

Lecture contents

- **Dielectrics. Polarization**
- **Linear polarizability**
- **Clausius-Masotti equation**
- **Frequency dependence of polarizability**
- **EM/optical properties of dielectrics**
- **Ferroelectrics and piezoelectrics**

Charge and Polarization

Polarization may be thought of as a bulk movement of the positive charges relative to the negative charges resulting in the bound charge density ρ_b . Consider three cases:

- **No polarization.** Charge density (ρ_b) in the medium is zero since the positive (ρ_+) and negative (ρ_-) distributions overlap.
- **Uniform polarization.** The relative shift of the charge densities leads to the appearance of surface charge densities (σ). The positive and negative charge densities in the bulk still cancel.
- **Nonuniform polarization.** The positive charge density is stretched out as well as displaced to the right. The charge density on the positive surface is greater than that on the negative surface. The polarization increases to the right.

$$\rho_b = -\nabla \cdot \vec{P}$$

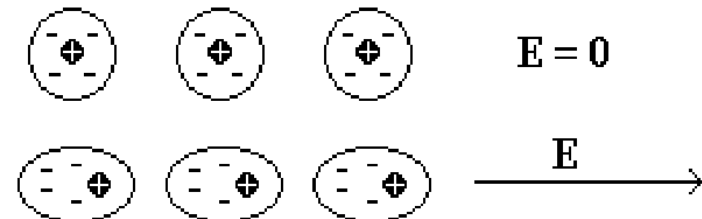
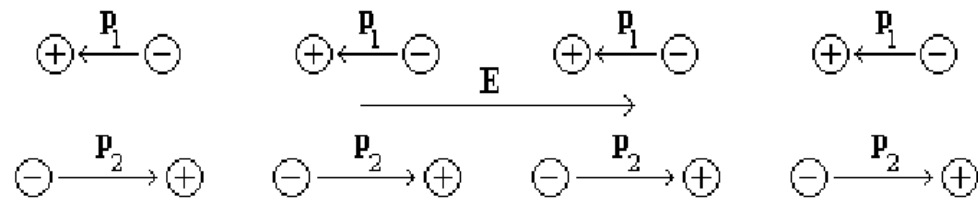
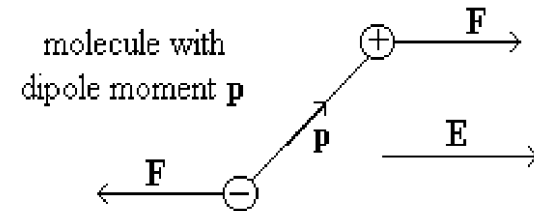
$$\begin{aligned} \rho_- &= \rho_+ \\ \rho_b &= 0 \\ \mathbf{P} &= 0 \end{aligned}$$

$$\begin{array}{c} \sigma_- \quad \left[\begin{array}{c} \rho_- = \rho_+ \\ \rho_b = 0 \\ \mathbf{P} \rightarrow \quad \mathbf{P} \rightarrow \end{array} \right] \quad \sigma_+ \\ \sigma_- = \sigma_+ \end{array}$$

$$\begin{array}{c} \sigma_- \quad \left[\begin{array}{c} \rho_- > \rho_+ \\ \rho_b < 0 \\ \mathbf{P} \rightarrow \quad \mathbf{P} \rightarrow \end{array} \right] \quad \sigma_+ \\ \sigma_- < \sigma_+ \end{array}$$

Dielectrics. Polarizability

- Three basic mechanisms of polarization:
 - **Dipolar (molecular) polarizability** due to reorientation (most significant in liquids and gases)
 - **Ionic polarizability** due to displacements of the positive and negative ions
 - Results in lattice distortions
 - May give rise to ferroelectricity
 - **Atomic (electronic) polarizability** due to redistribution of charge in any atom



Polarizability

- Problem: find electric response of dielectric material on electric field, in other words find polarization (P) vs. external electric field

$$[P] = \frac{[\text{dipole moment}]}{[\text{volume}]} = \frac{\text{Cm}}{\text{m}^3} = \text{Cm}^{-2}$$

- Linear response:

$$P = \epsilon_0 \left(\chi^{(1)} E + \chi^{(2)} E^2 + \dots \right)$$

$$\vec{P} = \epsilon_0 \chi \vec{E}$$

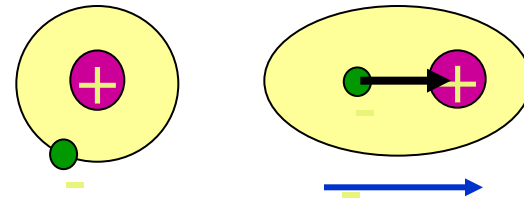
$$P = \chi^{(1)} E + \chi^{(2)} E^2 + \dots \quad \{\text{CGS}\}$$

$$\vec{P} = \chi \vec{E} \quad \{\text{CGS}\}$$

- Dipole moment of atom

$$p = lq = -e \int r n(r) dv$$

$\sum \psi^* \psi$



Electric Field

- Simplest case: linear scalar polarizability of atom, α (can be tensor)

$$p = \alpha E_{loc}$$

- Next, we need to find E_{loc}

Polarizability of atom

$$p = \alpha E_{loc}$$

TABLE Electronic Polarizabilities of Selected Atoms and Ions
(expressed as $\alpha/4\pi\epsilon_0$ in 10^{-30} m^3)

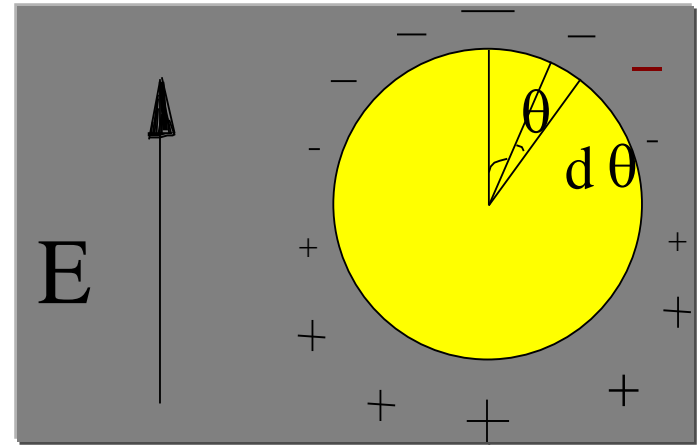
H	0.66	Ne	0.390	K ⁺	1.136
H ⁻	10.0	Na	27	Ca ²⁺	0.47
He	0.201	Na ⁺	0.312	Br ⁻	4.276
Li	12	Mg ²⁺	0.094	Kr	2.46
Li ⁺	0.029	Cl ⁻	3.063	Rb ⁺	1.758
Be ²⁺	0.008	Ar	1.62	Xe	3.99
O ²⁻	3.88	K	34	Cs ⁺	3.015
F ⁻	0.867				

Sources: A. M. Portis, *Electromagnetic Fields* (New York: Wiley, 1978); L. Pauling, *Proc. R. Soc. (London) Ser. A* 114: 181, 1927; J. Tessman, A. Kahn, and W. Shockley, *Phys. Rev.* 92: 890, 1953.

Local electric field -1

$$p = \alpha E_{loc}$$

- Next, we need to find E_{loc}
- Let's consider a sphere within a sample
- E_{loc} is a sum of
 - Applied external field, E_{appl}
 - E_1 is due to polarization charge on the sample surface (depolarizing field)
 - E_2 is due to the polarization charge on the sphere surface
 - E_3 is due to dipoles within the sphere

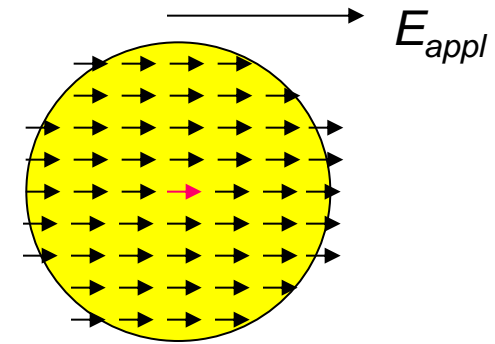


$$E_{loc} = E_{appl} + \underbrace{E_1 + E_2 + E_3}_{\frac{1}{4\pi\epsilon_0} \sum_k \left[\frac{3(p_k \cdot r_k) \vec{r}_k}{r_k^5} - \frac{\vec{p}_k}{r_k^3} \right]}$$

Sum over all the dipoles in the sample

Depolarizing field

- Field in a sample depends on its shape (bound surface charge distribution)



- Field due to dipoles in the center of dielectric sphere is a sum over all atoms

$$\vec{E}_{dip} = \frac{1}{4\pi\epsilon_0} \sum_k \left[\frac{3(\vec{p}_k \cdot \vec{r}_k) \vec{r}_k}{r_k^5} - \frac{\vec{p}_k}{r_k^3} \right]$$

- Considering both field and dipole moment along z-direction:

$$E_{dip} = \frac{p}{4\pi\epsilon_0} \sum_k \frac{3z_k^2 - r_k^2}{r_k^5} = \frac{p}{4\pi\epsilon_0} \sum_k \frac{2z_k^2 - x_k^2 - y_k^2}{r_k^5}$$

- Consider sample with cubic symmetry or amorphous

$$\sum_k \frac{z_k^2}{r_k^5} = \sum_k \frac{x_k^2}{r_k^5} = \sum_k \frac{y_k^2}{r_k^5}$$

- In a spherical sample with cubic crystal symmetry

$$E_{dip} = 0 \quad \text{and} \quad E_{loc} = E_{appl}$$

- For our problem:

$$E_3 = 0$$

Field E_2

- Field due to polarization charge on a sphere surface, E_2

- Charge density on the surface rings

$$-P \cos \theta$$

- Ring surface

$$2\pi r^2 \sin \theta d\theta$$

- Charge on the ring

$$dQ = -2\pi r^2 \sin \theta d\theta P \cos \theta$$

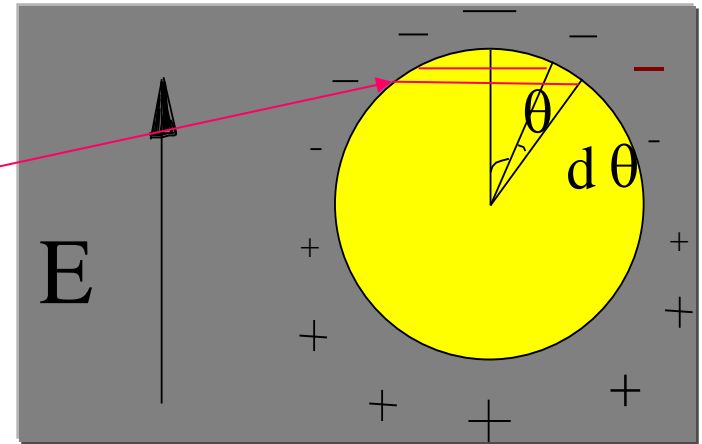
- Need to add up fields due to rings

$$dE = \frac{dQ}{r^2} \cos \theta$$

- Field in the center of the cavity
(Lorentz's field) :

$$E_2 = P \int_0^\pi 2\pi \sin \theta \cos^2 \theta d\theta = \frac{4\pi}{3} P$$

$$E_2 = \frac{P}{3\epsilon_0} \quad [\text{in SI}]$$



Clausius-Massotti equation

$$p = \alpha E_{loc}$$

- Polarization is a sum of dipole moments in unit volume of the sample:

$$P = \sum_k N_k p_k = \sum_k N_k \alpha_k E_{loc}$$

- We have found the local field:

$$E_{loc} = \underbrace{E_{appl} + E_1 + E_2 + E_3}_{\text{E- macroscopic field}} + \frac{4\pi}{3} P$$

O in cubic crystals

- Substituting

$$P = \sum_k N_k \alpha_k \left(E + \frac{4\pi}{3} P \right) \quad \text{And using} \quad P = \chi E = \frac{\epsilon - 1}{4\pi} E$$

- Finally obtain Clausius-Masotti equation

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \sum_k N_k \alpha_k$$

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{1}{3\epsilon_0} \sum_k N_k \alpha_k \quad [\text{in SI}]$$

Static dielectric constants of solids

TABLE Static Dielectric Constants of Selected Pure Solids at about 20 K

Solid	K	Solid	K
Aluminum oxide	9.5	Lead telluride	800
Ammonium chloride	7.22	Lithium fluoride	9.27
Barium fluoride	7.34	Lithium niobate	80
Cadmium iodide	68	Nickel monoxide	12.6
Cadmium telluride	11.00	Potassium bromide	4.7
Calcium fluoride	6.81	Potassium chloride	4.68
Cesium bromide	6.60	Potassium iodide	5.1
Cesium chloride	6.83	Selenium	
Cesium iodide	6.49	(amorphous)	6.0
Cobalt oxide	10.6	Sodium bromide	5.99
Europium oxide	24	Sodium chloride	5.8
Gallium arsenide	13.08	Sodium iodide	4.94
Germanium	15.3	Thallium iodide	20.4
Lead fluoride		Titanium dioxide	44.7
(cubic)	29.3	Zinc oxide	16.2

Sources: *Digest of Literature on Dielectrics*, published annually by the National Academy of Sciences; I. S. Zheludev, *Physics of Crystalline Dielectrics* (New York: Plenum, 1971).

Frequency dependence of polarizability

- Problem: dipole under oscillating electric field

- Two charges move with “spring” force β

$$\begin{cases} m_- \frac{d^2 r_-}{dt^2} = -\beta(r_- - r_+) - QE_{loc} \\ m_+ \frac{d^2 r_+}{dt^2} = -\beta(r_+ - r_-) + QE_{loc} \end{cases}$$

- Introducing dipole moment and reduced mass

$$p(t) = Q(r_+ - r_-) \quad M = \frac{m_+ m_-}{m_+ + m_-}$$

- To obtain oscillator equation, introduce dipole resonance frequency $\omega_0^2 = \beta/M$ and relaxation constant γ

$$\frac{d^2 p}{dt^2} + \frac{\beta}{M} p = \frac{Q^2}{M} E_{loc}$$

$$\frac{d^2 p}{dt^2} + \gamma \frac{dp}{dt} + \omega_0^2 p = \frac{Q^2}{M} E_{loc}$$

- Relaxation depends on state of material and temperature

for water at RT $1/\gamma = 3 \times 10^{10}$ 1/s

for ice at -20C $1/\gamma = 10^3$ 1/s

Frequency dependence of polarizability

$$\frac{d^2 p}{dt^2} + \gamma \frac{dp}{dt} + \omega_0^2 p = \frac{Q^2}{M} E_{loc}$$

- Under harmonic field $E_{loc} = E_0 e^{-i\omega t}$

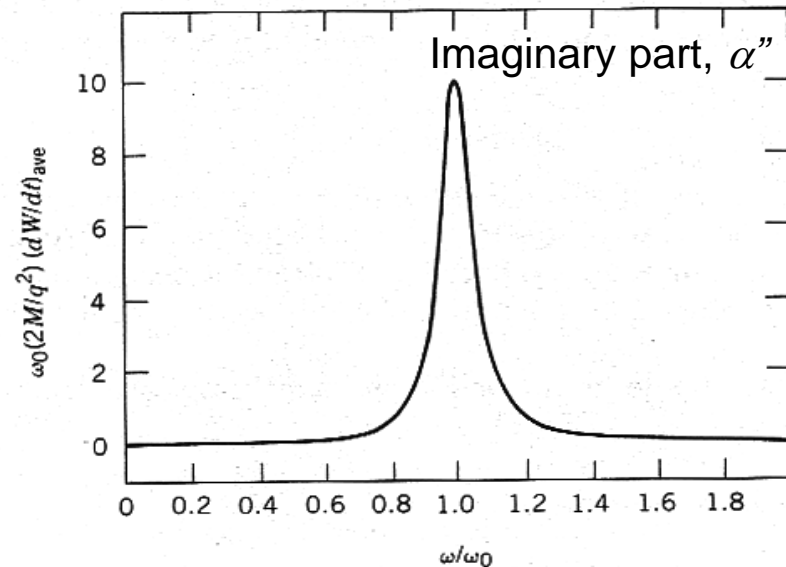
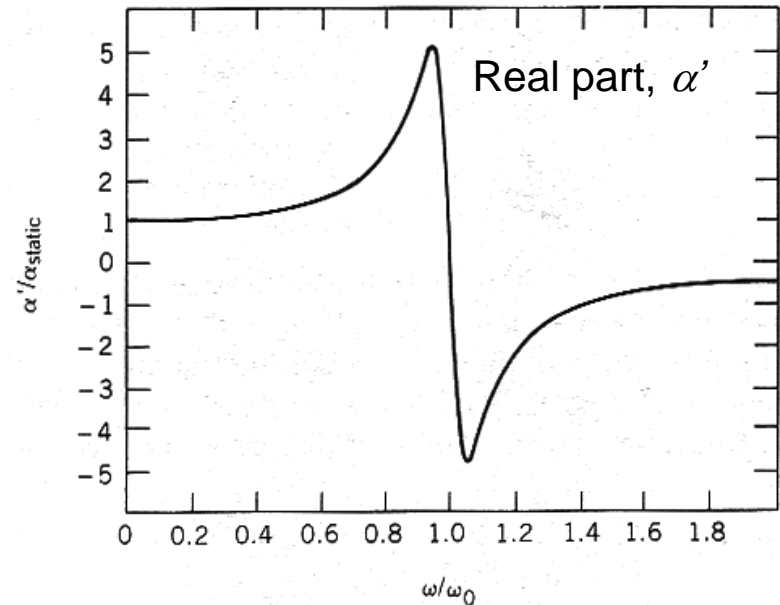
the polarizability $\alpha = p / E_{loc}$

is just a response of harmonic oscillator with damping

$$\alpha(\omega) = \frac{Q^2}{M} \frac{\omega_0^2 - \omega^2 + i\gamma\omega}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2}$$

- In solids, more accurately normal (optical) phonon modes should be considered instead of isolated dipoles
- Note another origin of imaginary part of dielectric function providing dissipation:

$$\left[\frac{dW}{dt} \right]_{ave} = \frac{1}{2} \alpha'' E_0^2$$

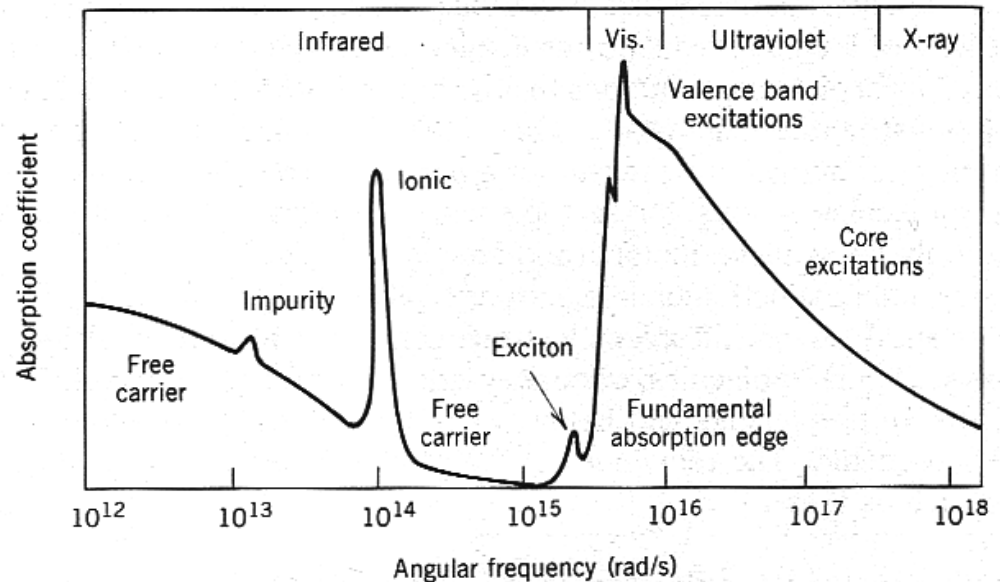
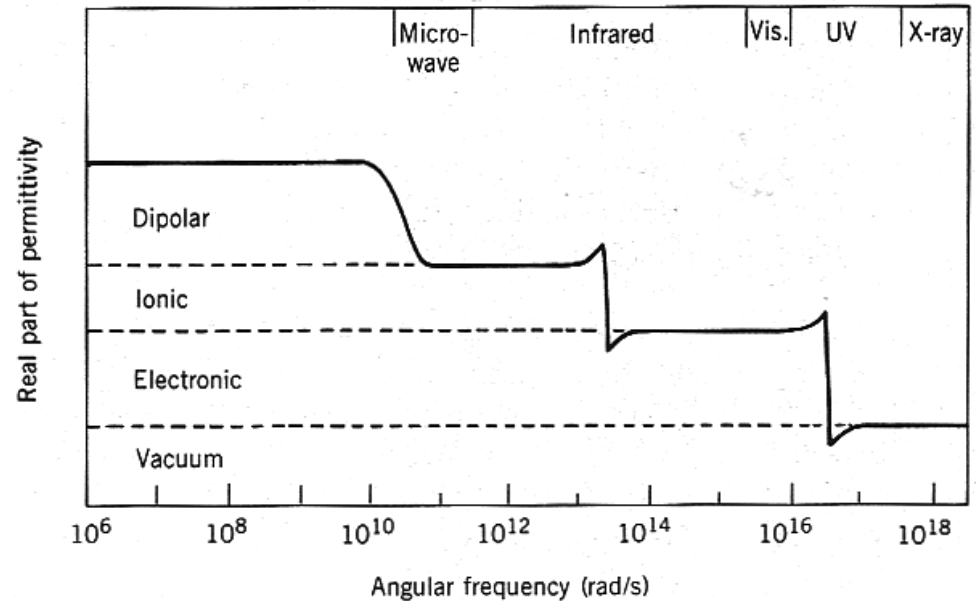


Frequency dependence of dielectric function

for $\mu = \mu_0$

$$\left\{ \begin{array}{l} \epsilon_1 = \epsilon_0 (n^2 - \kappa^2) \\ \epsilon_2 = 2n\kappa\epsilon_0 \end{array} \right.$$

$$\alpha = \frac{\omega}{nc} \frac{\epsilon_2}{\epsilon_0}$$



Dielectric function and reflection

- In general, by measuring the reflection spectrum in a wide photon energy range is enough to find both real and imaginary parts of the dielectric function
- Real and imaginary parts of the dielectric function are coupled with Kramers-Kronig dispersion relations:

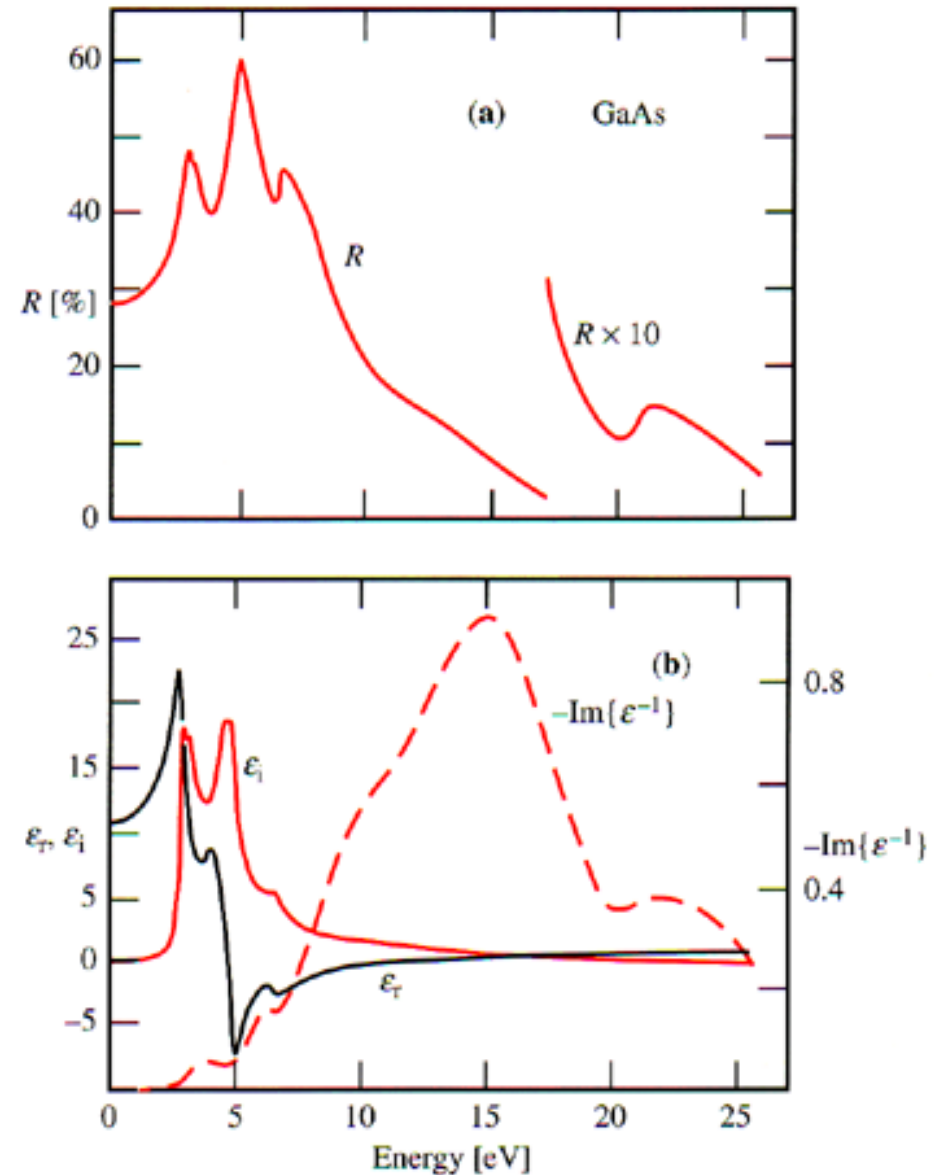
$$\epsilon_1(\omega) - 1 = \frac{2}{\pi} P \int_0^{\infty} \frac{\xi \epsilon_2(\xi)}{\xi^2 - \omega^2} d\xi$$

$$\epsilon_2(\omega) = -\frac{2\omega}{\pi} P \int_0^{\infty} \frac{\epsilon_1(\xi)}{\xi^2 - \omega^2} d\xi$$

- At high frequencies

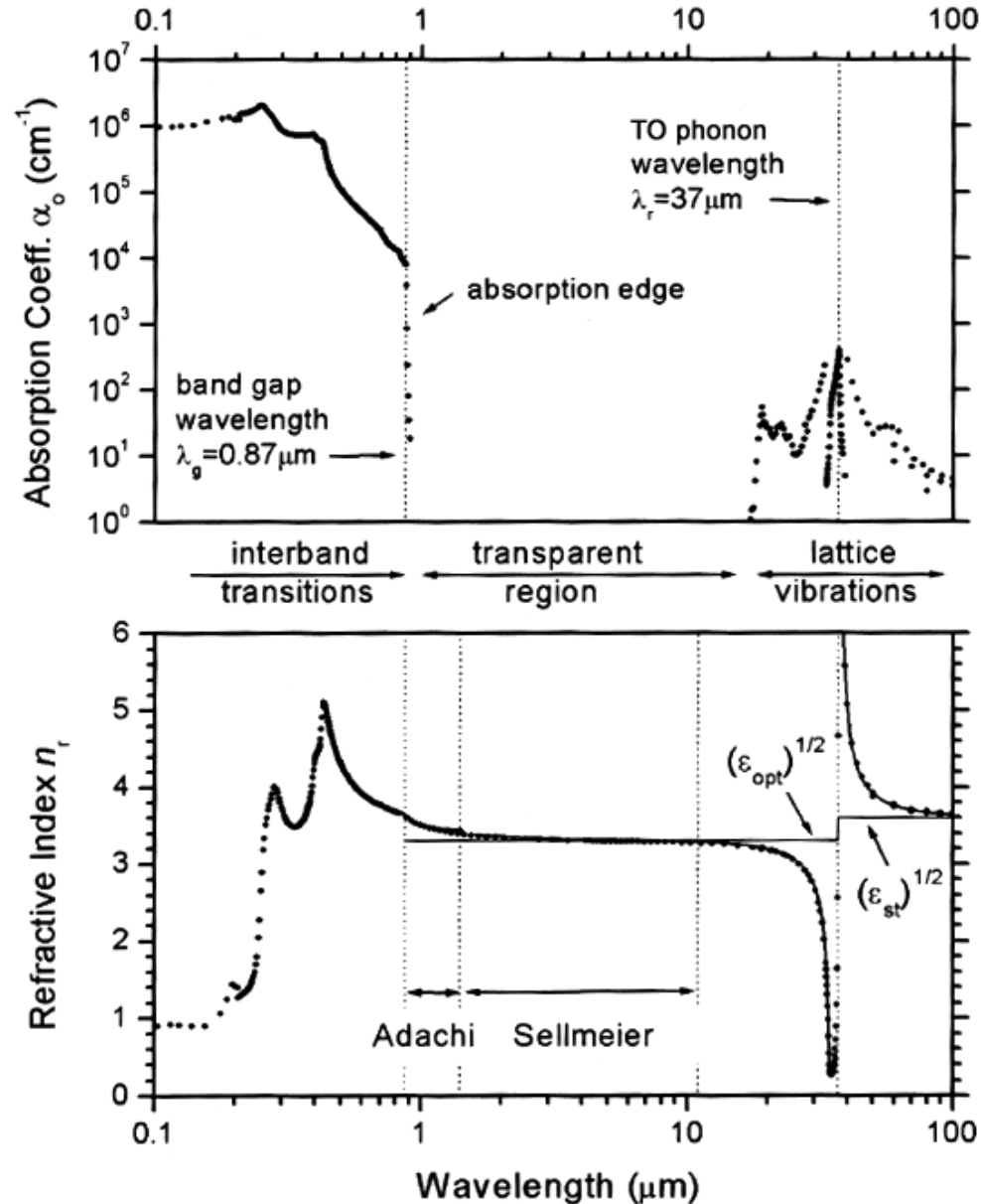
$$\epsilon(\omega) = 1 - \left(\frac{\omega_p}{\omega} \right)^2$$

Plasma frequency



Absorption coefficient and refractive index

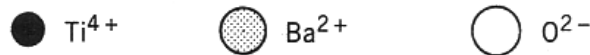
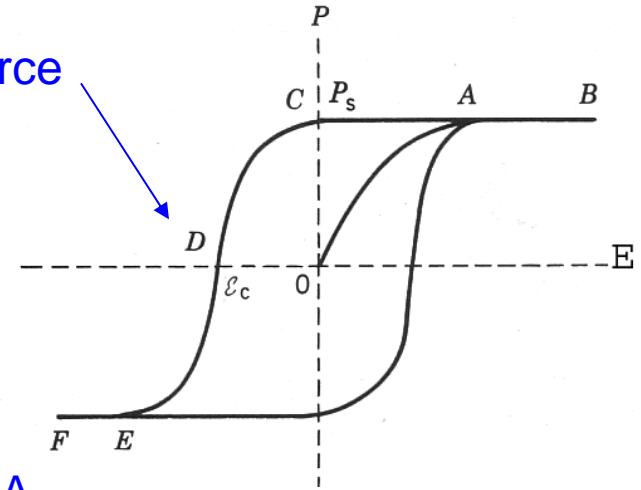
- In dielectrics and semiconductors, the usual choice of 2 medium (non-magnetic) parameters is absorption coefficient and refractive index
- Absorption coefficient:
 - low below bandgap energy,
 - high above bandgap (depends on density of states)
- Refractive index
 - Almost constant below bandgap
 - Reduced to unity above plasma frequency
 - Has a pole at TO optical phonon frequency



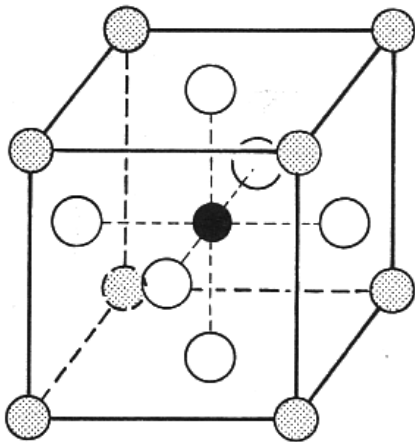
Ferroelectrics: general features

- Ferroelectrics are materials with spontaneous polarization (and hysteresis)
- Example: Crystalline BaTiO_3

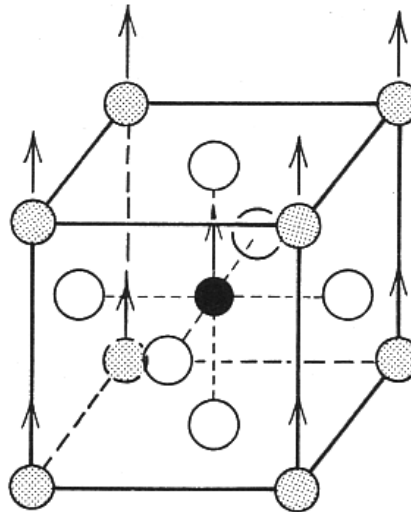
Coercive force



Displacements $\sim 0.13\text{\AA}$

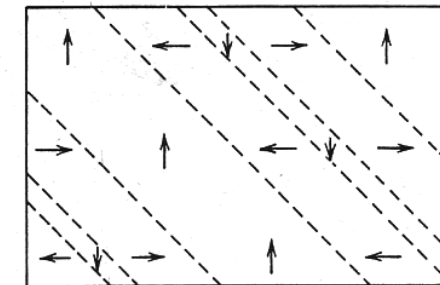
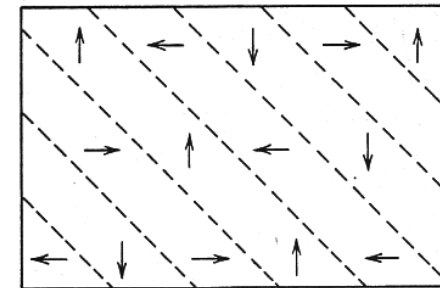


$T > 393\text{ K}$
Cubic perovskite
structure



$T < 393\text{ K}$
Tetragonal
distortion

Domain structure



\uparrow
E

1st order phase transition

Temperature dependence of dielectric constant

- Temperature dependence of susceptibility is described by Curie-Weiss law (paraelectrics)

$$\epsilon(T > T_c) = 1 + \frac{4\pi P}{E} = 1 + \frac{C}{T - T_c}$$

TABLE Spontaneous Polarization P_s (at temperature in parentheses), Curie Point T_c , and Curie Constant C for Selected Ferroelectrics

Material	P_s ($\mu\text{C}/\text{cm}^2$)	T_c (K)	C (K)
BaTiO ₃	26 (300 K)	293	1.6×10^5
PbTa ₂ O ₆	10 (300 K)	533	1.5×10^5
KNO ₃	6.3 (397 k)	397	4300
NaNO ₃	6.4 (416 K)	433	5000
NH ₄ HSO ₄	0.8 (200 k)	270	—
(NH ₄) ₂ SO ₄	6.4 (const)	-50	—
SbSI	25 (273 K)	295	—
NaKC ₄ H ₄ O ₆ • 4H ₂ O (Rochelle salt)	0.25 (278 K)	24	2240
C(NH ₂) ₃ Al(SO ₄) ₂ • 6H ₂ O	0.35 (300 K)	—	—
(NH ₂ CH ₂ COOH) ₃ H ₂ BeF ₄	3.2 (300 K)	70	2350

Source: J. C. Burfoot, *Ferroelectrics* (Princeton, NJ: Van Nostrand, 1967).

Piezoelectrics

- Polarization can result from strain (deformation).
- Example: in BaTiO_3 deformation leads to crystal cell distortion

- Sample under uniaxial stress T :

$$P = \chi\epsilon_0 E + dT$$

- Reversibly, strain depends on the applied field

$$e = sT + dE$$

- For quartz $d = 2.3 \cdot 10^{-12} \text{ m/V}$

d – polarization strain constant
 s – elastic compliance
 (typically both are tensors)

- For BaTiO_3 in (100) direction $d = 3 \cdot 10^{-10} \text{ m/V}$