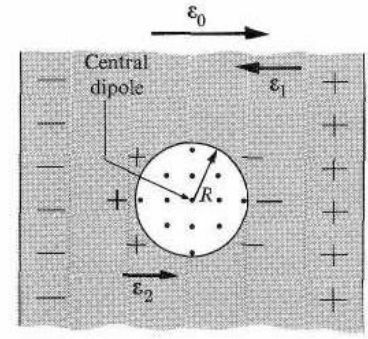


Unit V Dielectrics

Polarisation in dielectrics

Dielectrics are a class of material which respond to external electric fields. An external electric field can cause the center of positive and negative charges in the crystal to shift from their mean position. This separation of charges results in creation of dipoles in the system. The net dipole moment created per unit volume is called the polarization. The polarization in the material is dependent on the net electric field experienced by the dielectric.



If E_0 is the applied electric field applied to a parallel plate capacitor the surface charge density on the plates of the capacitor $\sigma = \epsilon_0 E_0$

If a dielectric material is placed between the plates of the capacitor, the surface density of charge due to polarization $\sigma_p = \epsilon_0 E'$ where E' is called the depolarization field.

The net electric field E between the plates is reduced by a factor which is the dielectric constant ϵ_r of the material i.e., $E = \frac{E_0}{\epsilon_r}$ or $E_0 = \epsilon_r E$

The net electric field $E = E_0 - E' = \epsilon_r E - \frac{\sigma_p}{\epsilon_0}$

Simplifying $\sigma_p = \epsilon_0 \epsilon_r E - \epsilon_0 E = \epsilon_0 (\epsilon_r - 1) E$

Hence the polarization in the material due to a net electric field is given by

$$P = \sigma_p = \epsilon_0 (\epsilon_r - 1) E$$

The polarisation of the material can also be written as

$P = \epsilon_0 \chi E$ where χ is the dielectric susceptibility of the material and is a measure of the ability to create dipoles in the material. The polarization is linearly proportional to the applied electric field for pure dielectrics.

This gives us the relation between susceptibility and dielectric constant

$$\chi = (\epsilon_r - 1) \text{ or } \epsilon_r = 1 + \chi.$$

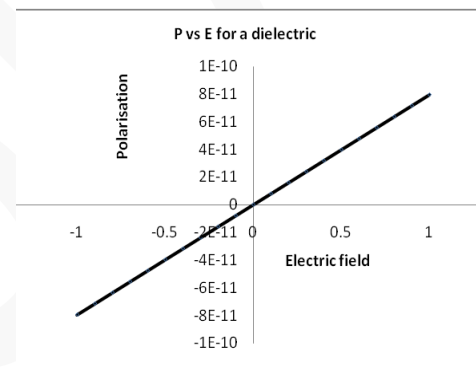
If N is the number of atoms per unit volume and α_e is the polarisability of the individual dipoles then the polarization can be written as $P = \epsilon_0 \chi E = N \alpha_e E$.

$$\text{Or } \chi = \frac{N \alpha_e}{\epsilon_0}$$

Polarization in dielectrics is thus proportional to the net electric field.

Electric fields in a dielectric material

To understand the polarization mechanism in totality, it is essential to understand the components of the electric fields. which exist in a real dielectric, apart from the applied electric field E and the depolarization



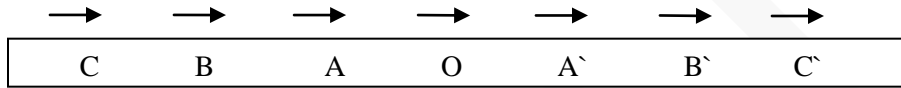
field \mathbf{E}' . In general the local electric field around a dipole inside the material experiences four components of electric field.

$$\mathbf{E}_{loc} = \mathbf{E}_o + \mathbf{E}_1 + \mathbf{E}_2 + \mathbf{E}_3$$

\mathbf{E}_o is the external applied electric field, \mathbf{E}_1 is the depolarization field, \mathbf{E}_2 is the Lorentz field on the surface of the spherical cavity and \mathbf{E}_3 is the field due to other dipoles lying within the sphere.

{ In the case of cubic structures the net Lorentz field can be shown to be zero. The electric field due to the dipoles inside the spherical cavity can be estimated as follows.

Consider a linear array of dipoles at A, B, C, A', B' and C' with dipole moment μ at regular intervals of d .



The electric field at A and A' are equal in strength and direction and equal to $\mathbf{E}_A = \mathbf{E}_{A'} = \frac{2\mu}{4\pi\epsilon_o d^3}$ and the net electric field $\mathbf{E}_{AA'} = \frac{\mu}{\pi\epsilon_o d^3}$.

The electric field at O due to the pair of dipoles equidistant from O can be written as

$\mathbf{E} = \mathbf{E}_{AA'} + \mathbf{E}_{BB'} + \mathbf{E}_{CC'} \dots = \frac{\mu}{\pi\epsilon_o} \left(\frac{1}{d^3} + \frac{1}{(2d)^3} + \frac{1}{(3d)^3} \dots \right) = \frac{\mu}{\pi\epsilon_o d^3} \sum \frac{1}{n^3} = \frac{1.2\mu}{\pi\epsilon_o d^3} = \frac{\gamma P}{\epsilon_o}$ where γ is a constant that depends on the geometry of the material. From the series we can evaluate the contribution of the nearest neighbors and find that only first few pair of neighbors contributes significantly to the electric field at any site. ###

In the case of a dielectric with a cubic structure the effective field can be written $\mathbf{E}_{in} = \frac{P}{3\epsilon_o}$

Thus the net electric field experienced by the dipoles will be greater by this factor and hence the polarization would be greater by this factor.

$$\mathbf{E}_{loc} = \mathbf{E} + \mathbf{E}_{in} = \mathbf{E} + \frac{\mathbf{P}}{3\epsilon_o}$$

From the definition of polarization we have $\mathbf{P} = N\alpha_e \mathbf{E}_{loc} = N\alpha_e \left(\mathbf{E} + \frac{\mathbf{P}}{3\epsilon_o} \right) = \epsilon_o(\epsilon_r - 1)\mathbf{E}$

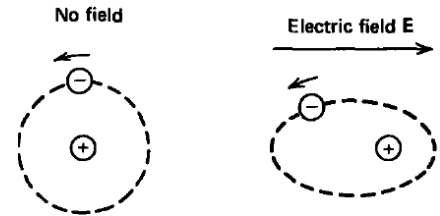
Solving this we get $\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{N\alpha_e}{3\epsilon_o}$. This is the Clausius Mosotti relation which relates the macroscopic dielectric constant to the microscopic polarisability of the material.

It is obvious that the effective microscopic polarisability is greater when the internal fields are considered and should evolve in a more realistic dielectric constant of the material.

Polarisation mechanisms

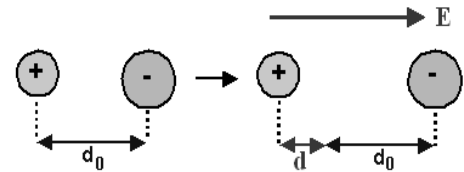
Electronic polarization : When an atom is subjected to an electric field E , the nucleus and the electron cloud will try to move in opposite directions. The nucleus moves in the direction of the applied field and the electron cloud in the direction opposite to that of the applied field. The centre of the negatively charged electron cloud no longer coincides with the positive nucleus and hence results in an induced dipole. The polarization produced due to this induced dipole is called “Electronic polarization”.

The electronic polarizability is $\alpha_e = 4\pi\epsilon_0 R^3$ where R is the radius of the atom. The electronic polarization is temperature independent since the size of the atom does not depend on temperature.



Ionic Polarisation

Dielectric materials with ionic bonding there exists regular arrangement of positive and negative ions. Ions between any two bond is then a dipole. Because of the symmetric arrangement of the dipoles in the material, the net dipole moment in the material may be zero.



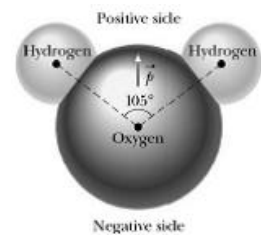
In the presence of an external electric field the elongation of the bond will result in an increased dipole moment along the direction of the field. However when the ions are displaced from their equilibrium position, a restoring force in the form of the coulombic force of attraction tends to constrain the bond elongation.

The displacement of the ions results in a net induced dipole moment per unit volume or the electric field induces polarization in the material. The ionic polarisability α_i is independent of temperature and depends on the Young's modulus of the material.

Orientational polarization:

Polar molecules have permanent dipole moments since the net charge centers are separated by a small distance. These dipoles can move and rotate freely (polar liquids - such as the water molecule). However due to the random motion of the molecules at normal temperatures, there is no net polarization in the material.

In the presence of an external field the dipoles tend to align in the direction of the field. This results in a net dipole moment for the material and is called orientational polarization.



The polarisation is given by
$$P = \frac{N\mu^2 E}{3kT}$$

Where N is the no of dipoles per unit volume, μ is the dipole moment of the individual molecules and T the temperature.

Increase in temperature increases the random motion of the dipoles and hence the orientational polarization is highly temperature dependent.

Space charge limited polarisation

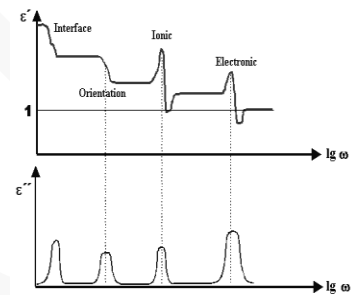
In general when two materials of different conducting phases meet at an interface, a potential barrier layer is formed resulting in an accumulation of charges of the opposite polarities on either sides of the interface. This can be modeled to be a polarization of charges in the bulk of the material. The width of the barrier is generally very small and can result in reasonably high capacitance. These are however very sensitive to voltages and frequencies and may not be effective at normal working conditions.

Frequency dependence of dielectric constant.

The response of the dielectric constant to an applied ac electric field can be understood by considering the ability of the individual dipoles in the material to follow the external AC field. The dielectric constant of an ideal dielectric which has all mechanism contributing to the polarization can be expressed as

$$\epsilon_r = \epsilon_{sp} + \epsilon_{or} + \epsilon_{io} + \epsilon_e$$

The AC electric field induces the dipoles due to the individual polarization mechanisms have to align in the direction of the field. At low frequencies, the dipoles due to all mechanisms tend to align with the electric field easily. As the frequency of the applied electric field increases, the dipoles alignment tends to lag behind the field (depending on the inertia of the dipole). This results in a effective decrease in the polarization of the material as the frequency increases.



The AC response of the dielectric constant can be represented as $\epsilon = \epsilon' + j\epsilon''$ where ϵ' is the real part of the dielectric constant and ϵ'' is the imaginary part of the dielectric constant which describes the losses in the dielectric.

At low frequencies of about 100Hz, the contribution to the dielectric constant from the space charge polarization disappears and hence the dielectric constant decreases. Beyond this and up to about 10^9 Hz remains constant implying all the other three polarization mechanisms are active. At round 10^9 Hz (the microwave region) the orientation polarization stops responding to the electric field and the contribution from this mechanism to the dielectric constant become zero and the effective dielectric constant of the material decreases to a lower value.

At this point only two polarization mechanisms are contributing to the dielectric constant – the ionic and electronic polarization mechanisms.

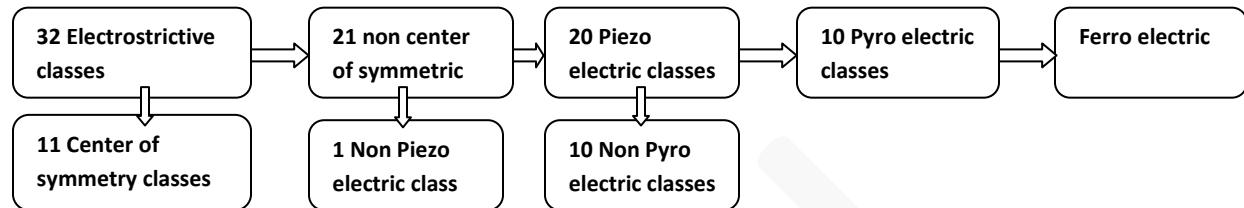
Around 10^{13} Hz (far infra red) the frequency of the AC field is in close to the vibrational frequencies of the bond and resonance phenomena sets in. The dielectric constant shows an initial increase and exhibits a resonance type of behavior around the resonant frequency.

Beyond this range the dielectric constant is only due to the electronic polarization. As the frequency of the AC approach 10^{15} Hz - the visible range which corresponds to the visible absorption frequency and a resonant condition sets in with a behavior similar to the ionic range.

The material may be treated as transparent to frequencies $> 10^{16}$ Hz and the dielectric constant should be that of vacuum or free space.

The dielectric loss ϵ'' represents the energy loss in the dipoles following the electric fields. As the frequency increases generally the inertia of the dipoles becomes significant and at particular frequency ranges the dipoles become inert to the increasing ac frequency. } }^{###}

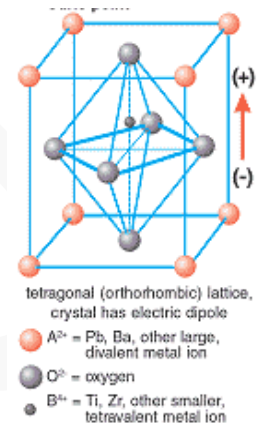
Classification of non linear dielectric materials



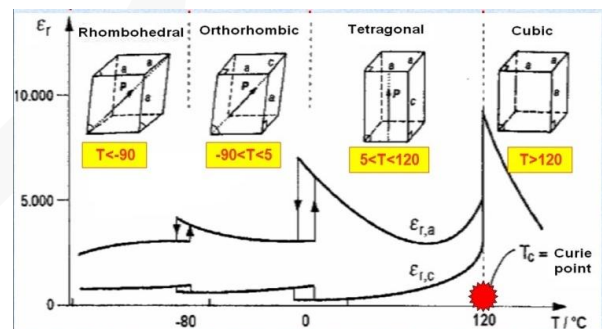
Non Centro-symmetric system

Out of a total of 32 crystal point groups (see the course related to structure of materials), 21 are non-centrosymmetric *i.e.* crystals not having a center of symmetry.

BaTiO₃ is a good example of a non centro symmetric crystal. The unit cell is cubic above the curie temperature of about 120 C, when the material is centro symmetric and behaves as a paraelectric. Between 5C and 120C the material is in the tetragonal phase exhibiting ferroelectric behavior. Below 5C and -90C the material has a orthogonal phase and below -90C the material is in the orthorhombic phase. In all these phases also the material exhibit ferroelectric behavior in varying proportions.



These dipoles arise due to the fact that in the tetragonal unit cell of BaTiO₃, the Ti⁴⁺ cation is surrounded by six O²⁻ anions in a slightly deformed octahedral configuration, and can occupy one of two asymmetrical sites. In either position, the Ti⁴⁺ cation is not coincident with the negative charge center of the oxygen anions by a small fraction of an Angstrom, creating an electric dipole. The energy barrier between the two possible Ti atom positions is sufficiently low to permit motion of the atom between sites by the coercion of an electric field, and the material can thus be directionally polarized with ease.



Non centro symmetric crystals can respond to an external stimulus producing polarization or surface charges which show up as a potential across the element. However these properties are highly anisotropic and could be described as a tensor (which describes the direction dependent properties of materials). Piezoelectric behavior is the response of these crystals to external mechanical pressures; Pyroelectric behavior is the response to thermal changes and Ferroelectric behavior is a response of the material to external electric fields.

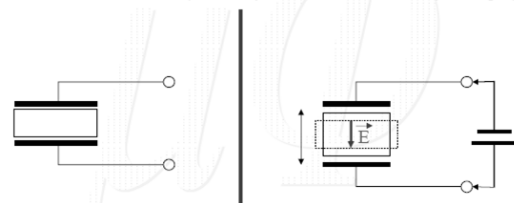
Piezoelectric materials

Piezoelectric Effect is appearance of an electrical potential across some faces of some crystals when a pressure is applied to the crystal. Pierre Curie and his brother Jacques discovered the effect in 1880.

Subsequently the inverse piezoelectric effect was observed as a distortion in the crystal when an electrical field is applied.

The term piezoelectricity refers to the fact that, when a crystal is strained, an electric field is produced within the substance. As a result of this field, a potential difference develops across the sample, and by measuring this potential one may determine the field. The inverse effect - that an applied field produces strain - has also been observed. It is explained by the displacement of ions, causing the electric polarization of the crystal's structural units. When an electrical field is applied, the ions are displaced by electrostatic forces, resulting in the mechanical deformation of the whole crystal.

– Mechanical strain (stress) \Leftrightarrow Electric field (charge)



The piezoelectric effect is very small. A field of 10^3 V/cm in quartz (SiO_2) produces a strain of only 10^{-7} . That is, a rod 1 cm long changes its length by 10\AA . Conversely, even small strains can produce enormous electric fields.

The piezoelectric effect is often used to convert electrical energy into mechanical energy, and vice versa; i.e., the substance is used as a transducer. For instance, an electric signal applied to the end of a quartz rod generates a mechanical strain, which consequently leads to the propagation of a mechanical wave - a sound wave - down the rod. The microscopic origin of piezoelectricity lies in the displacement of ionic charges within the crystal. In the absence of strain, the distribution of the charges at their lattice sites is symmetric, so the internal electric field is zero. But when the crystal is strained, the charges are displaced. If the charge distribution is no longer symmetric, then a net polarization, and a connected electric field, develops.

Piezo electric materials like PZT ($\text{Pb}(\text{Zr,Ti})\text{O}_3$), and Quartz find extensive application in electronics as sensors and actuators.

- Piezoelectric microbalances are used as very sensitive chemical and biological sensors.
- Atomic force and scanning tunneling microscopes for precision manipulation of sample at nano meter levels
- Transient pressure measurement to study explosives, internal combustion engines (knock sensors), and any other vibrations, accelerations, or impacts.
- Energy Harvesting from impact on the ground
- Electric igniters
- Transducers are used in electronic drum pads to detect the impact of the drummer's sticks.

Pyroelectric materials

Pyroelectricity is the ability of certain materials to generate an electrical potential when they are heated or cooled. Non centrosymmetric crystals with a net spontaneous polarization can be sensitive to external temperatures.

The change in temperature modifies the positions of the atoms slightly within the crystal structure, such that the polarization of the material changes. This polarization change gives rise to a voltage across the crystal. If the temperature stays constant at its new value, the pyroelectric voltage gradually disappears due to leakage current (the leakage can be due to electrons moving through the crystal, ions moving through the air, current leaking through a voltmeter attached across the crystal, etc.).

The pyroelectric coefficient may be described as the change in the spontaneous polarization vector P_s with temperature T

$$p_i = \frac{\partial P_s}{\partial T} \quad \text{where } p_i (\text{Cm}^{-2}\text{K}^{-1}) \text{ is the vector for the pyroelectric coefficient.}$$

It can be used to create a flow of current in an external circuit connected to a piece of the material. The effect has been known for many years but it is only since about 1960 that its technological applications have been seriously considered. These have been almost entirely in the field of the detection of electromagnetic radiation, especially in the two “atmospheric window” infrared (IR) bands of 3-5 μm and 8-14 μm . The ambient temperature operation of pyroelectric detectors, leading to low power consumption, low cost, compactness and lack of any requirement for logistical support in the form of cooling fluids or high-pressure gas, gives them a number of important advantages over photon detectors used in these wavebands, such as MCT or InSb. These must be cooled to cryogenic temperatures to obtain optimum performance. Hence, pyroelectric detectors have found a huge range of applications in products ranging from fire alarms to intruder detectors, in instrumentation such as gas analysis and laser beam characterization and in military/paramilitary applications such as thermal imaging.

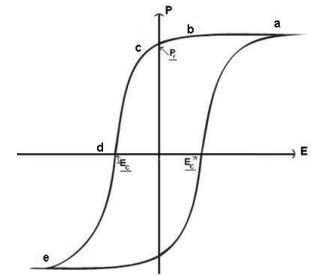
Ferroelectric materials

Charge displacements in dielectric and para electric ceramics, such as Al_2O_3 , mica, TiO_2 , are totally reversible, as ions / electron cloud return to their original position once an applied field is removed, and the polarization effect is linear.

Ferroelectrics are a class of non centro symmetric crystals which are also a subclass of the pyro electric / piezoelectric materials. These materials show a spontaneous polarization even in the absence of an electric field.

The spontaneous polarization observed in ferroelectric materials depends on the crystalline phase of the material (generally referred to as perovskites). BaTiO_3 is a classic example of a perovskite material.

Ferroelectric dielectrics differ from dielectric materials in their response to external applied electric field. Ferroelectrics display a nonlinear response of polarization to changing electric fields and display a hysteresis in the P versus E variations. The hysteresis loop is caused by the existence of permanent electric dipoles in classes of materials, which develop spontaneously below the Curie temperature. The polarisation state of the ferroelectric material has a memory effect and hence is used extensively in DRAMs and SRAMS.



The dielectric susceptibility of the material is highly temperature dependent and is given by $\chi = \frac{C}{T - T_c}$

for all $T > T_c$ where C is a constant dependent on the material and T_c is the Curie temperature. At temperature below T_c , the material shows spontaneous polarization and is classified as a ferroelectric material. At temperatures greater than T_c , the material is para electric with the susceptibility inversely proportional to temperature.

Ferro electric materials find numerous applications as sensors and actuators taking advantage of the temperature and field dependencies of the susceptibility (dielectric constant).

Problem Set:

1. If the molecular dipoles in a 10^{-3} m radius water drop are pointed in the same direction, calculate the polarisation of the water drop. Dipole moment of water molecule is 6×10^{-30} C m.
2. Assuming that the polarisability of Kr atom is 2.18×10^{-40} Fm⁻², calculate its dielectric constant. Kr has 2.7×10^{25} atoms per unit volume at NTP.
3. An elemental dielectric has $\epsilon_r = 12$ and contains 5×10^{29} atoms /m³. Calculate the electronic polarisability of the material.
4. Find the total polarisability of CO₂ if its susceptibility is 0.985×10^{-3} . Density of CO₂ is 1.977 Kg m⁻³.
5. On being polarised an oxygen atom shows a dipole moment of 0.5×10^{-22} C-m. If the distance of the center of the -ve charge cloud from the nucleus is 4×10^{-17} m, calculate the polarisability of oxygen.
6. A parallel plate capacitor without a dielectric is charged such that the surface charge density on the plates is 10^6 C-m⁻². If a slab of a material with dielectric constant 10 is inserted between the plates, calculate the polarisation in the material and the electric field due to induced surface charge on the dielectric.
7. A dielectric material has one species having an atomic polarizability value of 10^{-30} Cm²V⁻¹. It is found that when the dielectric sample is kept in a uniform electric field, the field reduces to one tenth of its original value. Estimate the number of atoms per unit volume of the material.
8. Electronic polarisability of Sulphur is 3.28×10^{-40} F-m². Calculate the dielectric constant of Sulphur if the density and atomic weight of Sulphur are 2.08×10^3 kg-m⁻³ and 32 respectively.