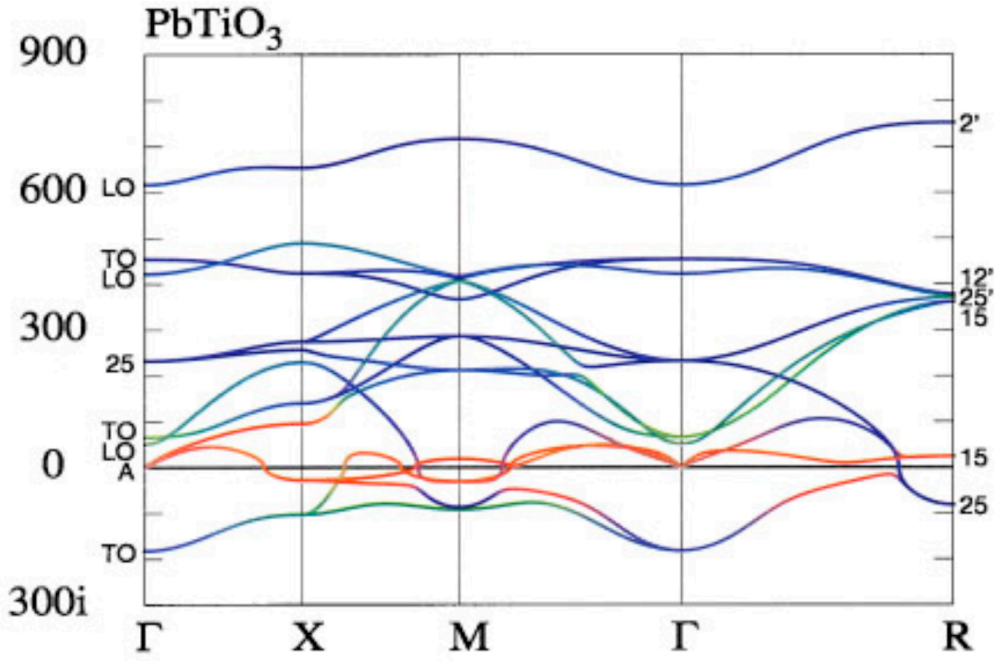
SCF → Polarization
Optimization → Polarization

Crystal system	Space group	Polarization		
		unrelaxed	relaxed	Experiment*
tetragonal	P4mm (#99)	XXX C/m^2	XXX C/m^2	**0.27 C/m^2**
orthorhombic	Amm2 (#38)	XXX C/m^2	XXX C/m^2	**0.36 C/m^2**
rhombohedral	R3m (#160)	XXX C/m^2	XXX C/m^2	**0.33 C/m^2**

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

$PbTiO_3$

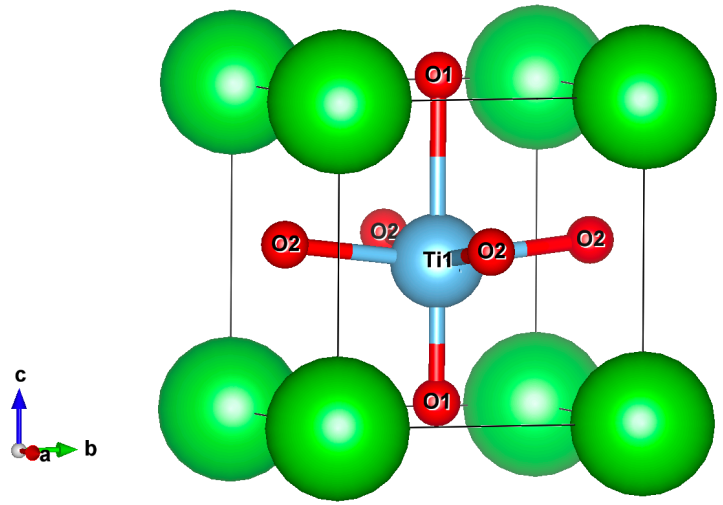
- **Typical Ferroelectric Material**
- **Phase Transition between Tetragonal ⇄ Cubic**
- **Larger Displacement than $BaTiO_3$ → Role of Pb**



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 z(O1)= 0.043 z(O2)= 0.533	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)= 0.4663 z(O1)= –0.1088 z(O2)= 0.3877	Ti-O1=1.764Å Ti-O2=1.977Å Pb-O2=2.529Å Pb-O1=2.795Å



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