Fundamental and Applications of Dielectric Ceramics

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Module No # 04
Lecture No # 17
Polarization mechanism

Hey so welcome to this again a new lecture of this course on fundamental and applications of dielectric ceramics. So, we will just let us just briefly recap the previous lecture.

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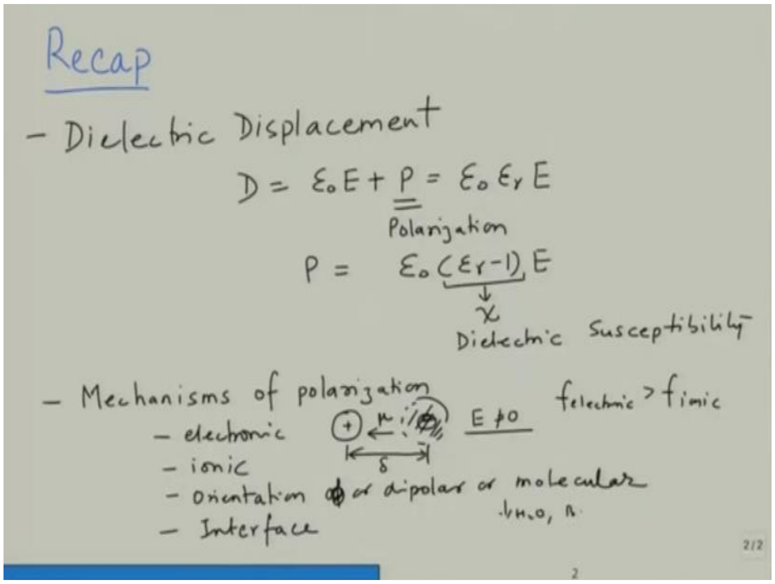

Recap

- Dielectric Displacement

$$D = \varepsilon_0 E + \underline{\underline{P}} = \varepsilon_0 \varepsilon_r E$$

Polarization

$$P = \varepsilon_0 \underbrace{(\varepsilon_r - 1)}_{\downarrow \atop \chi} E$$

Dielectric Susceptibility

- Mechanisms of polarization $f_{electronic} > f_{ionic}$
  - electronic $\underline{E \neq 0}$
  - ionic
  - orientation or dipolar or molecular
  - Interface

H_2O, ...

So, in the previous lecture we talked about dielectric displacement (D) which is basically after even certain electric in a parallel plate capacitor and it becomes this is equal $\varepsilon_0 E + P$ and this is equal to basically $\varepsilon_0 \varepsilon_r E$. So the P is the polarization which is because of insertion of the dielectric and this polarization and then we calculated as

$$P = \varepsilon_0(\varepsilon_r - 1)E$$

and this factor $(\varepsilon_r - 1)$ what is called as chi(χ) or dielectric susceptibility and higher the dielectric constant of the material is higher the dielectric susceptibility and more the material will be polarized.

Now you can see that we have written all this in scalar form but in reality, the polarization in the vector field is a vector dielectric permeability and susceptibility is they are tensors. So, we need to if you write them precisely by taking the direction into account then you need to consider the vector form the tensor form not the scalar but from most practical purposes we generally deal with the scalar form and then we moved on to discuss the mechanisms of polarization.

Because we have just said that polarization because of separation of charges but in a given solid the mechanisms are many fold depending upon the type of material. So, the mechanics which can exist in a material could be electronic then we can have ionic then we said we will have orientational or there are various names to it dipolar or molecular and then we have interface. So we discussed electronic polarization in which we said that as long as you have an atom and you apply electric field to it the positive charge of the atom and the electron cloud which is you know which is sort of smeared electron cloud which are center of mass here they gets separated by a distance δ and the dipole moment create as this μ.

So, this is the electronic polarization but this is only when there is $E \neq 0$ but the moment is equal to 0 the dipolar moment is also goes back to 0 okay. And then we said similar case happens in case of ion suppose you have a positive ion then you have a negative ion such as in ionic solid sodium chloride, potassium chloride, zirconium oxide any oxide dielectric or even non-oxide electrics as long as they contain anions and cations.

Ensemble of anions and cations they get displace with respect to each other and again similar to electronic polarization you have ionic polarization now only difference is in electronic polarization you are talking about charges at smaller mass scale whereas in ionic polarization you are talking about and big ions itself with respect to reach other. So, the mass goes up as a result it occurs at lower frequencies.

So if let us say $f_{electronic}$ will be more than f_{ionic} because of the mass difference of the entity which are involved in polarization and then the third or fourth third is because of orientation or dipolar molecular polarization this generally happens in materials which up where the molecules is permanent dipolar moment such as H_2O and this can also be you know barium titanate or another other molecule which as permanent dipole moment. So, molecule which show permanent dipole moment they show orientation or dipolar or molecular polarization.

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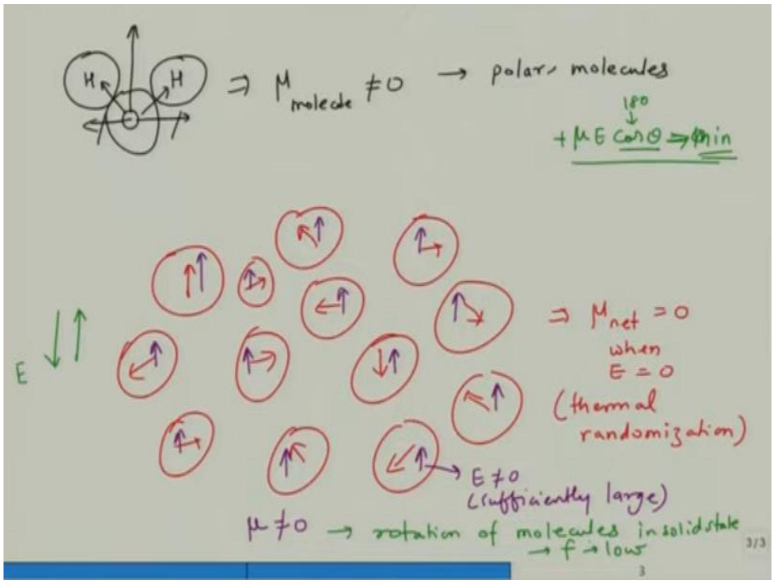

So, as we saw that in case of water molecule after this is a schematic of you have oxygen and you have H, H so you have 1 dipole moment in this direction another is in this direction. So, you have net component these two cancel out each other one component that remains in the vertical direction so as result this has a μ molecule is not equal to 0. So, such molecules in which $\mu \neq 0$ or called as polar molecules okay and they have.

So, If you now represent molecule as a entity then it has a dipole moment but if you have multiple water molecules then you say let us say they are all randomly distributed in the space and one dipole moment could be here and that could be here and this could be here this could be there and so on and hence so forth. So as a result, when you do not apply electric field the μ_{net} is equal to 0 when E = 0 and this is because of thermal randomization.

So, because of thermal randomization okay now when you apply electric field these dipole moments, they start aligning in. So if let us say direction of applied field is this and then they start aligning in this direction because you have the $\mu E cos\theta$ is the potential energy so this goes to this as long as it tends to become equal to 0 it will make them minimizing the energy and the they should co-align with each other they should become parallel to each other.

So, the μ is align that is for the sake of this will basically $-\mu E cos\theta$ sorry it should be minimum not 0 which should reach a minimum. So, when $cos\theta$ is 180 degree then it would be μE so sorry +

$\mu Ecos\theta$ theta I think $cos\theta$ will be 180 as a result this will reach $-\mu E$. So $-\mu E$ will be the minimum energy when they are perfectly anti-parallel to each other and this is where some people also tend to show it in this way that it be $-\mu Ecos\theta$ and they show μ and E parallel to each other which is not correct but this is a way some people write it but.

Basically, E points to positive and negative but μ points from negative to positive as a result you have to take the $-\mu E$ positive. So now when you apply electric field what might happens is so they tend to point in this direction at sufficiently large field they all become aligned in this direction and I am just drawing the ideal picture. So, this is the picture when E is not equal to 0 sufficiently large okay.

So, which means now μ is not equal to 0 so this is called dipole dipolar but here you can see there is problem that is not just displacement of molecule unlike in electronic and ionic here you have to rotate the molecule basically it is a rotation of molecule right. So, rotation of molecule basically takes place from one state to another so this involves rotation of molecules and rotation of molecules happen in generally we are dealing with dielectric and solid state the rotation has to happen within the solid state.

As a result, the molecule itself is heavier then it has to rotate as a function of applied field as strength in the solid itself. So, this causes so you can say in solid state typically this causes the frequency to be low basically time scales are larger and that is why this phenomena is at even lower frequencies.

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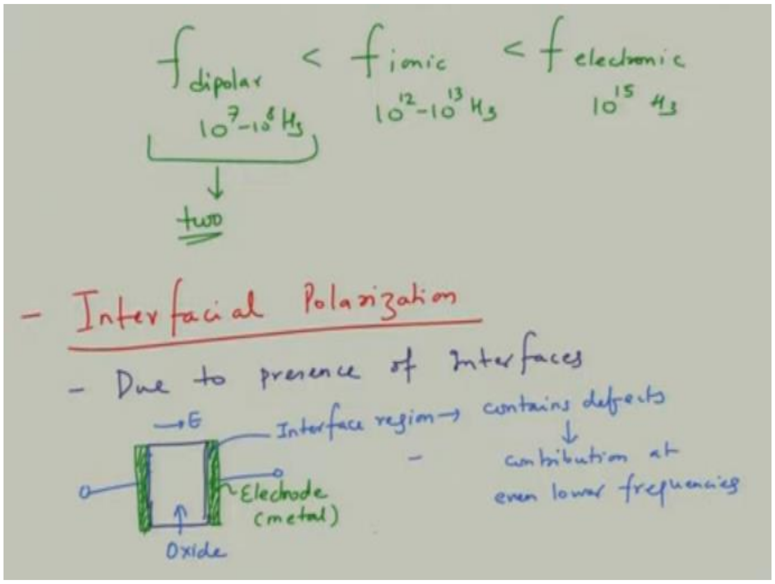

$f_{dipolar} < f_{ionic} < f_{electronic}$

$10^7 - 10^8$ Hz $10^{12} - 10^{13}$ Hz 10^{15} Hz

$\downarrow$ two

- Interfacial Polarization

- Due to presence of Interfaces

Interface regim → contains defects ↓ contribution at even lower frequencies

So you can say

$$f_{dipolar}(10^7 - 10^8\ Hz) < f_{ionic}(10^{12} - 10^{13}\ Hz) < f_{electronic}\ (10^{15}\ Hz)$$

and we will look at the magnitude they will depend upon system to system but generally this will happen at the frequency of 10^{15} Hz, this will happen up to 10^{12}-10^{13} Hz this will happen about 10^7 or 10^8 Hz depending upon mass of the mass of molecules like that.

So, these are the general trends I mean you might have molecular polarization also shows sometimes 2 types of orientation so as a result you have might 2 signatures. So, there is a low frequency contribution there is a high frequency contribution in some system you may observe that. So, we will see that in the frequency dependence and the 4th mechanism that is there is called as so interfacial polarization.

Interfacial polarization will occur as long as you have due to presence of interfaces so as I said molecular polarization is present in polar solids which are permanent dipole moments interfacial polarization will happen as long as you have interfaces and what kind of interfaces you may have in the material you have in interface for example you have a dielectric material like this. This is dielectric material when you make measurement the material has to have a electrode right. So, this is the electrode and this is generally a metal and here we have oxide.

So, because of differences in chemical and physical nature of oxides in metal because of differences in lattice parameter because of difference in coefficient thermal expansion the interface is far from being perfect. So, this is the interface region and this interface region contains defects and these defects basically these defects contributes to what we call as interfacial polarization and this generally happens at even lower frequency scale.

So, contribute to so basically you will have charge defects so presence of positive and negative charge defects and you apply electric field you get separation of them and that separation leads to so you might have some charge density here plus minus I do now know what kind of there could be some charges here and you apply a electric field let us say this direction you will have separation created between them and they will give the raise to interfacial polarization.

This generally happens to contribution at even lower frequencies not only you can have these electrode interfaces these are the most obvious one you might also have so this is because of electrodes.

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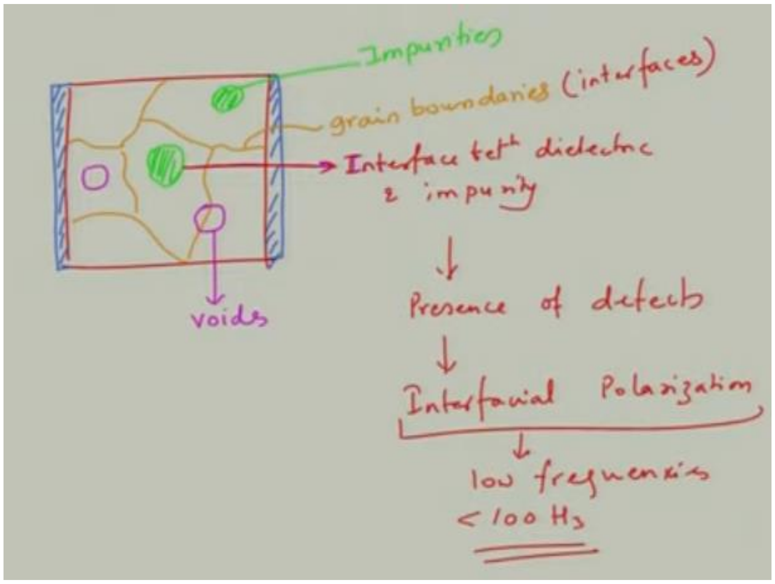

But let us say we have a dielectric solid like these and the electrode here these dielectric solids may have they may have grain boundaries they are also interfaces right? So these are grain boundaries right so you may have impurities these are impurities they may have voids so you may have voids these are all of these forms some sort of interfaces right so they will make so here this will be sort of cavity this is an interface again, interface between dielectric and impurity and then you will have these grain boundaries which are also.

All of these interfaces produce interfacial polarization because of defects at the interface interfaces are generally defective unless you have coherent interfaces with no defects at all you will have a defects could be lose bounds defects could be presence of vacancies it could be charge defects and so on and hence so forth. So, because of presence of defects of various kinds interface are generally defective and as a result so they will have presence of defects and because of defects you will have interfacial and by defects, I mean charge defects okay.

And this generally happens at low frequencies but the frequencies may vary depending upon the type of defect and what is the time scale of mass of the entity involved in so on and hence so forth generally this happens below 100 Hz so generally at lower frequencies like 0.01 Hz, 0.1 Hz and so on and hence so forth, So these are the 4 mechanisms of polarizations that we see in all materials.

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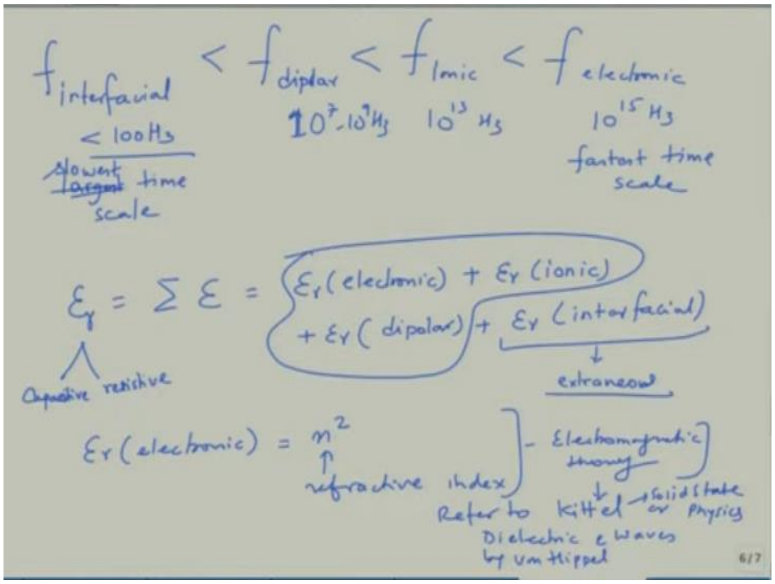

$f_{interfacial} < f_{dipolar} < f_{Ionic} < f_{electronic}$

$< 100\,Hz$ | 10^7-$10^9\,Hz$ | $10^{13}\,Hz$ | $10^{15}\,Hz$

Slowest ~~Largest~~ time scale

fastest time scale

$\varepsilon_r = \sum \varepsilon = \varepsilon_r(electronic) + \varepsilon_r(ionic) + \varepsilon_r(dipolar) + \varepsilon_r(interfacial)$

Capacitive

resistive

extraneous

$\varepsilon_r(electronic) = n^2$

refractive index

Electromagnetic theory

Refer to Kittel → Solid State Physics

or

Dielectric & Waves by von Hippel

So so now if you summarize this you have

$$f_{interfacial}(< 100\ Hz) < f_{dipolar}(10^7 - 10^9\ Hz) < f_{ionic}(10^{13}\ Hz) < f_{electronic}\ (10^{15}\ Hz)$$

we will see the length scale at time scale but generally this is 10^{15} Hz, this will be 10^{13} Hz this will be 10^7 or 10^9 Hz something like that this will be less than 100 Hz generally in the order of few milli hertz and point few hertz so on and hence so forth.

So, this is general scale so basically you can say that time is scales basically so this is the longest largest time scale and this is the fastest time scale we can say slowest okay. So this is how it will be now it also depends upon the type of materials that you will have so as result the dielectric constant that we measure it depends upon some of these contributions

$$\varepsilon_r = \sum \varepsilon = \varepsilon_r(electronic) + \varepsilon_r(ionic) + \varepsilon_r(dipolar) + \varepsilon_r(interfacial)$$

So we can see that while these three may be true contributions from the material this (interfacial) is something which is little extraneous and that is why we need to be little careful about it interfacial polarization and we make when we make dielectric constant measurements often we include interfacial component in the dielectric constant measurement and that is what Gibbs raise to overestimated values of dielectric constant as people report in the literature.

So one needs to be very careful and this requires one to make frequency dependence maybe dependent measurement do a detailed impedance spectroscopy to separate out various quantity and on top of that as we will say later on dielectric constant also is effected by the capacitive and resistive components because we basically we are making current measurements and those currents maybe as we will see later on they could have capacitive component resistant component which are again complicates the.

So now when we talk about the contributions this ε_r electronic is basically it is a fundamental mechanics which is present in every material whether it a gas whether it is a solid whether it is a liquid as long as you have atom you will have a electronic mechanism and so as a result we will not go into details but if you want to get in to details you can get you can look at the book by electrics and waves by von Happel or various of books by Kittel in fact you can look at the Kittel.

So ε_r electronic is equal to n^2 there is a mathematical treatment to do that we unfortunately do not have time to do that but so this is this basically scales at ε_r is equal to n^2.

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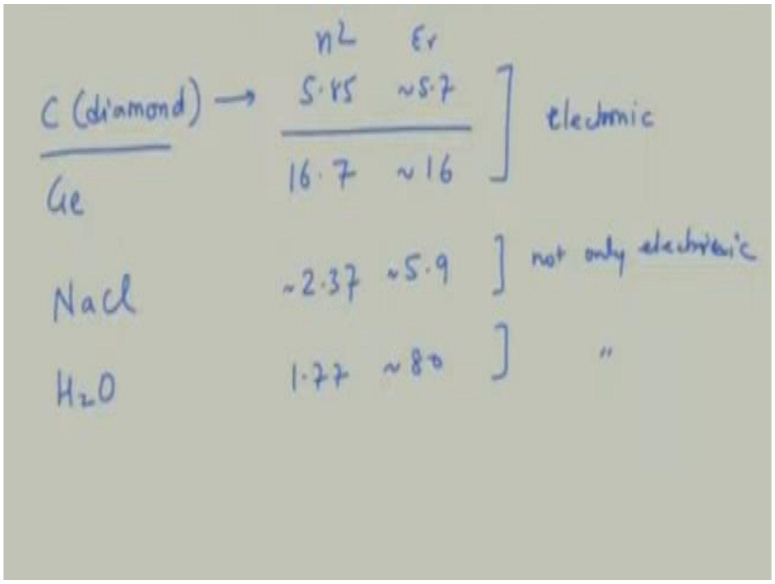

	n^2	ε_r	
C (diamond) →	5.85	~5.7	electronic
Ge	16.7	~16	
NaCl	~2.37	~5.9	not only electronic
H_2O	1.77	~80	"

So, for most materials let us see for something like diamond let us say this is basically so your n^2 square value of diamond is 5.85 the *n* is nothing but refractive because optical and electronic phenomena's are closely associated this is because of electrons as a result electronic mechanism is scales with n square and epsilon that you measure is approximately 5.7. So, the values are similar but on the other hand similarly if you do for the germanium for example germanium shows a value of n^2 square for about 16.7 and ε_r value is about 16.

So these 2 match closely well suggesting that you have electronics polarization however if you match for example for a NaCl shows you n square value of 2.37 but the measured value of electric constant is a approximately 5.9 which means it is not only electronic something else is there because the value is twice more than twice that off electronic. And if you measure for water for example H_2O molecules the dielectric constant for water is 1.7 and measured value is closed to 80. Again, this is electronic so something else right.

So, when you measure this dielectric constant that is where the frequency depends in dependence in dielectric constant is. So, this basically you can determine from electro-magnetic theory and I would say either you would say either Kittel or dielectric and waves okay aright Kittel solid state physics those who do not know the name and dielectric and waves by von Hippel.

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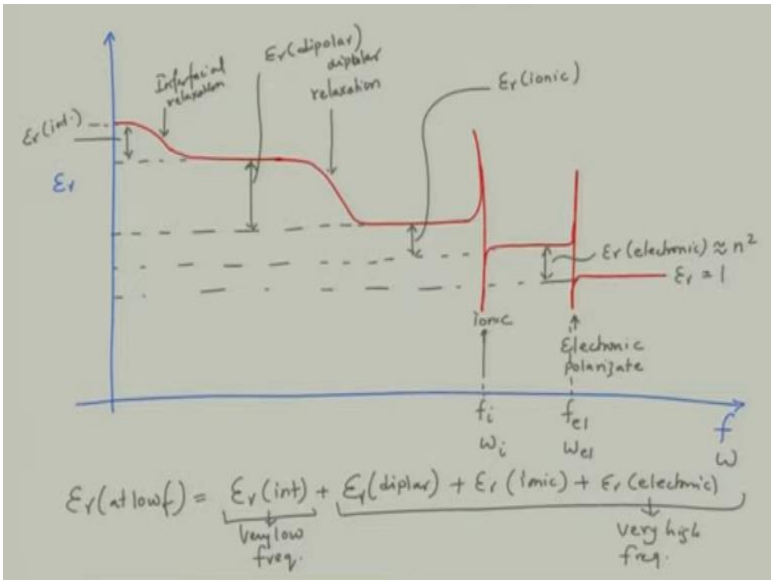

So, now in order to distinguish these contributions when we measure the dielectric constant we measure it as a function of frequency okay and what we see is quite interesting plot we see a plot of something like this is actually resonance peak okay so this is what this approximately let us say so this is we have various plateaus here we can mark this plateaus okay these are different plateaus.

So, at very high frequency we will have a contribution which is $\varepsilon_r(electronic)$ right in fact sorry when the electrons do not respond what will be when the electrons do not respond an ε_r when the material does not respond to frequency at all then it will be equal to $\varepsilon_r = 1$ it is as if you are in the free space. When electronic so this is a resonance that occurs when the frequency of the applied field matches with the frequency that is required for di-electronic dipoles to respond then you have at the onset of we call it onset of electronic polarization and this frequency will be f_e okay.

So, there is a resonance that happens and this difference will be $\varepsilon_r(electronic)$ and what is difference is equal to n^2 okay. So as long as you are in these two frequencies ranges the material will show only electronic contribution the moment go to little lower frequencies then ionic resonance occurs and this frequency is f_i let us say okay. If you write it as omega (ω) this will be ω_e or l ω_i okay and this plateau is now $\varepsilon_r(ionic)$ and this is not resonance this is basically what we call as a relaxation.

So we will get into details of what is relaxation is what resonance is but then you enter into the regime of what we call as dipolar so this is $\varepsilon_r(dipolar)$ or orientation or molecular and then we reached the region of interface interfacial relaxation here it could be dipolar relaxation and then this contribution will be ε_r interface. So basically, at lower frequency is ε_r at low f will be equal to $\varepsilon_r(interfacial) + \varepsilon_r(dipolar) + \varepsilon_r(ionic) + \varepsilon_r(electronic)$ on top of 1 okay.

So, this is what basically dielectric constant will be this will be at very high frequency and this will be at very low frequency. So, when you want to measure that dielectric constant depending upon the type of material you have to choose your frequencies quite wisely. So, for example you have a material where you have lot of interfacial contributions you may want to avoid that you want to make that measurement completely but you may want to subtract that from total because these three are intrinsic in nature this is not intrinsic in nature this comes from defects and interfaces in variety of other things okay.

So, this will vary depending upon how you prepare the material how you what kind of electrodes you put on it and under what conditions you measure so this will be variable where other three are fundamental contributions because of nature of the material itself okay. So that is why you see for a something like germanium (Ge) does not have ions so for Ge this will not be there is no molecule in Ge you still might have some interfacial contribution depending upon what kinds of electrodes you put on germanium to measure.

But Ge only contribution that will come from material will be $\varepsilon_r(electronic)$of you look at MgO for example magnesium oxide. Magnesium oxide, aluminum oxide or they contain ions they will have not only electronic contribution but also ionic contribution but these are if these are centro-symmetric molecules they do not have a permanent dipole moment which mean they will have only these 2-contribution ionic and electronic.

On the other hand if you have a molecule like ahh you know H_2O or you now barium titanate or lead titanate or zinc oxide non-centro symmetric zinc oxide which are piezoelectric, ferroelectric in nature for electric in nature they will not only in electronic because they have an atoms they have ionic because they will have ions of 2 types or 3 types they will have dipolar because they will have permanent dipole moment which is randomly orientated in the beginning but when you apply electric field of certain frequency it aligns itself in that direction.

And then interfacial is dependent upon the defects and interfaces in the materials okay so this is how basically that dielectric constant of different materials will be manifested.

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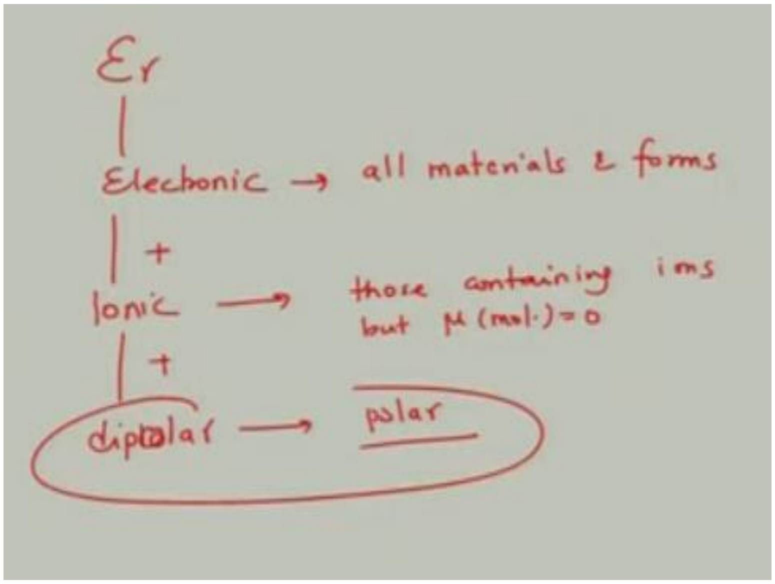

So, you have 4 components you have epsilon r intrinsic components are electronic ionic and dipolar. So electronic will be in all materials and forms as long as you atom ionic will be those containing ions but µ (molecule)is equal to 0 non polar materials. And dipolar will be for any polar material which has dipolar moment will show dipole it adds so on. So electronic plus ionic plus dipolar.

So, dipolar material will have all the 3 contributions ionic material will have only electronic and ionic contribution electronic material will have only electronic contribution. So, this is the basically summary of mechanism of dielectric polarization that we have next we will deal with another quantity called as electric polarizability whose analytic treatment will do thank you.