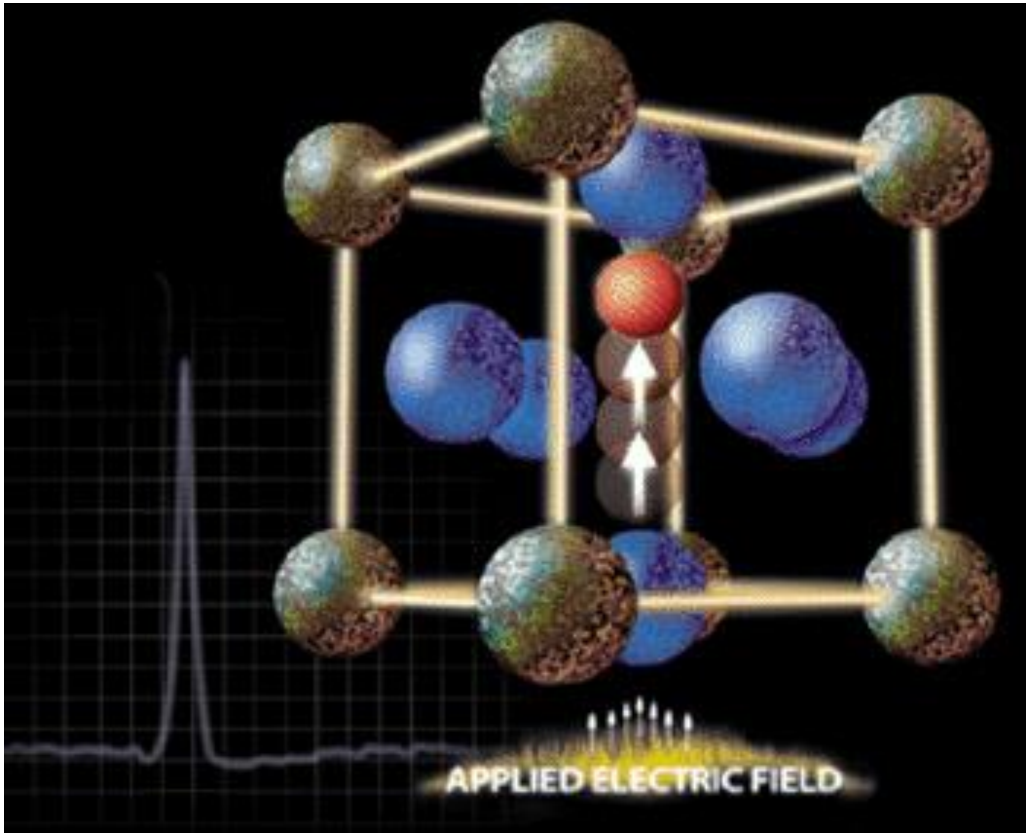
Ferroelectricity



Polarization, Capacitance, Dielectric Properties

Capacitance $$C = \frac{q}{V}$$

Capacitance of a parallel plate capacitor

$$C = \varepsilon\varepsilon_0 \frac{A}{L}$$

Relative Dielectric Constant

$$\varepsilon = \frac{C}{C_{Vac}}$$

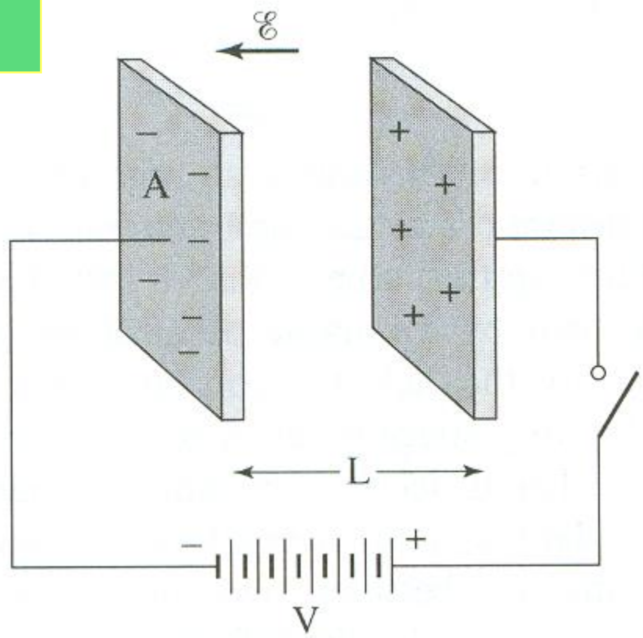


Figure 9.16. Two metal plates, separated by a distance, L, can store electric energy after having been charged momentarily by a battery.

Polarization, Capacitance, Dielectric Properties

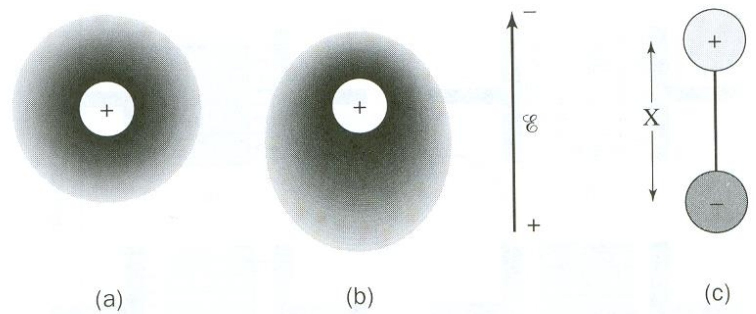


Figure 9.17. An atom is represented by a positively charged core and a surrounding, negatively charged, electron cloud (a) in equilibrium and (b) in an external electric field. (c) Schematic representation of an electric dipole as, for example, created by separation of the negative and positive charges by an electric field, as seen in (b).

Electric Dipole Moment

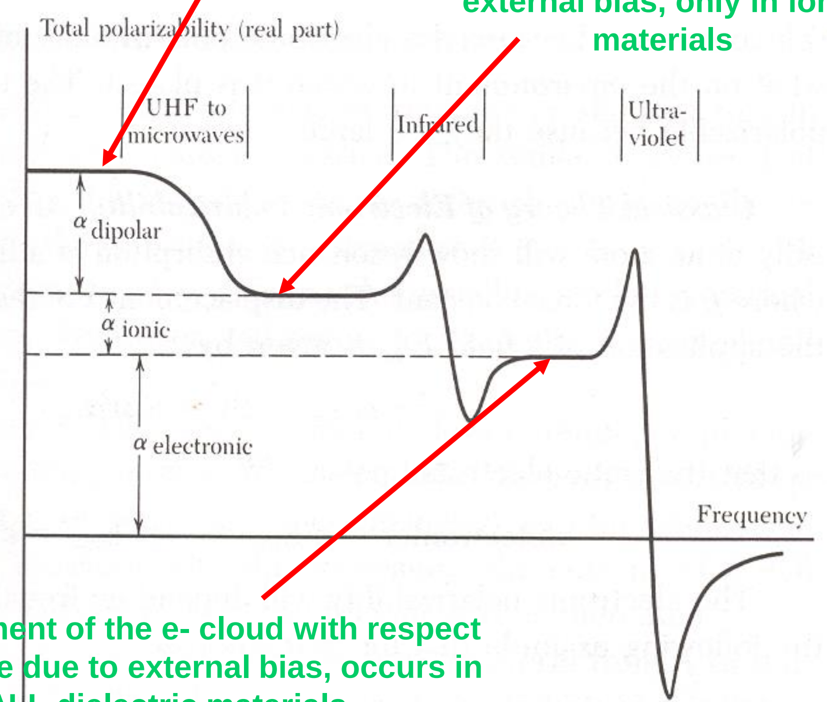
$$p = q \cdot x$$

Polarization

$$P = \frac{p}{V} \equiv \frac{q}{A}$$

Materials *already* possesing permanent dipoles, H_2O, $BaTiO_3$, oils, waxes, amorphous polymers,…

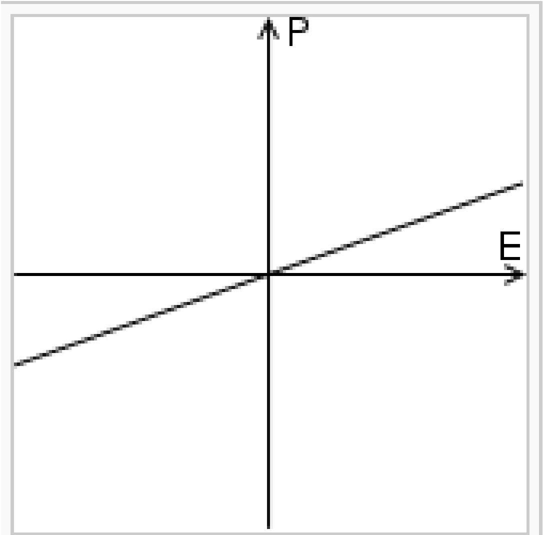
Displacement of ions with respect to each other due to external bias, only in ionic materials



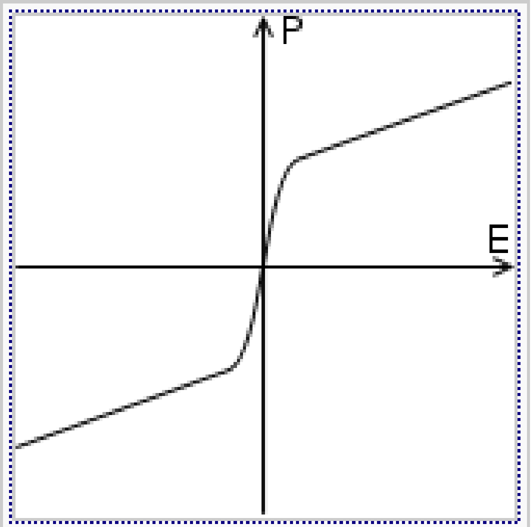
displacement of the e- cloud with respect to the core due to external bias, occurs in ALL dielectric materials

Frequency dependence of the several contributions to the polarizability.

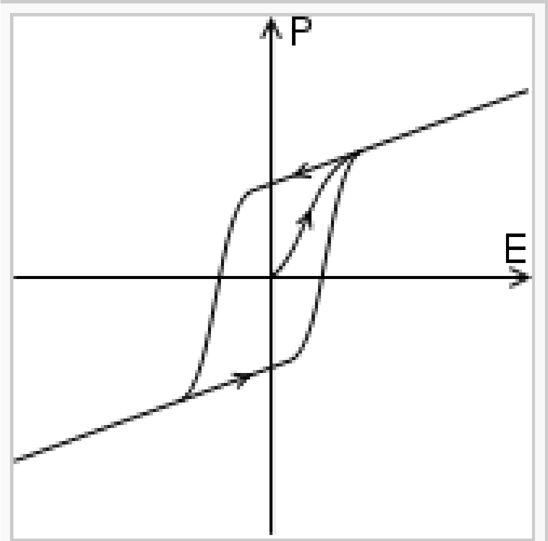
Dielectrica, Paraelectrica and Ferroelectrica



Dielectric polarization



Paraelectric polarization



Ferroelectric polarization

Induced dipoles

Permanent dipoles

Permanent dipoles
With spontaneous
polarization

Some Important Definitions

D: electrical displacement

ε: dielectric constant

E: electrical field

E_c: coercive field

d_{ijk}: piezoelectric coefficient (third rank tensor)

p: pyroelectric coefficient

Q_{ijkl}: electrostrictive coefficient (fourth rank tensor)

$$D = P_S + E\varepsilon$$

Consider Gauss's Law in the presence of a dielectric:

$$\nabla \cdot \mathbf{E} = \frac{1}{\varepsilon_0} \rho_{\text{total}}$$

$$= \frac{1}{\varepsilon_0} \left(\rho_f + \rho_b \right)$$

ρ_{total} : Total charge density

ρ_f : Free charge density

ρ_b : Bound charge density

$$\because \rho_b = -\nabla \cdot \mathbf{P}$$

$$\therefore \varepsilon_0 \nabla \cdot \mathbf{E} = \rho_f - \nabla \cdot \mathbf{P}$$

$$\Rightarrow \nabla \cdot \underbrace{\left(\varepsilon_0 \mathbf{E} + \mathbf{P}\right)} = \rho_f \qquad \boxed{\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}}$$

electric displacement D

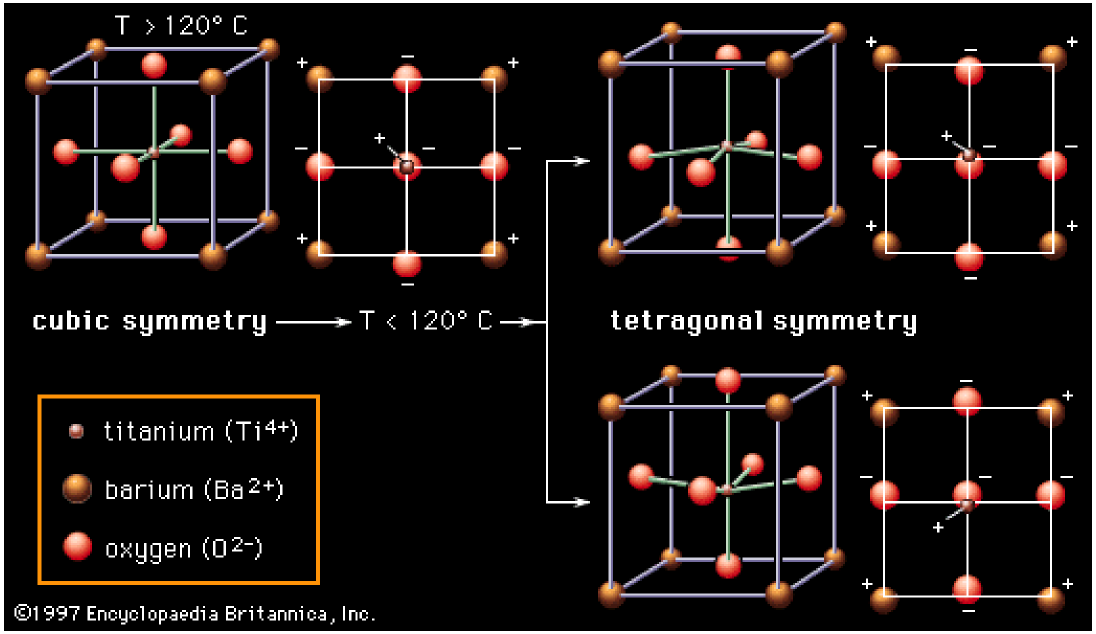
Then,

$$\nabla \cdot \mathbf{D} = \rho_f$$

Integral form:

$$\oint_{\text{surface}} \mathbf{D} \cdot d\mathbf{a} = Q_{f\text{enc}}$$

Perovskite Structure



Typical Perovskite Ferroelectrics

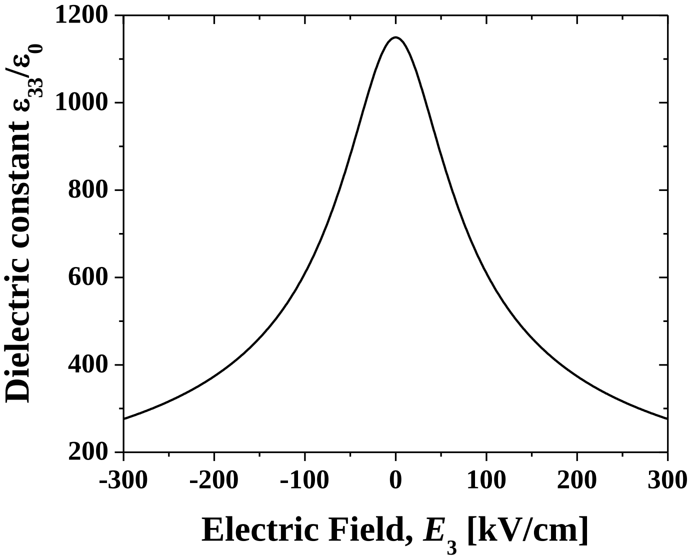
- $Pb(Zr,Ti)O_3$-PZT
- $Ba(Sr,Ti)O_3$-BST
- $KNbO_3$ and $LiNbO_3$
- $Pb(Ca,Ti)O_3$ -PCT
- $Pb(Sr,Ti)O_3$ –PST
- $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$

Properties

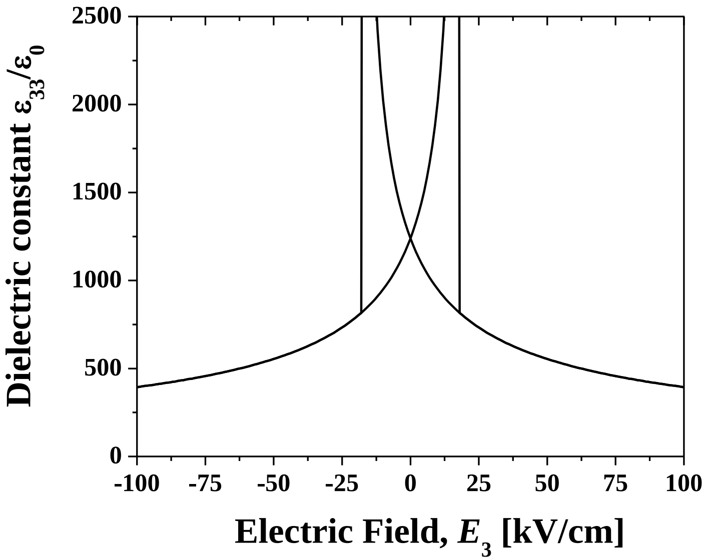
- ✓ Spontaneous polarization in the absence applied electrical field.
- ✓ Extremely high dielectric constant (~500-15,000).
- ✓ Strong non-linear dielectric response to an applied electrical field.
- ✓ High strain response to applied electrical field ⇨ **piezoelectricity**
- ✓ Strong variation in polarization with temperature ⇨ **pyroelectricity**

Dielectric Constant: Slope of the *P* vs. *E* curve

$$P_i = \varepsilon_0 \varepsilon_{ij} E_j$$



Paraelectric

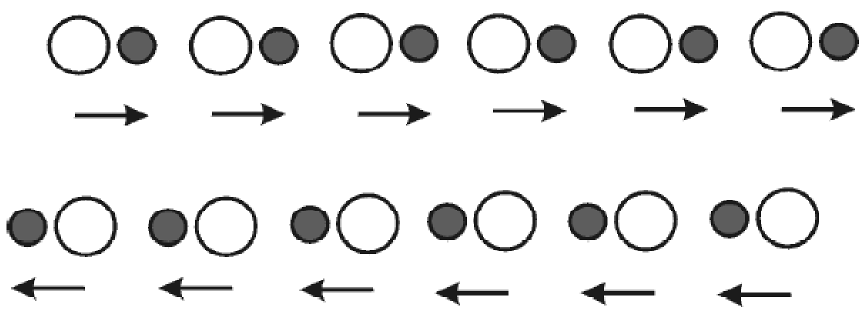


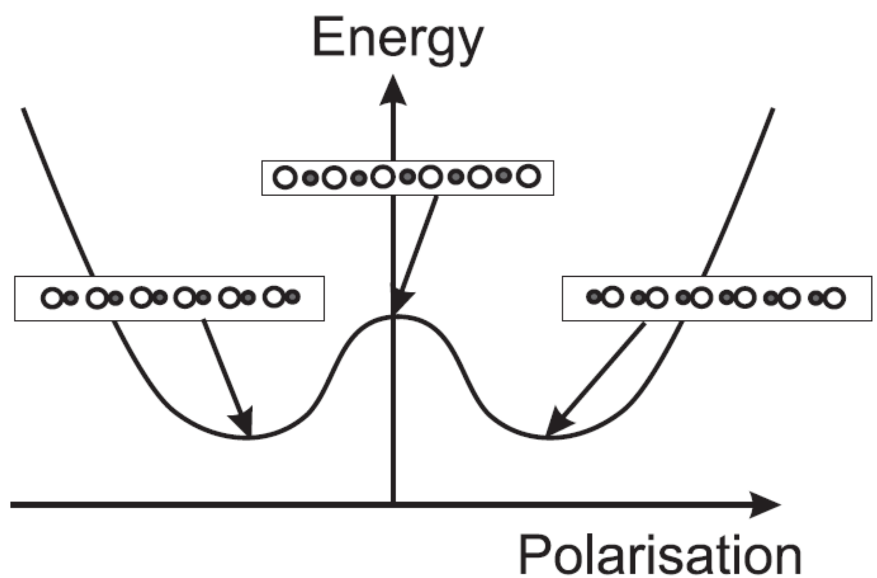
Ferroelectric

Field dependence of dielectric permittivity → **Tunability**

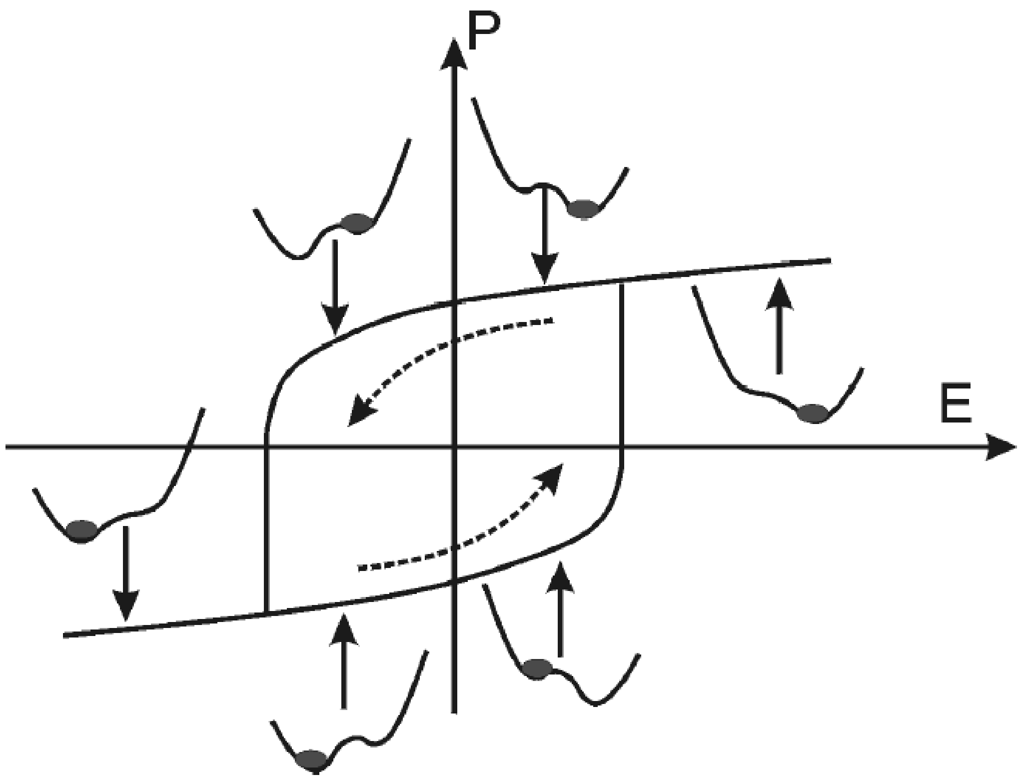
Ferroelectrica:

Two polarized states of equal energy but opposite direction





Spontaneous Polarization and the Hysteresis



Spontaneous Polarization and the Hysteresis

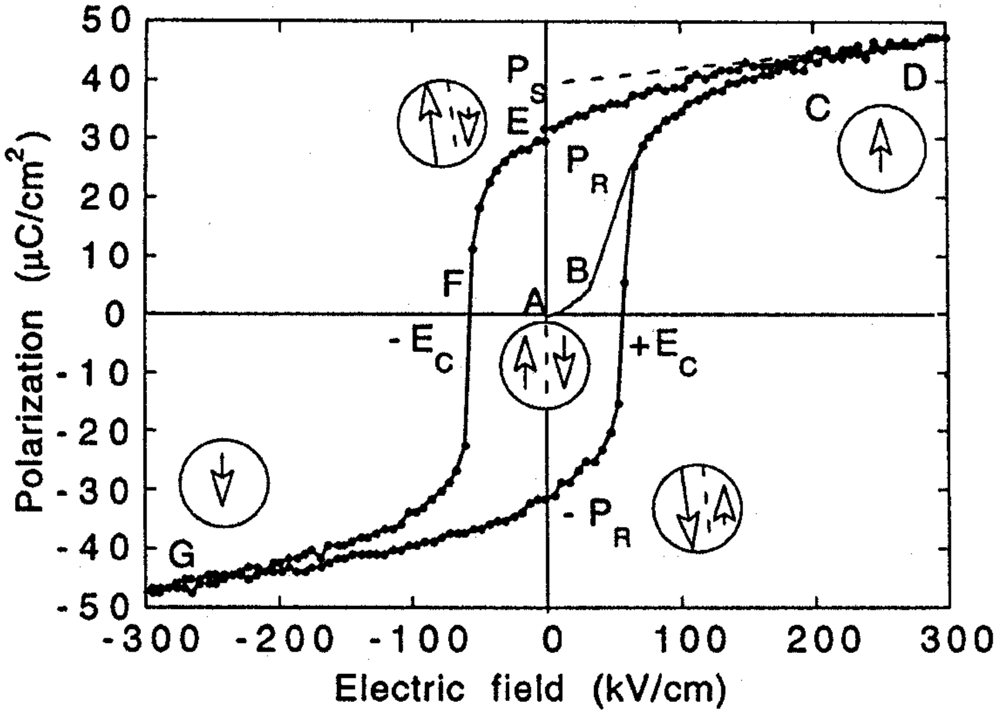


Figure 8. Ferroelectric (*P–E*) hysteresis loop. Circles with arrows represent the polarization state of the material at the indicated fields. The symbols are explained in the text. The actual loop is measured on a (111)-oriented 1.3 μm thick sol-gel $Pb(Zr_{0.45}Ti_{0.55})O_3$ film. (Experimental data courtesy of D V Taylor.)

Free energy is that portion of energy that is available to perform thermodynamic work; *i.e.*, work mediated by thermal energy.

Most useful to describe properties of solid materials at constant pressure that can expand or shrink as a function of temperature.

$$F = U - TS$$

Where U is the internal energy stored in a certain volume

Natural variables: $T, V, \{N_i\}$

Differential: $$\mathrm{d}F = -p\,\mathrm{d}V - S\mathrm{d}T + \sum_i \mu_i\,\mathrm{d}N_i$$

Ginzburg Landau Theory of Phase Transitions

Any crystal in thermodynamic equilibrium can be completely specified by the values of a number of variables:
Temperature T, entropy S, electric Feld **E**, polarization **P**, stress σ and strain s.

We are applying externally electric fields **E** and elastic stresses σ, the crystal responds with the polarization and strain.

Expand the free energy in powers of the dependent variables, with unknown coefficients.

Simple example: a single component of the polarization, and ignore the strain field.

$$\mathcal{F}_P = \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + ... - EP$$

Finding the minima of F: $$\frac{\partial \mathcal{F}}{\partial P} = 0$$

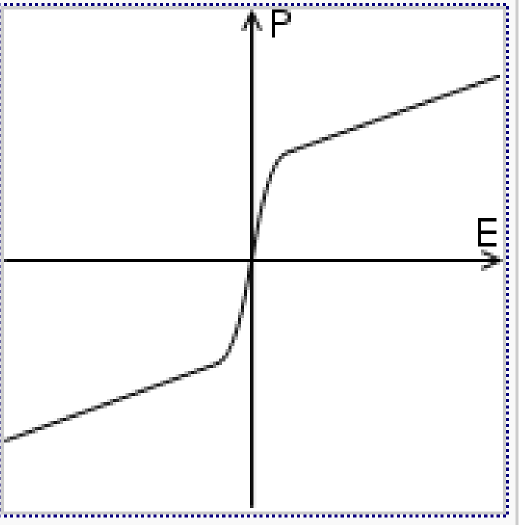
Paraelectric Materials:

If **a; b; c** are all positive, the free energy (for **E** = 0) has a minimum at the origin.

$$\frac{\partial \mathcal{F}}{\partial P} = aP - E = 0$$

This provides a relationship between the polarizability and the field (in linear response, **for small electric field**) which defines the dielectric susceptibility

$$\chi = \frac{P}{E} = \frac{1}{a}$$



Paraelectric polarization

Ferroelectric Materials:

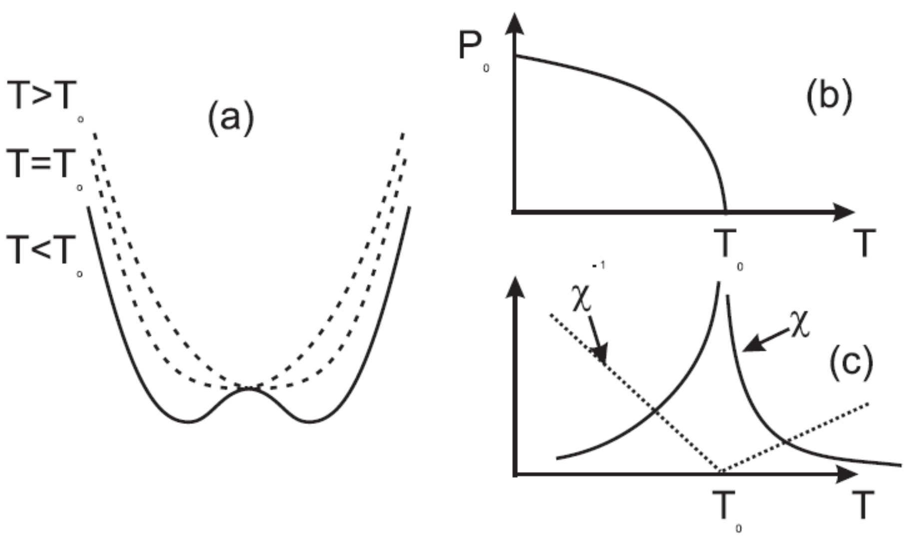
If **a < 0**, while **b; c > 0**: The free energy will have a double minimum at a finite polarization P.

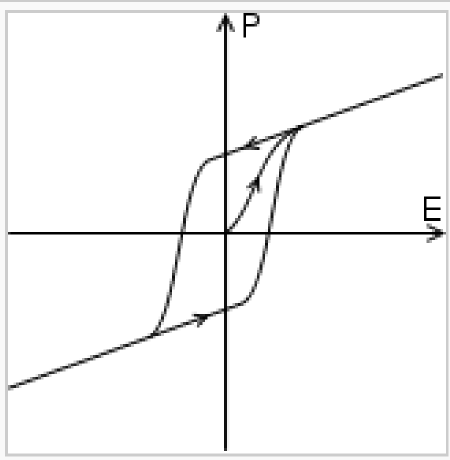
The ground state has a spontaneous polarization and is a ferroelectric.

A phase transition happens if **a** changes continuously with temperature and changes sign at a temperature T_o.

Assuming a linear variation of a(T) with temperature: $a_0 \sim (T - T_o)$.

A **second-order**, or **continuous phase transition.** The order parameter (here spontaneous polarization) vanishes continuously at the transition temperature $T_c = T_o$.





Ferroelectric polarization

If **b < 0** (while c remains positive).

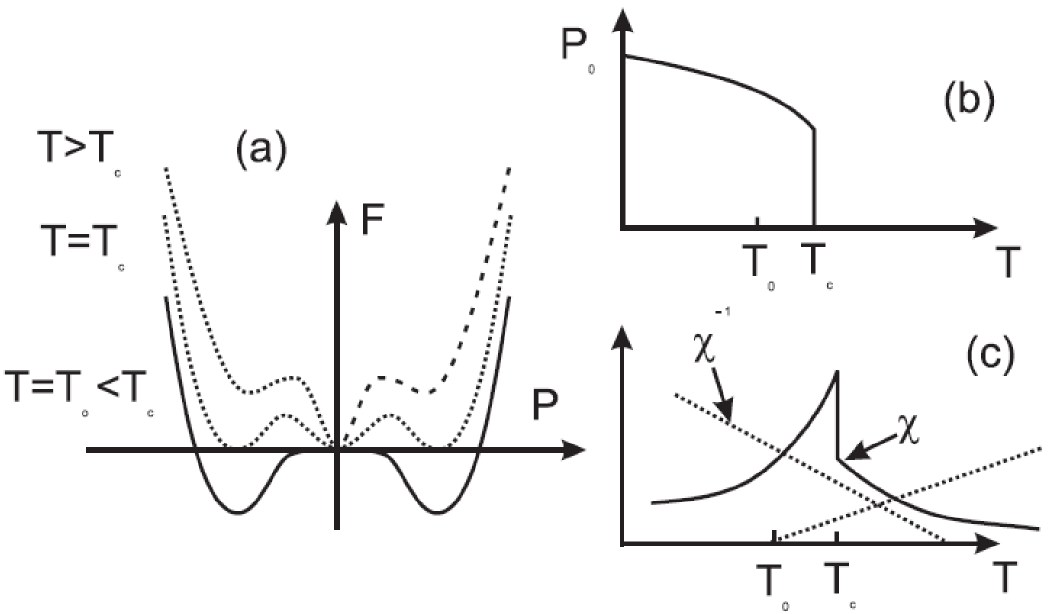
$T > T_o$ the free energy may have a subsidiary minimum at non-zero P.

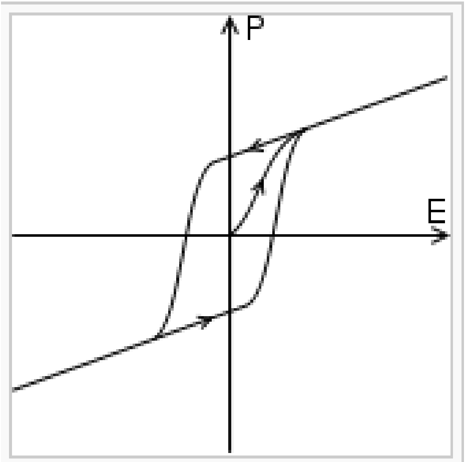
As **a** is reduced (temperature lowered), this *minimum will drop in energy to below that of the unpolarized state*, and will be the thermodynamically favored configuration.

This happens at the Curie temperature T_c, which is higher than T_o.

At any temperature between T_c and T_o the unpolarized phase exists as a local minimum of the free energy.

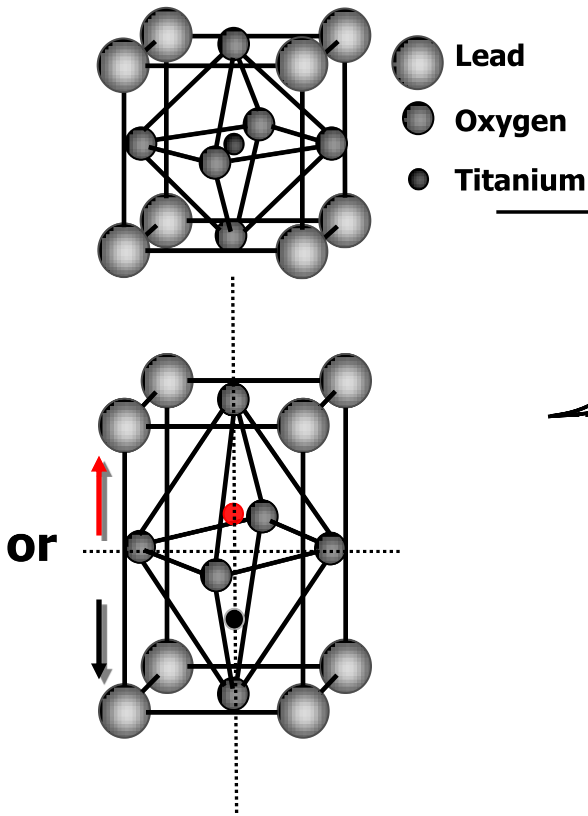
The order parameter jumps discontinuously to zero at T_c.
First-order or **discontinuous transition**.

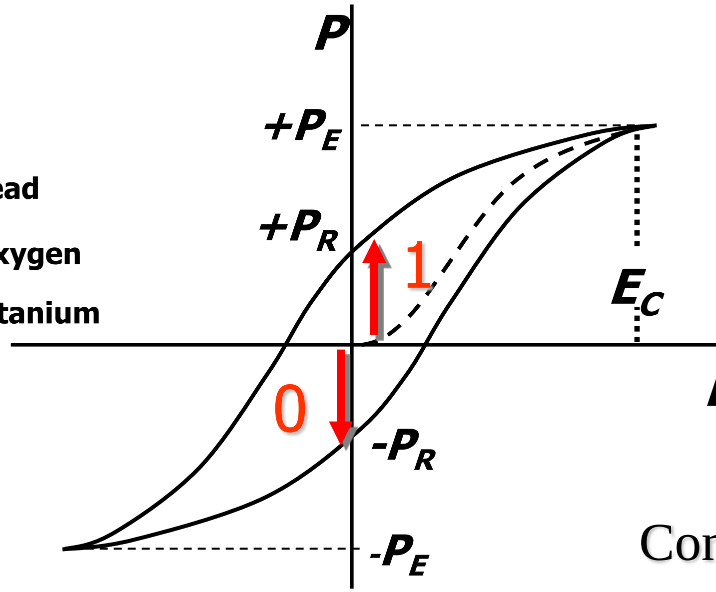




Ferroelectric polarization

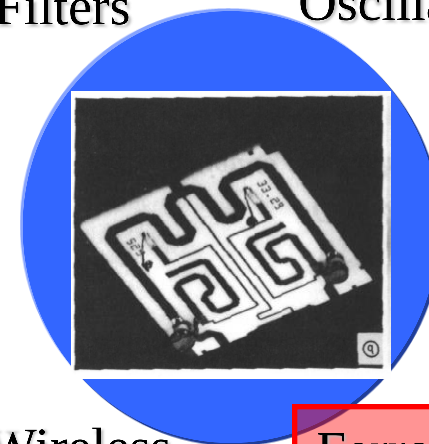
Why Ferroelectrics?





Filters

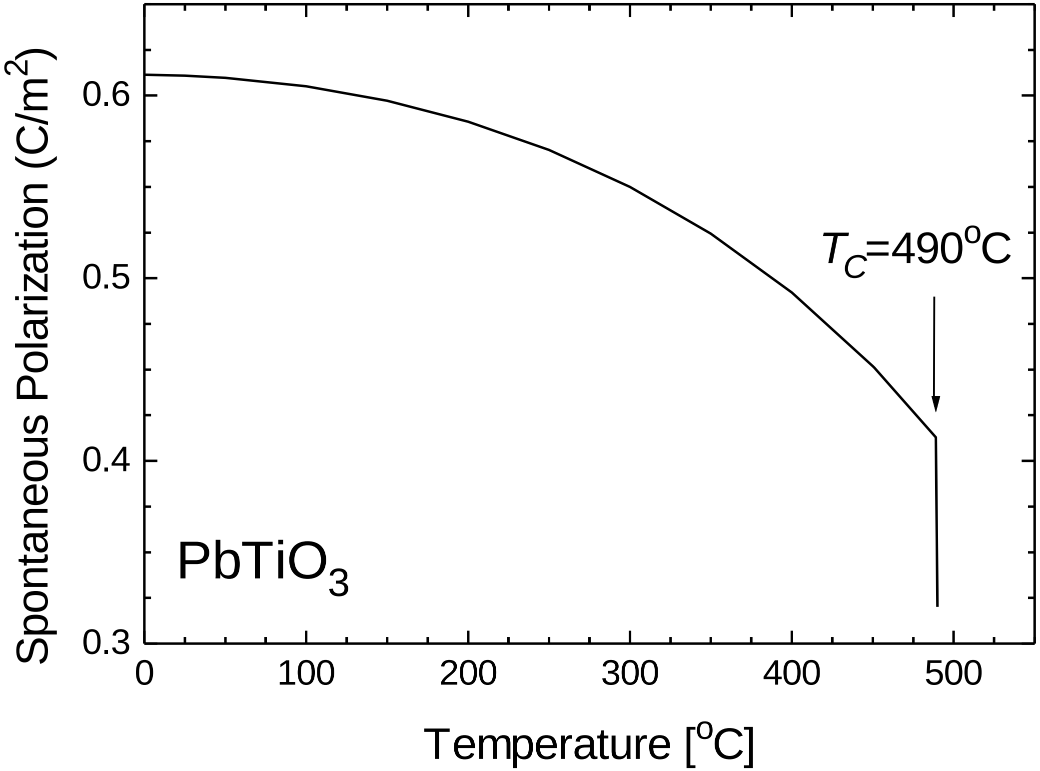
Oscillators

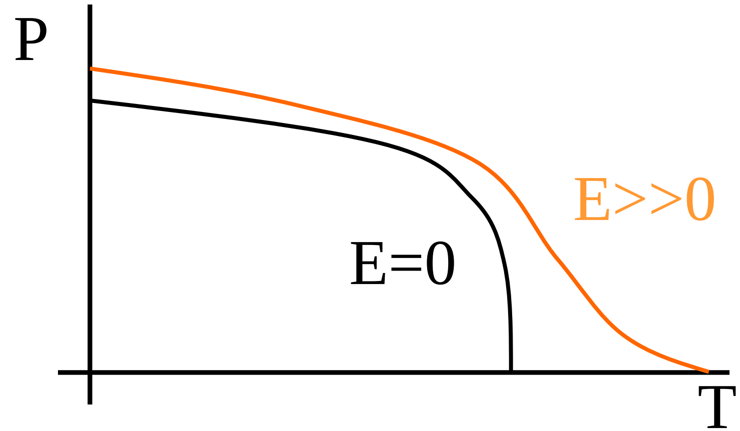


Wireless Communications

Ferroelectric Memories

Temperature Dependence of Spontaneous Polarization

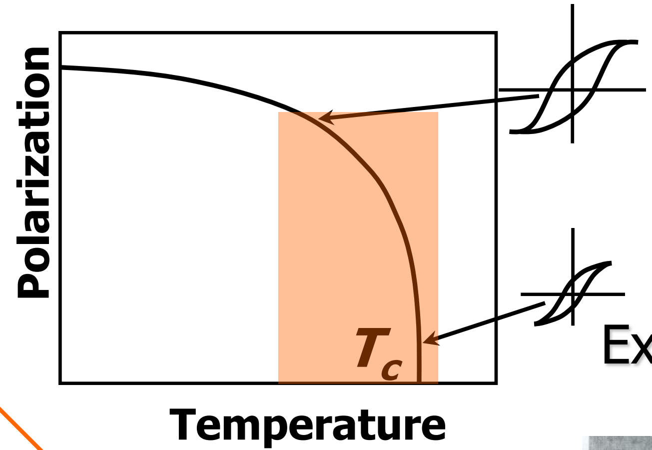


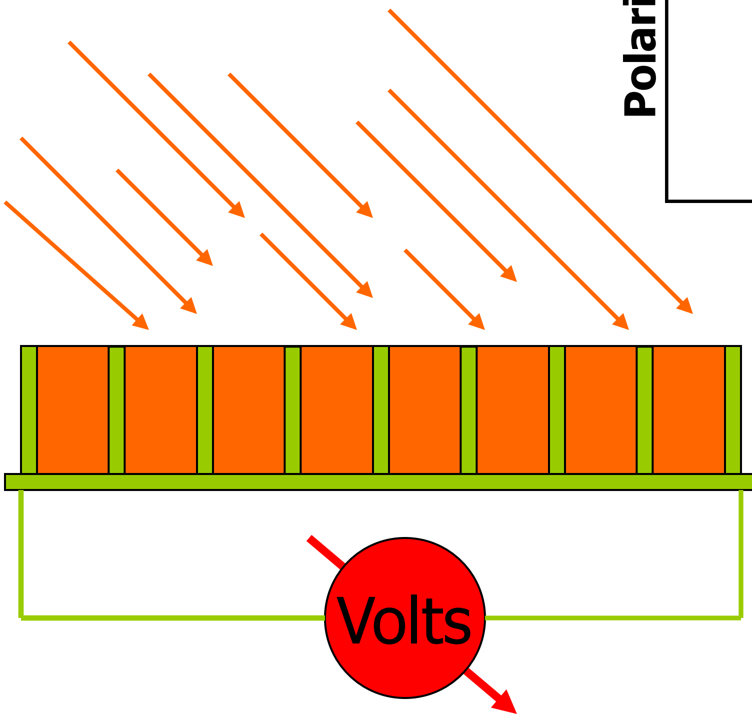


Pyroelectricity

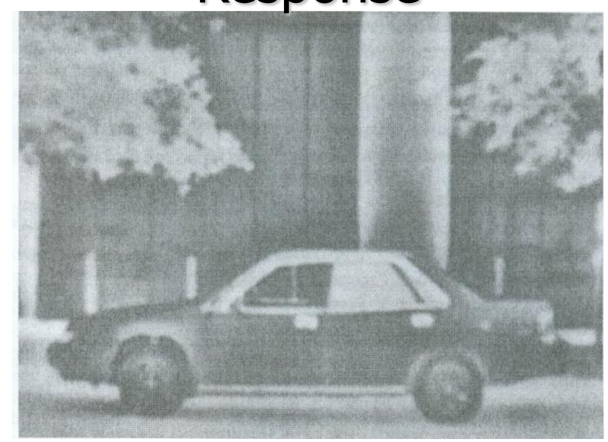
$$p = \left(\frac{\partial D}{\partial T}\right)_E = \frac{\partial P_S}{\partial T} + E\frac{\partial \varepsilon}{\partial T}$$

Why Ferroelectrics?





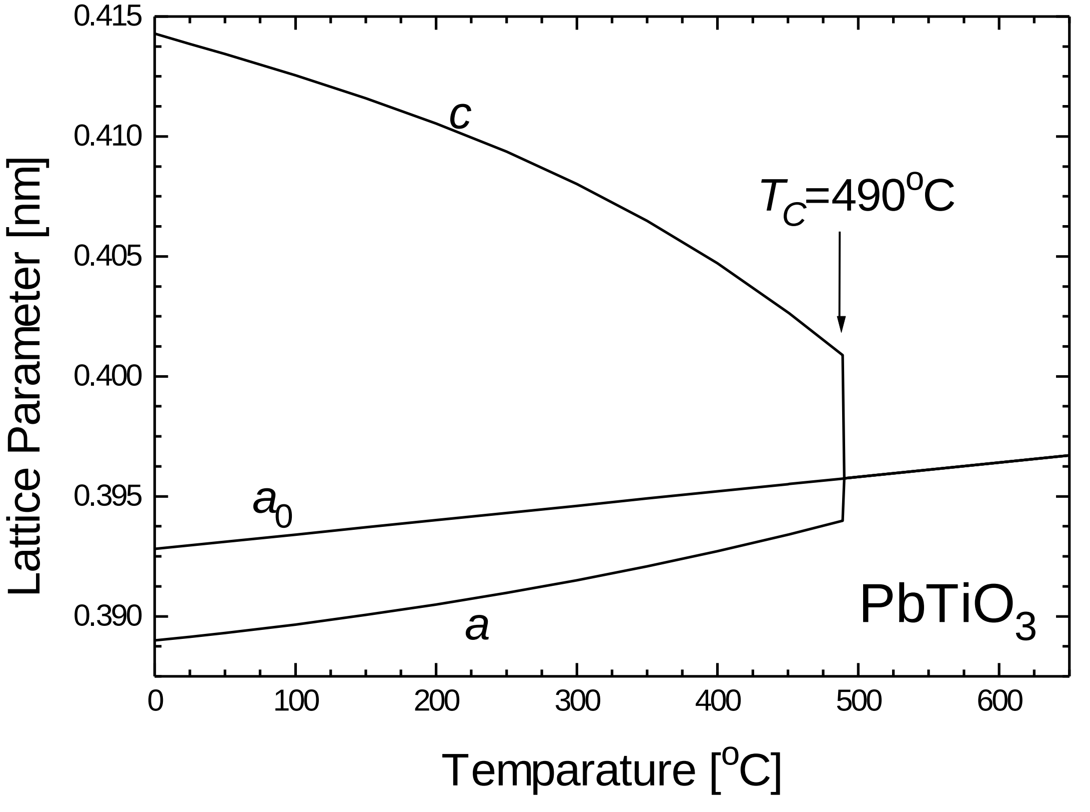
Exceptional Pyroelectric Response



Pyroelectricity

$$p = \left(\frac{\partial D}{\partial T}\right)_E = \frac{\partial P_S}{\partial T} + E\,\frac{\partial \varepsilon}{\partial T}$$

Electrostriction: Coupling between Polarization and Self-Strain



Piezoelectric effect: Strain due to an applied electric field

$$x_{ij} = d_{kij} E_k$$

Strain due to combined Electrostrictive and Piezoelectric effect

$$x_{ij} = d_{kij} E_k + Q_{ijkl} P_k P_l$$

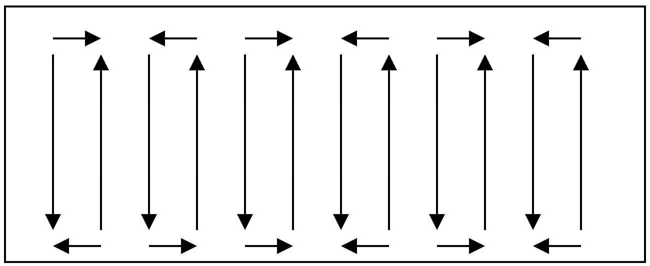
$$= \frac{1}{\varepsilon_0} d_{kij} \varepsilon_{ki}^{-1} P_j + Q_{ijkl} P_k P_l$$

Under non-zero external stress

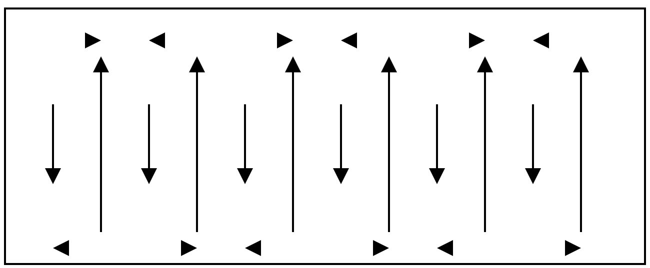
$$x_{ij} = d_{kij} E_k + Q_{ijkl} P_k P_l + S_{ijkl} X_{kl}$$

Polarization Switching by an Electric Field

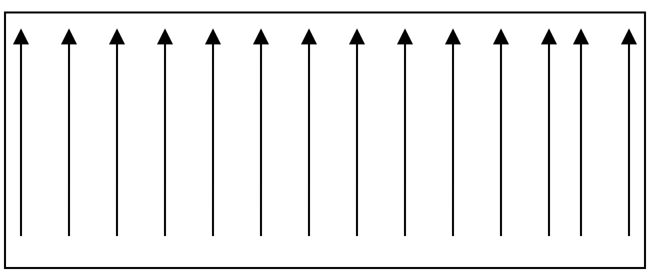
E=0

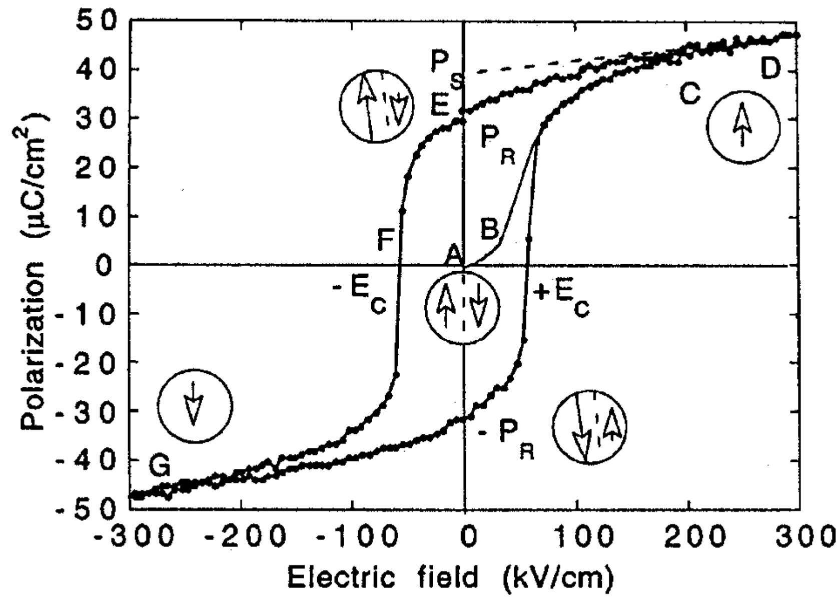


E>0



$E \approx E_C$





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Polarization Switching by an Electric Field

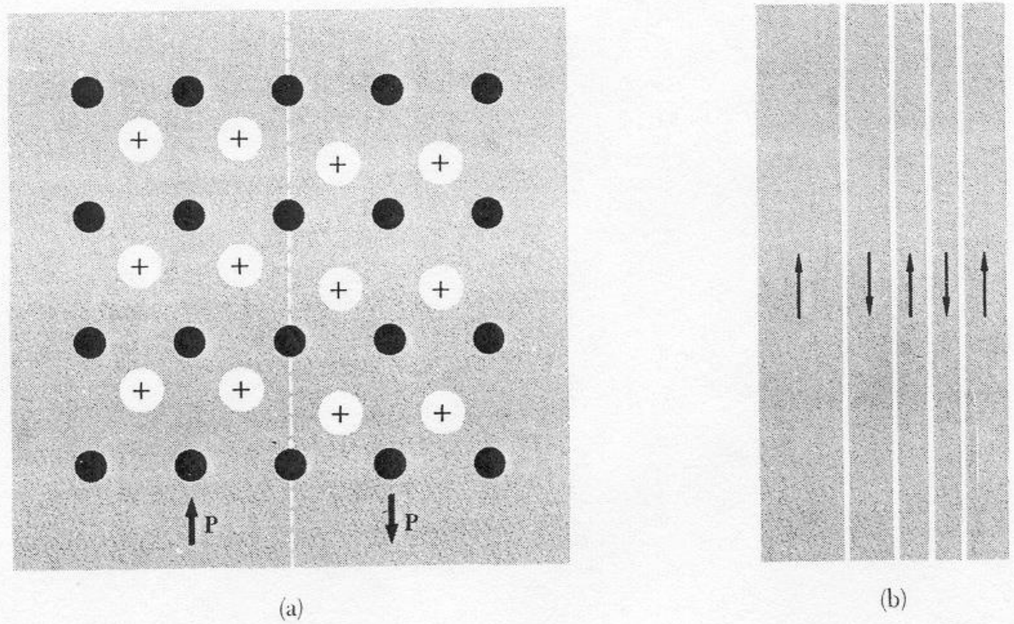


Figure 21 (a) Schematic drawing of atomic displacements on either side of a boundary between domains polarized in opposite directions in a ferroelectric crystal; (b) view of a domain structure, showing 180° boundaries between domains polarized in opposite directions.

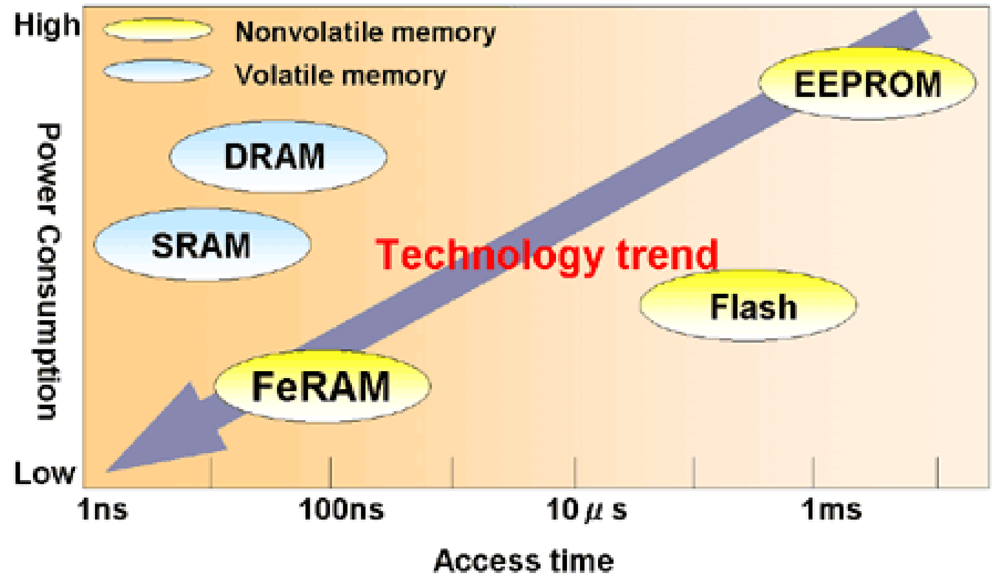
Electrical (or 180^0-domains) to minimize depolarization.

Applications of Ferroelectrics

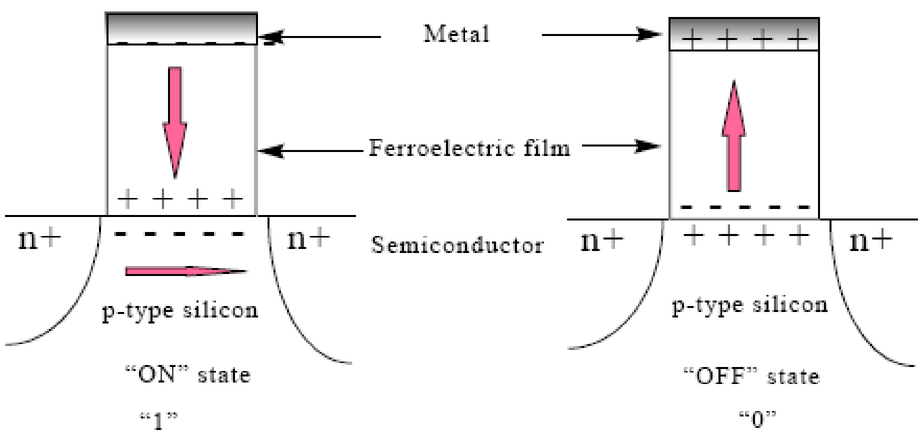
- ✓ Non-Volatile RAMs (memory)
- ✓ Dynamic RAMs (capacitors)
- ✓ Tunable Microwave Devices
- ✓ Pyroelectric Detectors/Sensors
- ✓ Optical Waveguides
- ✓ Piezoelectric Sensors/Actuators, MEMS

Non-Volatile RAMs (memory)

RAMTRON



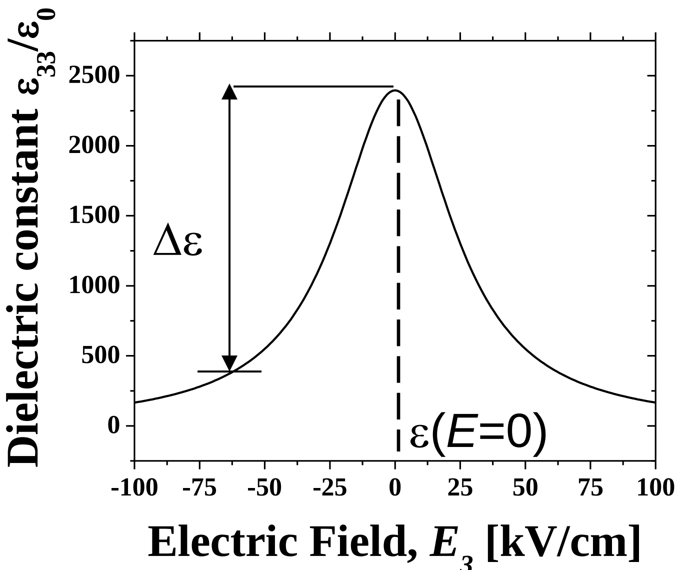
1-transistor memory structure



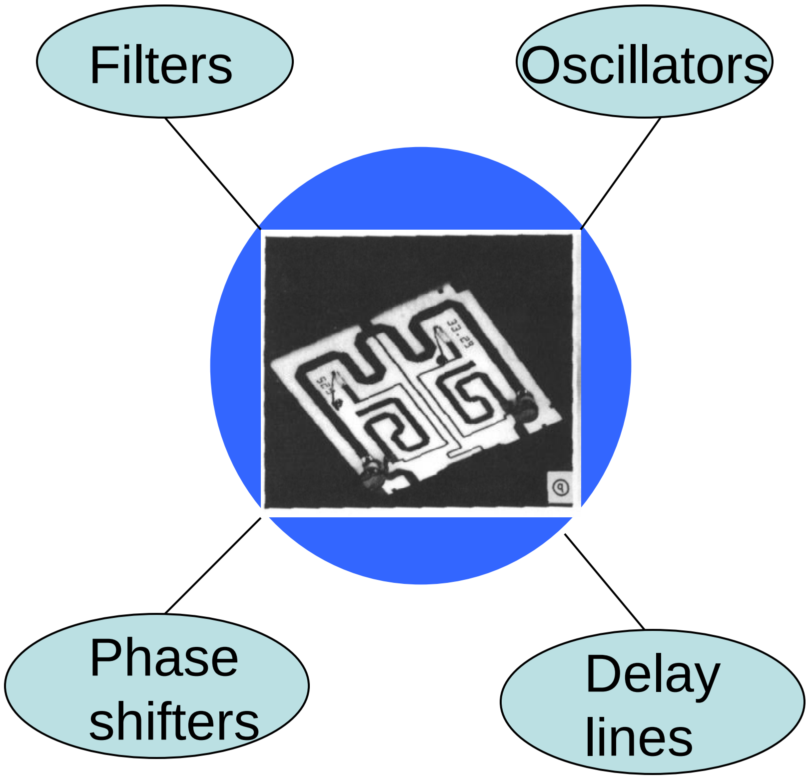
Non-Volatile RAMs (memory)

Smart cards use ferroelectric memories. They can hold relatively large amounts of information and do not wear out from use, as magnetic strips do, because they use contactless radio frequency input/output. These cards are the size and shape of credit cards but contain ferroelectric memory that can carry substantial information, such as its bearer's medical history for use by doctors, pharmacists and even paramedics in an emergency. Current smart cards carry about 250 kilobytes of memory.

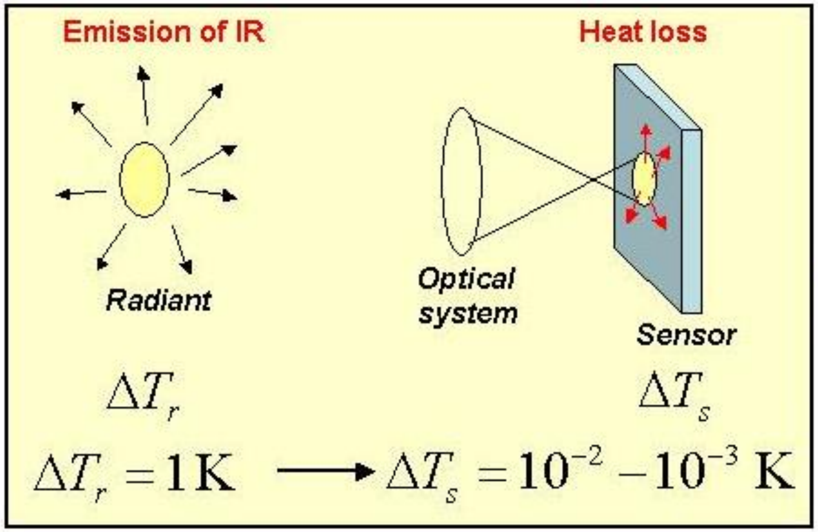
Tunable Microwave Devices / Optical Waveguides

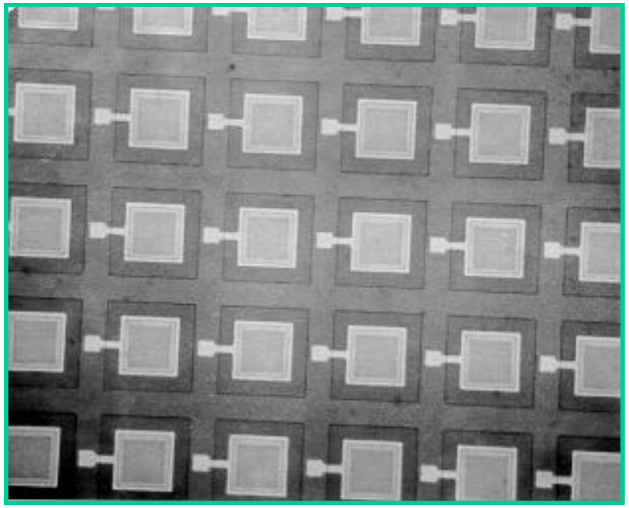


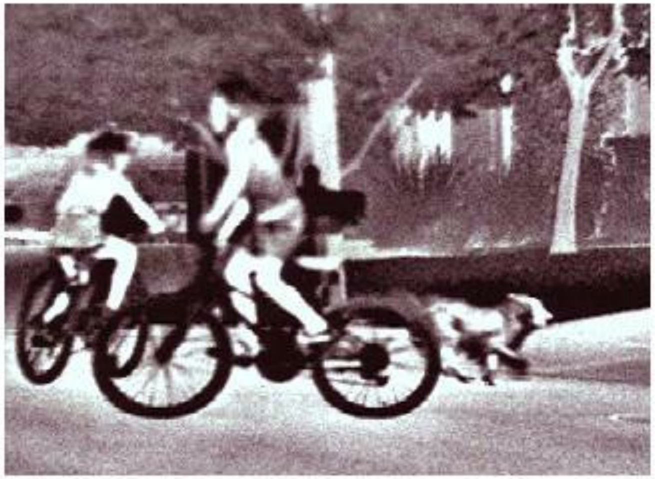
$$tunability = \Phi = \frac{\Delta\varepsilon}{\varepsilon(E=0)}$$



Pyroelectric Detectors/Sensors







Piezoelectric Sensors/Actuators, MEMS