Non - Metallic Materials
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Module - 05
Electrical, magnetic and thermal properties of non - metallic materials
Lecture - 23
Dielectric and piezoelectric behavior

Welcome to my course Non-Metallic Materials and we are in module number 5 Electrical, magnetic and thermal properties of non-metallic materials. And this is lecture number 23, where I will be talking about Dielectric and piezoelectric behavior of non-metallic materials.

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Concepts Covered

- Relative permittivity and polarization
- Concept of polarizability and its relation to relative permittivity
- Clausius Mossoti relationship
- Frequency dependence of polarizability and relative permittivity
- Estimation of polarizability
- Concept of piezoelectric and pyroelectric effect

So, I will introduce the concept of relative permittivity and the polarization which is dipole moment per unit volume. Then, we will be talking about the concept of polarizability and its relation to relative permittivity. The Clausius Mossotti relationship will be derived and explained.

Then, we will talk about the frequency dependence of the polarizability and relative permittivity. Then, there are certain rules, which is adopted to estimate the polarizability, particularly for ionic as well as electronic polarizability, this will be illustrated. And finally, we will talk about the concept of piezoelectric and pyroelectric effect in a non-centrosymmetric non-metallic materials.

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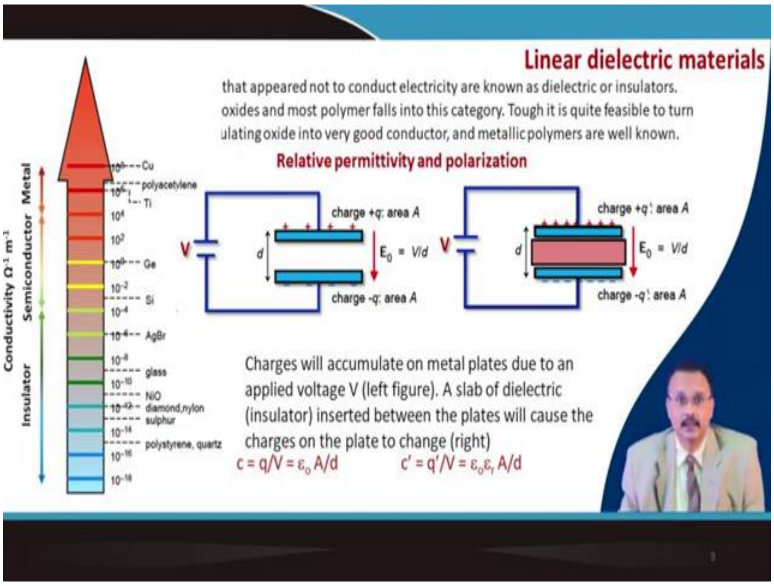

Linear dielectric materials

that appeared not to conduct electricity are known as dielectric or insulators. oxides and most polymer falls into this category. Tough it is quite feasible to turn ulating oxide into very good conductor, and metallic polymers are well known.

Relative permittivity and polarization

Charges will accumulate on metal plates due to an applied voltage V (left figure). A slab of dielectric (insulator) inserted between the plates will cause the charges on the plate to change (right)

$c = q/V = \varepsilon_0 A/d$ $c' = q'/V = \varepsilon_0 \varepsilon_r A/d$

So, you know that the solid you can differentiate based on how good or how bad they can conduct electricity. So, a dielectric material is basically an insulator which does not conduct electricity. This is a very crude term because now it is possible and partially, you will be able to understand it also.

That introduction of the defect could be responsible to make a otherwise insulating material at least semiconducting and certain oxides of the material for example, ruthenium oxide, strontium ruthenium, they exhibits metal like conductivity; but those are not usual terms.

So, if you can see here, the scales the metal is at the top and the highly insulating materials like quartz or polystyrene, diamond, they are in the bottom having the conductivity in the range of 10 to the power minus 14 Ohm per meter. So, when you take two simple parallel plate electrode which is separated by vacuum and then, you apply a DC potential, so, this plate will be positively charged and this will be negatively charged.

So, you can estimate the capacitance of this parallel plate in a simple relation q by V; V is the applied voltage and q is the charge which is accumulated and which is basically a geometric capacitance which depends on the area of this electrode A and the separation of the distance between this two electrode d.

So, you can write a relation that it relates the capacitance with the permittivity of the vacuum and otherwise, it is all geometric A and d. Now, once in this particular parallel plate capacitor you replace the so called vacuum or air with a insulating material then, you will see that the capacitance will change.

So, c will be c prime and the charge, surface charge density also will change because of the insertion of the relative dielectric permittivity of this material. So, now your q dash has changed, capacitance has changed, and now the capacitance is given by epsilon 0 into epsilon r into A by d. So, the charges will accumulate on metal plate due to an applied voltage and insertion between the plates will cause the charge on the plate to change, that is the right side of the figure.

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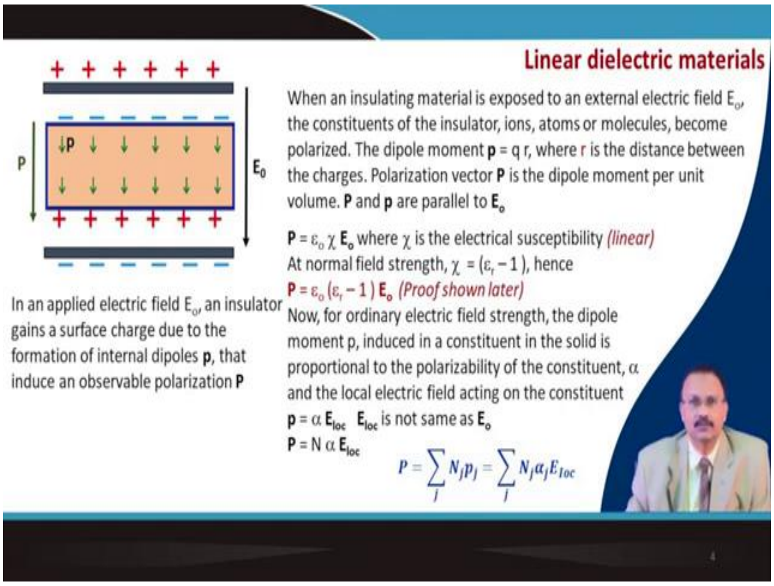

Linear dielectric materials

In an applied electric field E_o, an insulator gains a surface charge due to the formation of internal dipoles **p**, that induce an observable polarization **P**

When an insulating material is exposed to an external electric field E_o, the constituents of the insulator, ions, atoms or molecules, become polarized. The dipole moment **p** = q r, where r is the distance between the charges. Polarization vector **P** is the dipole moment per unit volume. **P** and **p** are parallel to $\mathbf{E_o}$

$\mathbf{P} = \varepsilon_o \chi \mathbf{E_o}$ where χ is the electrical susceptibility *(linear)*

At normal field strength, $\chi = (\varepsilon_r - 1)$, hence

$\mathbf{P} = \varepsilon_o (\varepsilon_r - 1) \mathbf{E_o}$ *(Proof shown later)*

Now, for ordinary electric field strength, the dipole moment p, induced in a constituent in the solid is proportional to the polarizability of the constituent, α and the local electric field acting on the constituent

$\mathbf{p} = \alpha \mathbf{E_{loc}}$ $\mathbf{E_{loc}}$ is not same as $\mathbf{E_o}$

$\mathbf{P} = N \alpha \mathbf{E_{loc}}$

$$P = \sum_j N_j p_j = \sum_j N_j \alpha_j E_{loc}$$

So, the situation what is happening can be explained by this figure. So, initially you have charge here and then, you have inserted a dielectric material. So, something is happening in this material, you can see that in the material itself, there are small dipole moment that is being created.

So, dipole moment is nothing but charge separated by a distance. So, this dipole moment usually we denote it by this small p and that leads to what we call polarization which is this creation of the dipole moment per unit volume of this material. So, the polarization this field this is the vector quantity is exactly identical to the field of the applied voltage whatever you are applying, it is in the same potential.

So, this polarization is related to this applied electric field by this relation. It is a linear relationship. So, polarization is directly proportional to the field through electrical susceptibility. So, this is the slope term as you can see y equal to m x, there is no c term here. So, this is a straight line and the slope is nothing but electrical susceptibility.

So, this kind of feature is actually exhibited by the material which we call it is a linear dielectric material. So, at normal field strength when the field strength is not exorbitantly high, then your dielectric susceptibility is nothing but relative permittivity minus 1. So, if you put it back here, so your polarization value will be epsilon 0 into epsilon r minus 1 into the applied electric field.

So, this can be proved; in fact, we have proved it in the next slide. So, for the ordinary field strength, the dipole moment small p induced in a constituent in the solid is proportional to the polarizability of the material. What is this polarizability? I will just explain in a moment. So, this polarizability of the constituent material which is present in this dielectric, this is acting on the constituent.

So, you can always define the dipole moment is actually, again linearly proportional to the localized field which is acting on those typical constituents and this localized field is certainly not equal to the global field with whatever you are applying. So, if you now assume that there are N dipole moment and polarizability is alpha, then polarization you can write by this relation. Polarization is number of dipole into its polarizability of this individual constituents and the localized field whatever is acting.

Now, there are there could be different types of polarizability. So, it is basically a summation. So, you can sum the different types of polarizability and their number and the local field whatever is acting. So, if you add it up, that basically will give you the total polarization of this material.

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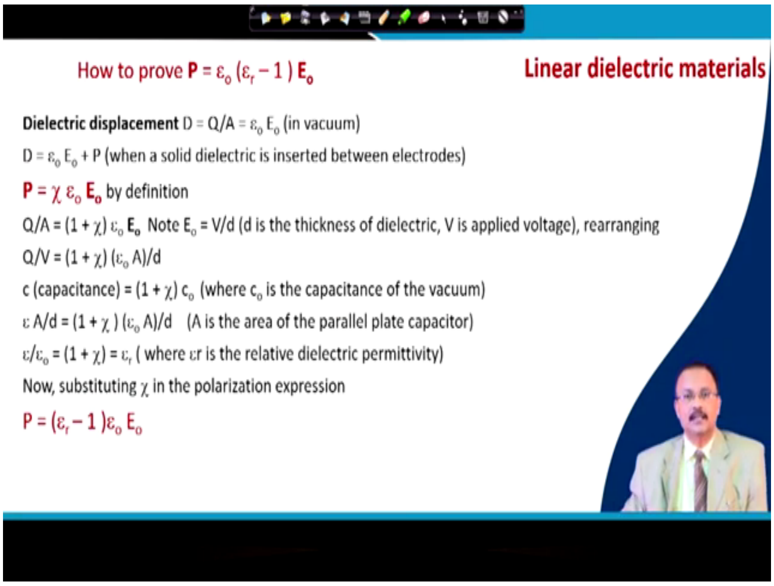

How to prove **P** = ε_0 (ε_r − 1) $\mathbf{E_0}$

Linear dielectric materials

Dielectric displacement D = Q/A = ε_0 E_0 (in vacuum)

D = ε_0 E_0 + P (when a solid dielectric is inserted between electrodes)

P = χ ε_0 $\mathbf{E_0}$ by definition

Q/A = (1 + χ) ε_0 $\mathbf{E_0}$ Note E_0 = V/d (d is the thickness of dielectric, V is applied voltage), rearranging

Q/V = (1 + χ) (ε_0 A)/d

c (capacitance) = (1 + χ) c_0 (where c_0 is the capacitance of the vacuum)

ε A/d = (1 + χ) (ε_0 A)/d (A is the area of the parallel plate capacitor)

$\varepsilon/\varepsilon_0$ = (1 + χ) = ε_r (where εr is the relative dielectric permittivity)

Now, substituting χ in the polarization expression

P = (ε_r − 1)ε_0 E_0

Now, as I told that this can be proved, this polarization and dielectric field, this linear relationship is given by this relation, it can be proved. So, we will introduce a term which is called dielectric displacement, which is nothing but the surface charge density. Q is the surface charge and area is involved here.

So, this D is proportional to your applied electric field and the proportionality constant is the dielectric permittivity in vacuum. So, by definition, we have shown that this polarization is related to the electric susceptibility and dielectric permittivity in vacuum and the value of the electric field.

So, you can substitute it Q by A is given by this relation and then, this electric field is the applied voltage divided by thickness of the electrode, the electrode separation. So, that is d. So, you substitute that, you get the relation Q by V is given by this relation. So, the capacitance you know that capacitance again, Q equal to c into V.

So, you just replace it. So, you get the relation between capacitance susceptibility. And now, by the definition of capacitance, you put the value. It is dielectric permittivity into area divided by d, this is equal to 1 by 1 plus kappa into again you just expand the term for c 0.

So, epsilon by epsilon 0 that is the relative dielectric permittivity, this is 1 plus electric susceptibility and that is basically dielectric relative dielectric permittivity. Now, you substitute this value here, you get P is equal to epsilon r minus 1 into epsilon 0 into E 0. This is just for the sake of simplicity I decided to derive this relationship.

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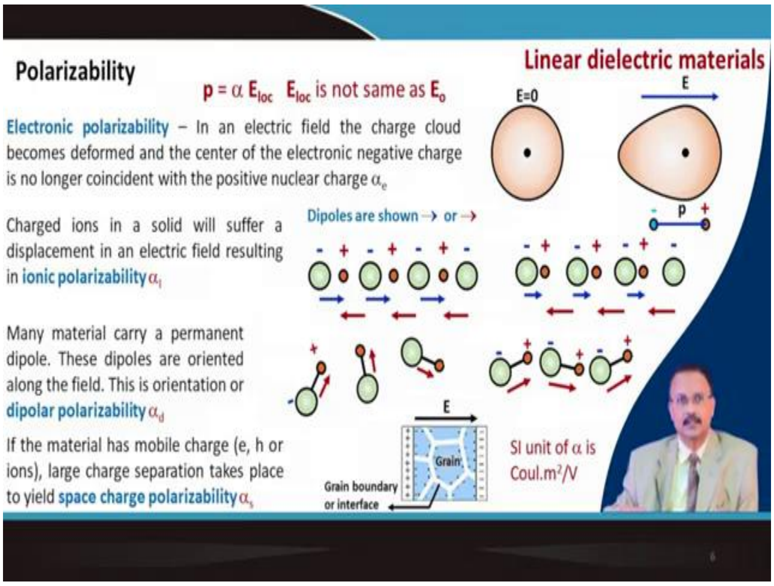

Polarizability

$p = \alpha E_{loc}$ E_{loc} is not same as E_o

Electronic polarizability – In an electric field the charge cloud becomes deformed and the center of the electronic negative charge is no longer coincident with the positive nuclear charge α_e

Charged ions in a solid will suffer a displacement in an electric field resulting in **ionic polarizability** α_i

Many material carry a permanent dipole. These dipoles are oriented along the field. This is orientation or **dipolar polarizability** α_d

If the material has mobile charge (e, h or ions), large charge separation takes place to yield **space charge polarizability** α_s

Linear dielectric materials

Dipoles are shown → or →

SI unit of α is Coul.m^2/V

Now, as I said polarization could be of different types and remember, this basic relation that this dipole moment is related directly proportional to the field that is being applied to this different types of polarizability. The first type of polarizability is electronic polarizability, when you are applying a field in the positive direction.

Then, your nucleus and electronic cloud which were symmetric, otherwise without the application of any field, then your electron cloud will go towards the positive field direction. So, there will be separation of charge and separation of charge will lead to dipole moment and dipole moment per unit volume is polarization.

So, due to the electronic polarizability that contribution will be given to the total polarization of this material. So, again for an ionic solid, there also will be shift, relative shift of the positive and negative cation leads to the ionic polarizability. So, electronic polarizability, I have defined it with alpha e; ionic polarizability is alpha i.

Certain material, they have permanent dipole; water is one of them. So, orientation when you are applying a field, then it is not ion or it is not the movement of electron with respect to its nucleus, the whole dipole will start to move along with their field direction. So, this kind of polarizability, we have defined as dipolar polarizability.

And if certain material is having mobile charge, you know about the defect we have talked about. So, it is having a mobile charge then this kind of shift of the charge may be very large. For all these cases, the separation, the distance is relatively very small. Think of ionic polarizability, cations are ions are there inside a material inside your lattice.

So, they cannot have a long-range kind of distance, it cannot travel. So, this is a little bit very small shift. Dipolar polarization also, there is a small shift; but in case of space charge polarizability, there is a large shift and usually through the grain, this charge will move and grain boundary, there it will be shielded.

So, this kind of builds polarizability is also apparent in a dielectric material. So, in all we have four different mechanisms; one is electronic polarizability, ionic polarizability, dipolar polarizability or orientation and polarizability and finally, the space charge polarizability is there.

And you can easily define the unit for polarizability is coulomb into meter square per volt that is from the definition. Polarization definition, as I have told that this is dipole moment per unit volume. So, you can easily calculate in SI unit, what is the unit of the polarizability.

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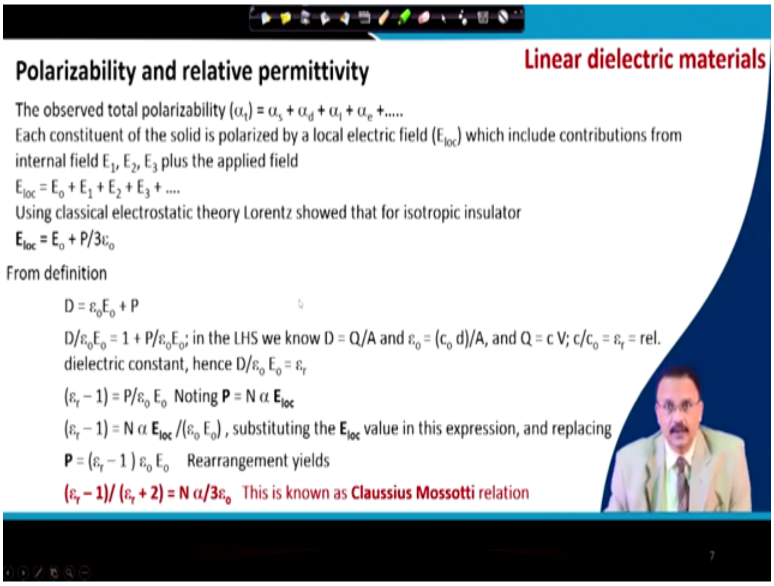

Polarizability and relative permittivity

Linear dielectric materials

The observed total polarizability (α_t) = $\alpha_s + \alpha_d + \alpha_i + \alpha_e + \ldots\ldots$

Each constituent of the solid is polarized by a local electric field (E_{loc}) which include contributions from internal field E_1, E_2, E_3 plus the applied field

$E_{loc} = E_0 + E_1 + E_2 + E_3 + \ldots.$

Using classical electrostatic theory Lorentz showed that for isotropic insulator

$\mathbf{E_{loc}} = E_0 + P/3\varepsilon_0$

From definition

$D = \varepsilon_0 E_0 + P$

$D/\varepsilon_0 E_0 = 1 + P/\varepsilon_0 E_0$; in the LHS we know $D = Q/A$ and $\varepsilon_0 = (c_0\, d)/A$, and $Q = c\,V$; $c/c_0 = \varepsilon_r$ = rel. dielectric constant, hence $D/\varepsilon_0\, E_0 = \varepsilon_r$

$(\varepsilon_r - 1) = P/\varepsilon_0\, E_0$ Noting $\mathbf{P} = N\, \alpha\, \mathbf{E_{loc}}$

$(\varepsilon_r - 1) = N\, \alpha\, \mathbf{E_{loc}} / (\varepsilon_0\, E_0)$, substituting the $\mathbf{E_{loc}}$ value in this expression, and replacing

$\mathbf{P} = (\varepsilon_r - 1)\, \varepsilon_0\, E_0$ Rearrangement yields

$(\varepsilon_r - 1)/(\varepsilon_r + 2) = N\, \alpha / 3\varepsilon_0$ This is known as **Claussius Mossotti** relation

Now, one can actually relate this different types of polarizability with the relative permittivity, whatever I talked about the relative permittivity, it is the ratio of the capacitance with or without dielectric. So, that epsilon r can be related with this individual polarizability.

And this observed total polarizability is your electronic plus ionic plus dipolar or orientational plus space charge right. Now, each constituent of the solid is polarized by a local electric field, which include contributions from the internal field and this also you can write. This is a series.

So, localized field is also say E 0 for one type of polarizability, E 1, E 2, E 3 etcetera. So, if you use classical electrostatic theory by Lorentz and it has been derived in a book by Solid State Physics by Kittel, you can have a look. For isotropic insulator this localized field is nothing but this E 0, the field that you are applying, then the polarization divided by 3 into epsilon 0.

So, this you will have to take for this estimation. So, now, the dielectric displacement is epsilon 0 into E 0 that is without any dielectric plus polarization is there, once you inserted the dielectric material between these two parallel plate, so, you can have this relation. Then you just do this divide both side by epsilon 0 into E 0.

So, you get this is the relation and we know that this D is nothing but surface charge density and c 0 is sorry; epsilon 0 is c 0 into d by A and Q equal to c V. So, all this relation already we have used. So, you can end up with this relation epsilon r minus 1 is equal to polarization by epsilon 0 into the applied electric field.

Now, we have just defined that the polarization is number of dipole into its respective polarizability and the local electric field. So, local electric field value, you substitute it and you get this relation and this relation you rearrange it and you get basically a relation between the polarizability.

This is the total polarizability and the dielectric permittivity; epsilon r minus 1 divided by epsilon r plus 2 is equal to number of these constituent dipoles into polarizability divided by 3 into epsilon 0. This relation is known as Clausius Mossotti relationship.

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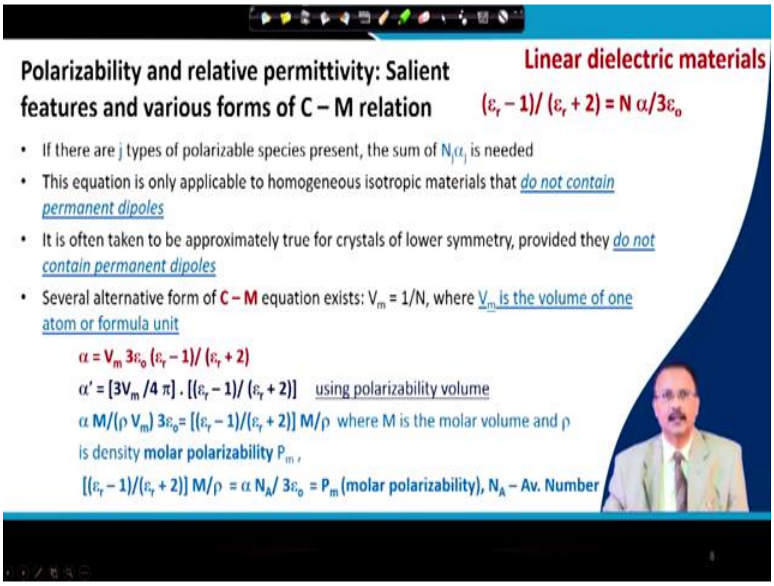

Polarizability and relative permittivity: Salient features and various forms of C – M relation

Linear dielectric materials

$(\varepsilon_r - 1)/(\varepsilon_r + 2) = N\alpha/3\varepsilon_0$

- If there are j types of polarizable species present, the sum of $N_j\alpha_j$ is needed
- This equation is only applicable to homogeneous isotropic materials that *do not contain permanent dipoles*
- It is often taken to be approximately true for crystals of lower symmetry, provided they *do not contain permanent dipoles*
- Several alternative form of **C – M** equation exists: $V_m = 1/N$, where V_m is the volume of one atom or formula unit

$\alpha = V_m 3\varepsilon_0 (\varepsilon_r - 1)/(\varepsilon_r + 2)$

$\alpha' = [3V_m/4\pi] . [(\varepsilon_r - 1)/(\varepsilon_r + 2)]$ using polarizability volume

$\alpha M/(\rho V_m) 3\varepsilon_0 = [(\varepsilon_r - 1)/(\varepsilon_r + 2)] M/\rho$ where M is the molar volume and ρ is density **molar polarizability** P_m,

$[(\varepsilon_r - 1)/(\varepsilon_r + 2)] M/\rho = \alpha N_A/3\varepsilon_0 = P_m$ (molar polarizability), N_A – Av. Number

Now, this Clausius Mossotti relationship that relates polarizability and relative dielectric permittivity. So, if there are jet number j types of different polarizable species, then you will have to use the summation term. That is quite obvious number of that particular polarizability into the individual polarizability and this equation is valid only for homogeneous isotropic material.

So, it should not contain any anything which contains permanent electric dipole which is not in strict sense valid, this relationship. So, it is only a valid for ionic and electronic polarizability. Several alternate form of this Clausius Mossotti relationship is possible and this is just three different types of relationship that you can think of and I have a certain assignment problem set for this.

The first one is I replace it with molar volume. So, this is molar volume is replaced. Second one is using a polarizability volume. So, this is the same relationship; but for the sake of simplicity, I just algebraically you do this thing and you get different forms of the same relation.

And the third one is called molar polarizability, where in the both side, we are multiplying with the M and the M is the molar volume and density. So, these three different form of the Clausius Mossotti relationship is possible.

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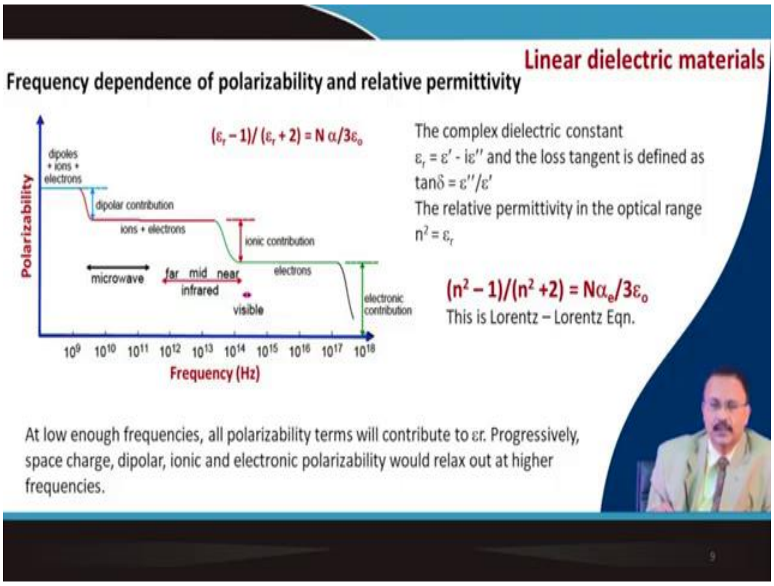

Linear dielectric materials

Frequency dependence of polarizability and relative permittivity

The complex dielectric constant $\varepsilon_r = \varepsilon' - i\varepsilon''$ and the loss tangent is defined as $\tan\delta = \varepsilon''/\varepsilon'$

The relative permittivity in the optical range $n^2 = \varepsilon_r$

$(n^2 - 1)/(n^2 + 2) = N\alpha_e/3\varepsilon_o$

This is Lorentz – Lorentz Eqn.

At low enough frequencies, all polarizability terms will contribute to εr. Progressively, space charge, dipolar, ionic and electronic polarizability would relax out at higher frequencies.

So, in an AC electric field, all this different polarized will source will not be actually contributing. So, at very high frequency, all this polarizability will relax out because they cannot actually follow the kind of the speed is not enough for ionic polarization or the dipolar polarization to follow it.

So, but the electronic polarizability is very fast. So, it will be there. So, at high frequency, your polarizability and thereby, your dielectric permittivity is minimum; whereas, at lower frequency in millihertz range, it is maximum because all these polarizations are contributing to the dielectric constant.

So, at very high frequency, this Lorentz-Lorentz equation is valid and it says that the dielectric permittivity can be replaced by the refractive index square. So, I have just in Clausius Mossotti relationship, I just replace the value of epsilon r by refractive index to get the Lorentz-Lorentz equation.

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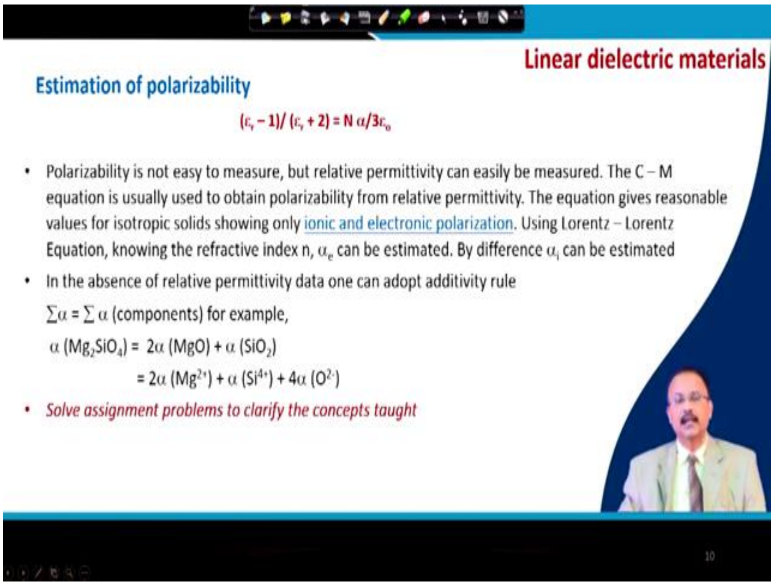

Linear dielectric materials

Estimation of polarizability

$(\varepsilon_r - 1)/(\varepsilon_r + 2) = N\alpha/3\varepsilon_0$

- Polarizability is not easy to measure, but relative permittivity can easily be measured. The C – M equation is usually used to obtain polarizability from relative permittivity. The equation gives reasonable values for isotropic solids showing only ionic and electronic polarization. Using Lorentz – Lorentz Equation, knowing the refractive index n, α_e can be estimated. By difference α_i can be estimated
- In the absence of relative permittivity data one can adopt additivity rule

  $\sum\alpha = \sum\alpha$ (components) for example,

  $\alpha(Mg_2SiO_4) = 2\alpha(MgO) + \alpha(SiO_2)$

  $= 2\alpha(Mg^{2+}) + \alpha(Si^{4+}) + 4\alpha(O^{2-})$
- *Solve assignment problems to clarify the concepts taught*

And now particularly, for ionic polarizability and electronic polarizability, you can separate it out the individual component. I will just hint you how to do that, but exact assignment problems are illustrated just to make you understand this concept. So, this is my equation of polarizability and that its relationship with dielectric permittivity.

So, this polarizability usually it is not very easy to actually experimentally verify, but you can get this value epsilon r. So, in a composite system, if you know its refractive index and then, you can just delineate the electronic contribution, the dielectric permittivity due to electronic polarizability, whatever is left out is your ionic polarizability.

So, that is one way to do that. Otherwise, you can adopt this additive rule where it says that the polarizability if you do a summation that is the summation of all individual components. So, if you take say for example, magnesium silicate. So, that is due to magnesium oxide and silicon dioxide in the first instance and then, again you can divide it to magnesium ion, silicon ion and oxygen ion.

So, just by breaking it into different constituents, it is possible for you to actually estimate the individual polarizability. Things will be clear when I will solve certain assignment problem to illustrate this phenomena better.

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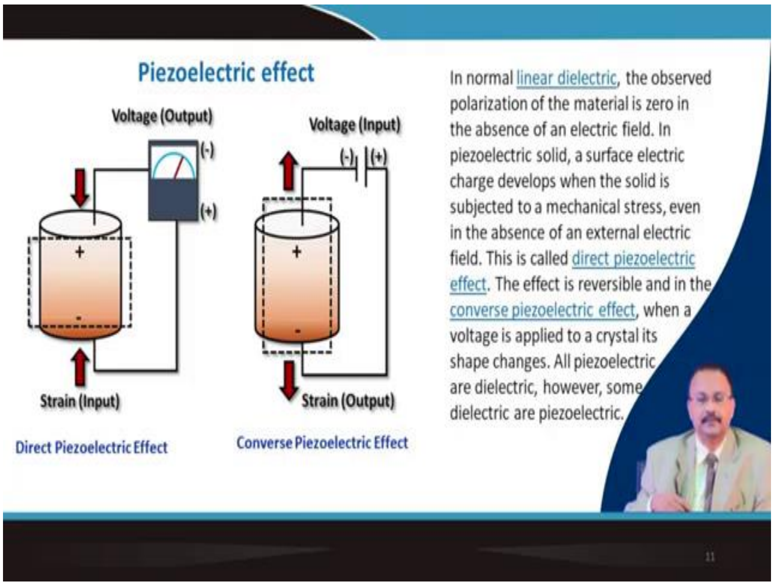

Piezoelectric effect

Direct Piezoelectric Effect

Converse Piezoelectric Effect

In normal linear dielectric, the observed polarization of the material is zero in the absence of an electric field. In piezoelectric solid, a surface electric charge develops when the solid is subjected to a mechanical stress, even in the absence of an external electric field. This is called direct piezoelectric effect. The effect is reversible and in the converse piezoelectric effect, when a voltage is applied to a crystal its shape changes. All piezoelectric are dielectric, however, some dielectric are piezoelectric.

Now, we will talk about the piezoelectric effect. Mostly, there are two types of piezoelectric effect. In certain material when you are applying a stress, then you will see that it generates electricity. So, the polarization is related to the stress and not due to electric field.

And there is a converse effect, when you are applying a voltage, then depending on the voltage whether it is a DC or AC voltage, there is a expansion of the material. So, the first one is called direct piezoelectric effect and the second phenomena is called inverse piezoelectric effect or converse piezoelectric effect.

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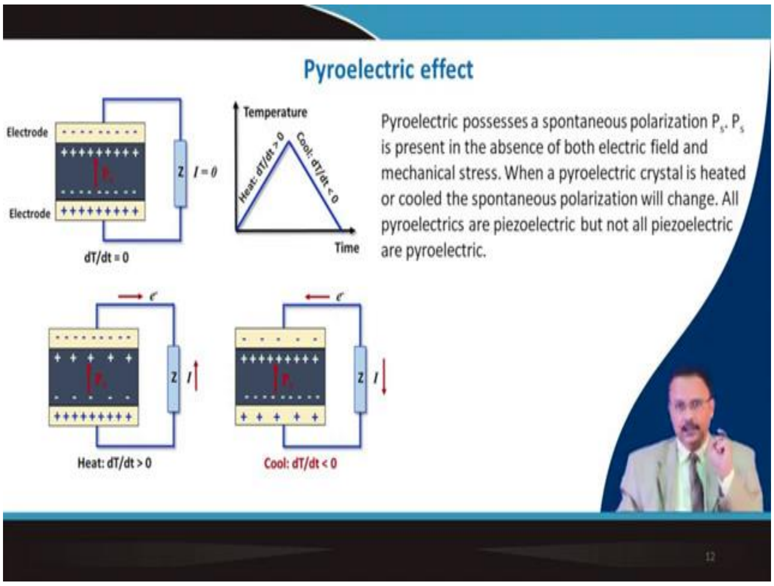

Pyroelectric effect

Pyroelectric possesses a spontaneous polarization P_s. P_s is present in the absence of both electric field and mechanical stress. When a pyroelectric crystal is heated or cooled the spontaneous polarization will change. All pyroelectrics are piezoelectric but not all piezoelectric are pyroelectric.

This type of material insulating material, sometimes it is also possible for you to change its polarization. Because what you are doing? You are changing the polarization that means the dipole moment per unit volume either by application of electric field. In case of linear dielectric, once you are applying the electric field, then the polarization is there. Once you take out the field, then the polarization is 0.

In case of piezoelectric material, you are applying a stress and you are getting polarization. There is a converse effect also. You apply a voltage; you get strain out of it. In case of pyroelectric material, you change the temperature and you will see that the polarization changes. We will not talk much about the pyroelectric material in this lecture.

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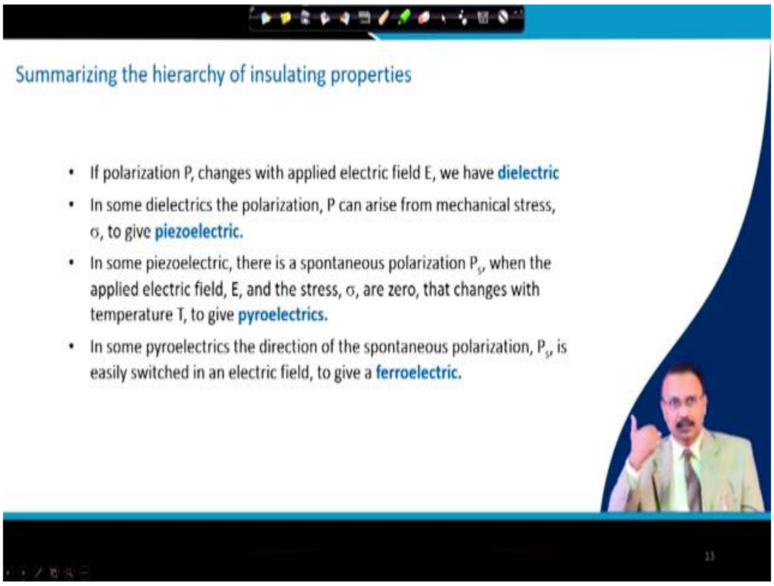

Summarizing the hierarchy of insulating properties

- If polarization P, changes with applied electric field E, we have **dielectric**
- In some dielectrics the polarization, P can arise from mechanical stress, σ, to give **piezoelectric.**
- In some piezoelectric, there is a spontaneous polarization P_s, when the applied electric field, E, and the stress, σ, are zero, that changes with temperature T, to give **pyroelectrics.**
- In some pyroelectrics the direction of the spontaneous polarization, P_s, is easily switched in an electric field, to give a **ferroelectric.**

So, polarization as I said that certain material could be dielectric material, certain material can be piezoelectric in nature when polarization is changed by stress, some material can be pyroelectric in nature, where the polarization can be changed by the application of temperature change and in certain material, this polarization value is switchable.

So, not only change of the polarization value, but you can switch the polarization direction from one direction to other direction those materials are called ferroelectric material.

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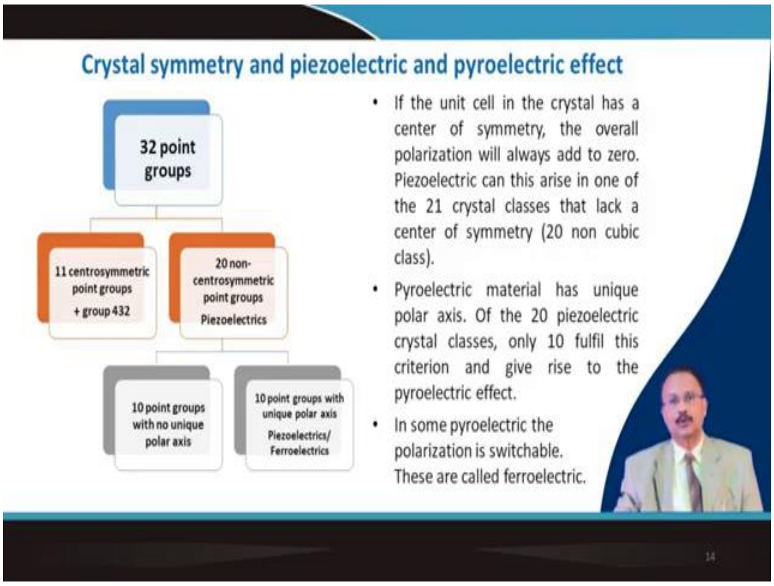

Crystal symmetry and piezoelectric and pyroelectric effect

32 point groups

11 centrosymmetric point groups + group 432

20 non-centrosymmetric point groups Piezoelectrics

10 point groups with no unique polar axis

10 point groups with unique polar axis Piezoelectrics/ Ferroelectrics

- If the unit cell in the crystal has a center of symmetry, the overall polarization will always add to zero. Piezoelectric can this arise in one of the 21 crystal classes that lack a center of symmetry (20 non cubic class).
- Pyroelectric material has unique polar axis. Of the 20 piezoelectric crystal classes, only 10 fulfil this criterion and give rise to the pyroelectric effect.
- In some pyroelectric the polarization is switchable. These are called ferroelectric.

So, this set of material, this multi functionality is dependent on the point group on the symmetry. There is no scope for me to go into details about the details of the point group, but there are 11 centrosymmetric point group material and which are not piezoelectric in nature.

Out of that 20 is piezoelectric in nature and out of this 20, 10 are 10 point groups are having no unique polar axis. But other 10 is having a unique polar axis. So, those materials can be either pyroelectric or they could be ferroelectric in nature.

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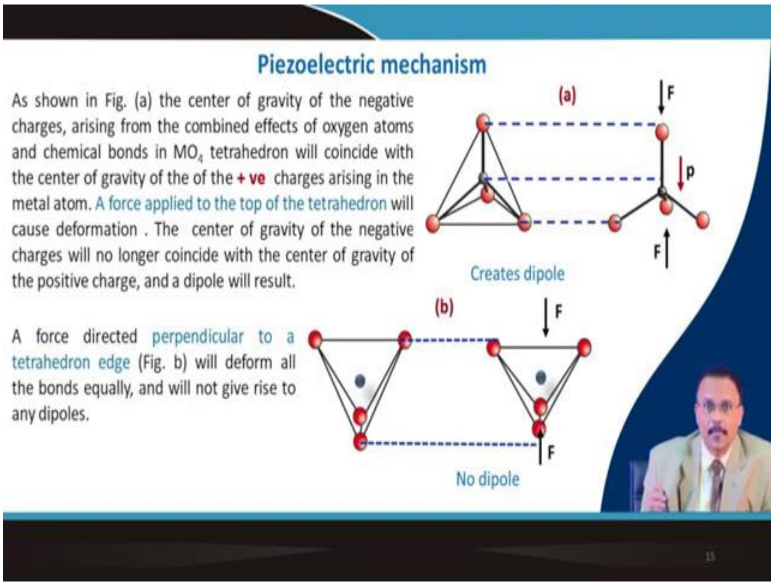

Piezoelectric mechanism

As shown in Fig. (a) the center of gravity of the negative charges, arising from the combined effects of oxygen atoms and chemical bonds in MO_4 tetrahedron will coincide with the center of gravity of the of the **+ ve** charges arising in the metal atom. A force applied to the top of the tetrahedron will cause deformation . The center of gravity of the negative charges will no longer coincide with the center of gravity of the positive charge, and a dipole will result.

A force directed perpendicular to a tetrahedron edge (Fig. b) will deform all the bonds equally, and will not give rise to any dipoles.

So, the piezoelectric mechanism can be understood by this fictitious tetrahedral material and as you can see that if I apply a stress here, then this cation which is sitting in the tetrahedral void, they will be shifted here. So, the electric lines of force of this orange atom will not coincide with the electric lines of force of this positive cation.

So, there will be creation of dipole. So, the stress will generate the dipole only when you are applying the force along with the bond line; but if you are alloy, if you are applying the force along with the edge of this tetrahedra, then there will not be significant change in the respective charges, they will not separate. So, you will not get any dipole.

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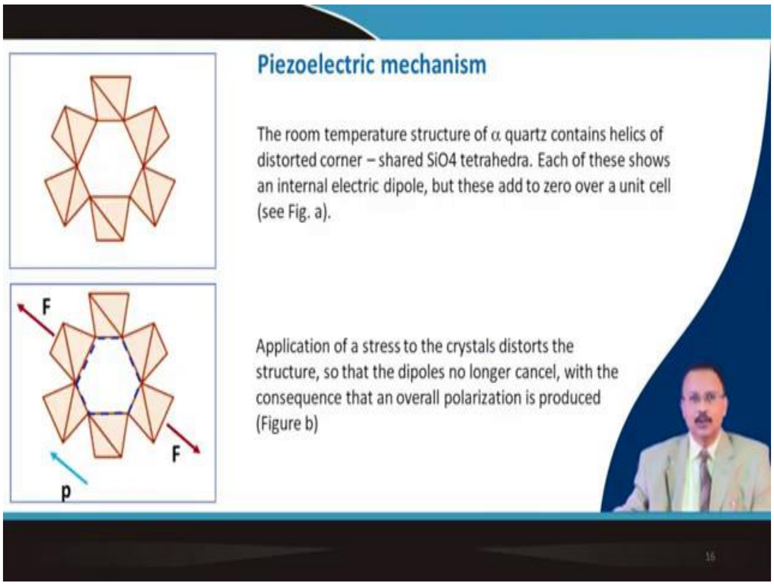

Piezoelectric mechanism

The room temperature structure of α quartz contains helics of distorted corner – shared SiO4 tetrahedra. Each of these shows an internal electric dipole, but these add to zero over a unit cell (see Fig. a).

Application of a stress to the crystals distorts the structure, so that the dipoles no longer cancel, with the consequence that an overall polarization is produced (Figure b)

So, similar thing happens in quartz crystal. In quartz crystal, it forms a helix structure like this. So, here your Si ions are there in the oxygen tetrahedra. Once, you are applying a force then these lines of force are not matched. So, then it generates the so called piezoelectric effect in quartz crystal.

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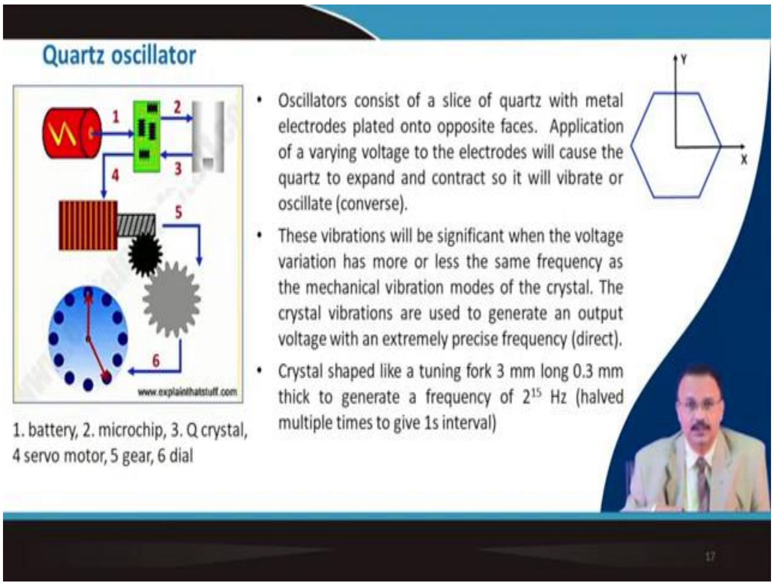

Quartz oscillator

1. battery, 2. microchip, 3. Q crystal, 4 servo motor, 5 gear, 6 dial

- Oscillators consist of a slice of quartz with metal electrodes plated onto opposite faces. Application of a varying voltage to the electrodes will cause the quartz to expand and contract so it will vibrate or oscillate (converse).
- These vibrations will be significant when the voltage variation has more or less the same frequency as the mechanical vibration modes of the crystal. The crystal vibrations are used to generate an output voltage with an extremely precise frequency (direct).
- Crystal shaped like a tuning fork 3 mm long 0.3 mm thick to generate a frequency of 2^{15} Hz (halved multiple times to give 1s interval)

And this quartz is a time keeper. You know that the quartz crystal is used to make the watch and this is due to the fact if you take a single crystalline quartz and you can have various types of cut; X cut, Y cut or XY cut. This is possible and what is happening that this quartz crystal, it is in the form of a tuning fork.

So, once you apply voltage due to the converse piezoelectric effect, it will try to vibrate and the cut is made such that the vibration frequency is very specific so that one second, you can divide it out of it. So, it is a very precise cut which is required to make this kind of vibration and this vibration in turn can generate a voltage.

So, this voltage will drive this server motor servo motor which is connected with a gear. So, very specific movement of the frequency, it will drive this motor to push the hand, the second hand very precisely and this actually is the working principle of the so called quartz watch.

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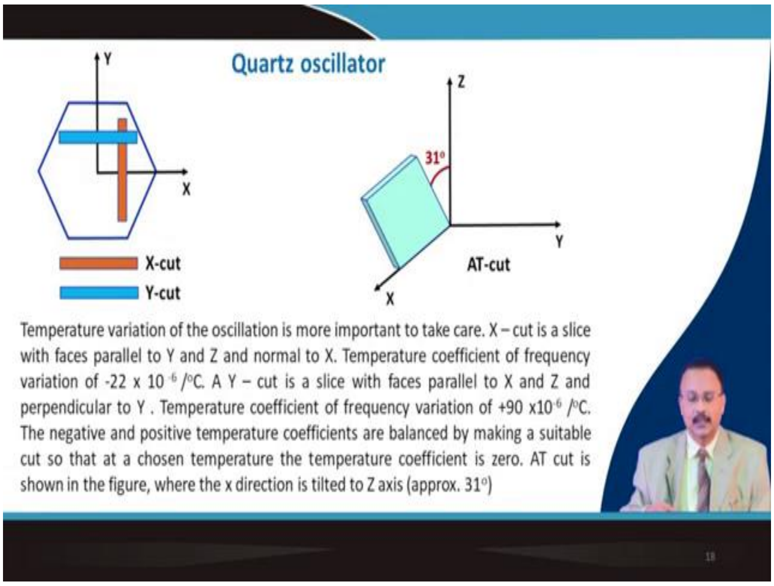

Quartz oscillator

Temperature variation of the oscillation is more important to take care. X – cut is a slice with faces parallel to Y and Z and normal to X. Temperature coefficient of frequency variation of -22×10^{-6} /°C. A Y – cut is a slice with faces parallel to X and Z and perpendicular to Y . Temperature coefficient of frequency variation of $+90 \times 10^{-6}$ /°C. The negative and positive temperature coefficients are balanced by making a suitable cut so that at a chosen temperature the temperature coefficient is zero. AT cut is shown in the figure, where the x direction is tilted to Z axis (approx. 31°)

Now, as I said that this kind of cut is very important because you will have to take care of the thermal expansion coefficient. Thermal expansion coefficient should not change with the temperature. So, therefore, this special cut, we call it is a AT-cut, where this X axis is slightly tilted to the Y axis.

It is a very special cut of that tuning fork which makes the quartz. So, that is usually done to balance this temperature coefficient problem. So, it is having a 0 temperature coefficient. So, your frequency does not change with temperature and therefore, the clock does not the gives a proper exact time irrespective of the temperature change.

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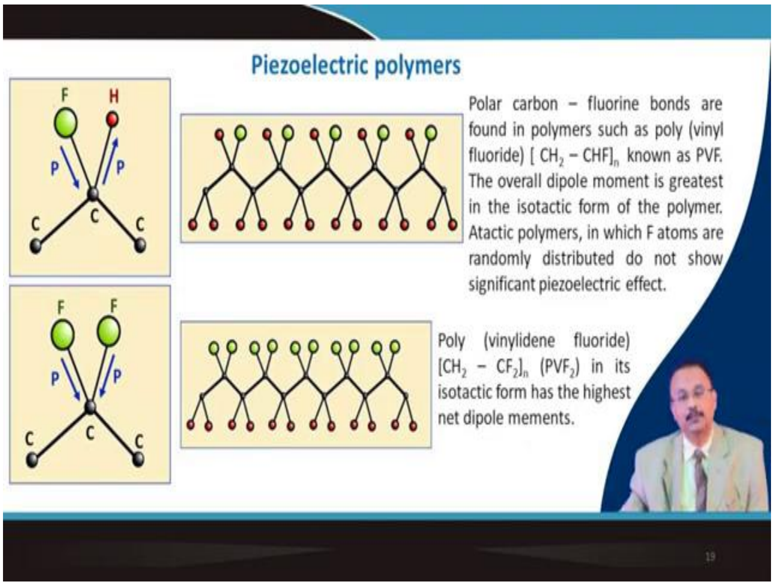

Piezoelectric polymers

Polar carbon – fluorine bonds are found in polymers such as poly (vinyl fluoride) [$CH_2 - CHF]_n$ known as PVF. The overall dipole moment is greatest in the isotactic form of the polymer. Atactic polymers, in which F atoms are randomly distributed do not show significant piezoelectric effect.

Poly (vinylidene fluoride) $[CH_2 - CF_2]_n$ (PVF_2) in its isotactic form has the highest net dipole mements.

In certain polymer also this piezoelectricity is apparent and I have cited the example of polar carbon fluorine kind of bond which is having a intrinsic dipole. So, it depends that how this dipoles are oriented, whether you remember that we talked about isotactic kind of arrangement of the polymer.

So, this kind of arrangement of the dipoles are extremely important for certain polymer to behave like a normal piezoelectric and polyvinylidene fluoride is one of them which is nowadays being used for energy harvesting purpose.

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References

- **Richard J.D. Tilley** Understanding solids, The science of materials 2nd Edition, Wiley, Chapter 11 pp 326 – 340 (Study material)
- **W.D. Kingery, H.K. Bowen, and D.R. Uhlmann,** Introduction to Ceramics, 2nd Edition, John Wiley & Sons Ltd. Chichester Chapter - 18
- **Michael W Bersoum** Fundamental of Ceramics, 2nd Edition, CRC Press

So, this study material for this particular lecture is the is from the book by Tilley, the oxide material and W. D. Kingery and Barsoum is the other two textbook which you can follow.

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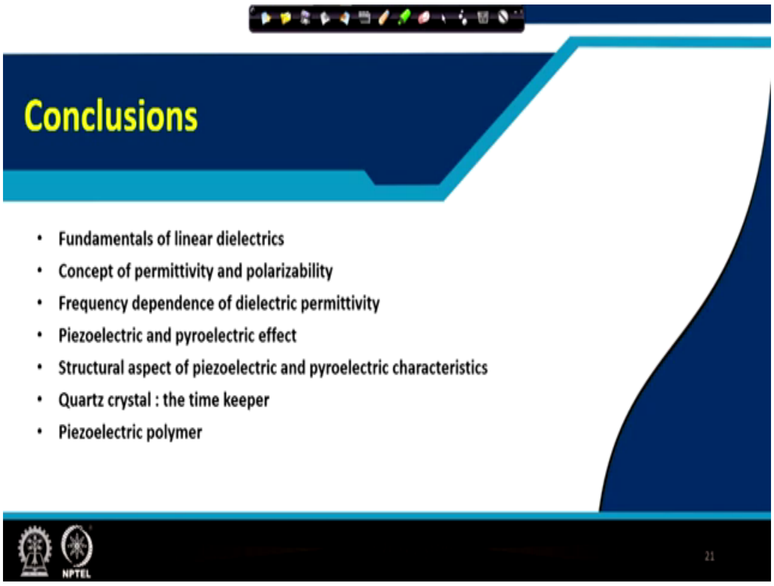

Conclusions

- Fundamentals of linear dielectrics
- Concept of permittivity and polarizability
- Frequency dependence of dielectric permittivity
- Piezoelectric and pyroelectric effect
- Structural aspect of piezoelectric and pyroelectric characteristics
- Quartz crystal : the time keeper
- Piezoelectric polymer

So, in this lecture, I have described the fundamentals of linear dielectrics then concept of permittivity and polarizability is introduced. Frequency dependence of the dielectric permittivity is introduced. The basics of the piezoelectric, and pyroelectric effect is illustrated.

Then, structural aspect of the piezoelectric, pyroelectric and ferroelectric material is identified. Quartz crystal function has been illustrated and finally, we have introduced the piezoelectric behavior in certain polymeric material.

Thank you for your attention.