Fundamental and Applications of Dielectric Ceramics
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Module No # 04
Lecture No # 18
Dielectric Polarizability

So welcome again to the new lecture of the course fundamental and applications of dielectric ceramics.

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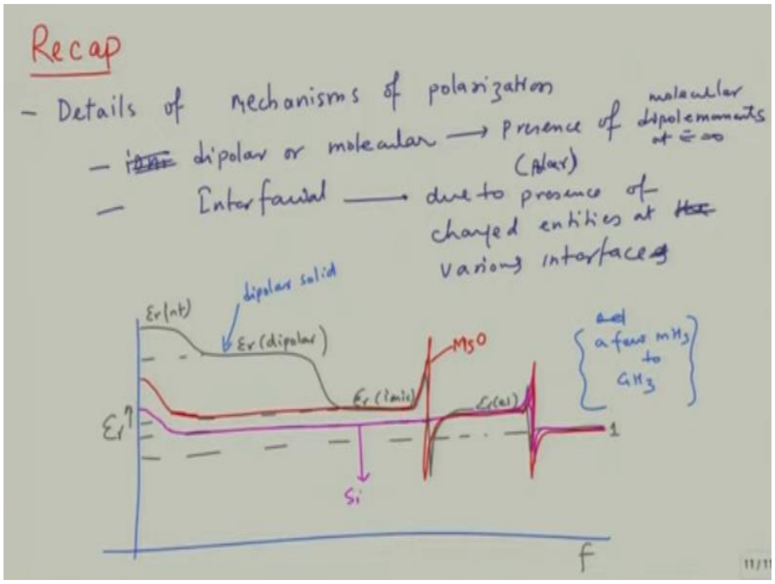

Recap

- Details of mechanisms of polarization
  - dipolar or molecular → presence of molecular dipole moments at $E=0$ (Polar)
  - Interfacial → due to presence of charged entities at ~~the~~ various interfaces

So we will briefly look at what we did in the last lecture so in the last lecture we learnt about details of mechanism of we looked at details of ironic polarization sorry ionic we looked at in the previous lecture but in the last lecture we looked at dipolar polarization or molecular and then we looked at interfacial. This happens because of presence of dipole moments at $E=0$ molecular dipole moments let us say.

So, this is basically talk in polar materials right and then we have interfacial due to presence of charged entities or defects at various interfaces right. Now because of masses of entities involved and they are frequency dependent so some are sluggish some are faster and as a result they have a very large frequency dependence as we saw in a last lecture that our dielectric constant variable something like this so sort of rough plot okay.

So here we have one this is epsilon r electronic this is epsilon r ironic this is $\varepsilon_r(dipolar)$ and this is $\varepsilon_r(interfacial)$.

$$\varepsilon_r(interfacial) + \varepsilon_r(dipolar) + \varepsilon_r(ionic) + \varepsilon_r(electronic)$$

So, these are the contributions that you get from different regimes okay and this is frequency this is so. So this what we should get ideally for every material if you have only gases you will see this part so if you wanted to draw only for gas you will have only this or a monoatomic solid you will have you may have some sorry for a let me have the different color for a monoatomic solid you may have something like these you may have some interfacial polarization depending upon the type of interfaces that you have but basically you will have this is the curve that you get for something like let us say silicon okay.

If you wanted to have something like NaCl or MgO you may have something like this but the values may change depending upon the type of the system because the masses of atomic masses of that different in so on and hence so forth but approximately you will get something like this for let us say MgO and Mg is you know atomic mass of Mg is different than silicon as a result there will be some changes in the values with respect to but let us ignore that right now.

For something like water that is what you will get this is for basically a dipolar solid okay. So these are the sort of curve that you likely to obtain but in reality you will dielectric measurement are generally made at frequencies from you know point 1, a few milli hertz(Hz) to few giga Hz let us say and they show various kinds of behaviors because of contribution from other factors as a result the curves are often deviate from ideal curves and as a result there is a whole new area of dielectric analysis whole area search of electric analysis and impedance spectroscopy which one needs to conduct in details.

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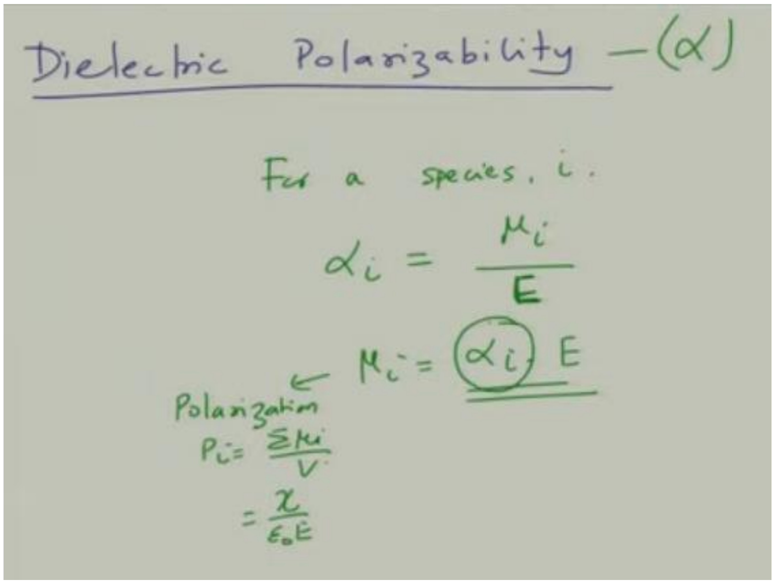

Dielectric Polarizability — (α)

For a species, i.

$$\alpha_i = \frac{\mu_i}{E}$$

$$\leftarrow \mu_i = \boxed{\alpha_i}\, E$$

Polarization

$$P_i = \frac{\Sigma \mu_i}{V}$$

$$= \frac{\chi}{\varepsilon_0 E}$$

Anyway, so now another quantity that we introduce here is called as dielectric polarizability basically dielectric polarizability is ability of dielectric material to polarized okay. So higher the electric polarizability more the dipole moment is going to be. So that electric polarizability of an of its species so dielectric polarizability is defined as sorry it called as α so for a species i defined α_i and this is equal to μ_i/E.

Now, this E is often taken as local electric field or microscopic electric field but let us not worry about that is different treatment altogether let us just worry about the macroscopic field so basically $\alpha = \mu/E$. So this is called as dielectric polarizability so it defines the and it is also essentially you can say as the when alpha is higher so you can say that $\mu_i = \alpha_i \cdot E$ okay and μ is related to polarization because polarization $P_i = \frac{\sum \mu_i}{V}$ and $P_i = \frac{\chi}{\varepsilon_0 E}$.

So basically, what we are saying is that higher the polarizability of the system is more the polarization of the system will be which is because of higher dielectric constant of the material that is there. So, let us so polarizability is a quantity that can be analytically defined using the simple treatments so that is why we will do analysis of polarizability of different classes of materials.

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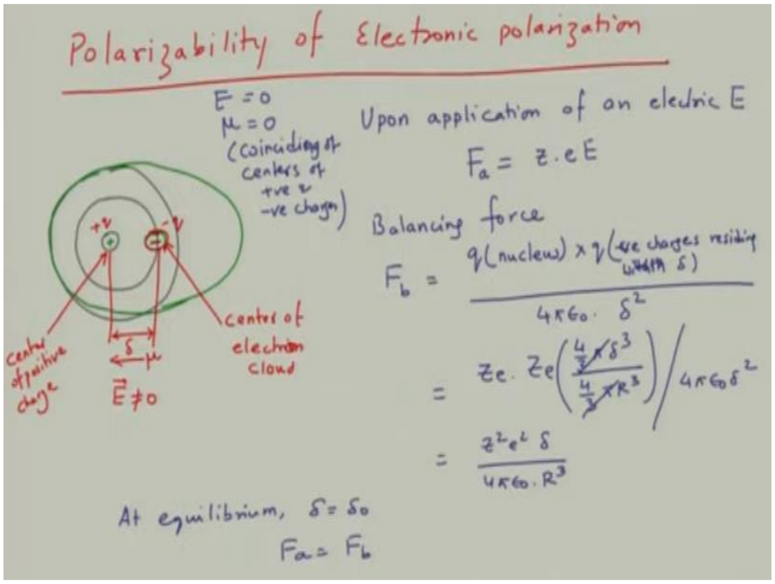
Polarizability of Electronic polarization

$E = 0$
$\mu = 0$
(coinciding of centers of +ve & -ve charges)

Upon application of an electric E

$$F_a = z \cdot eE$$

Balancing force

$$F_b = \frac{q(\text{nucleus}) \times q(\text{-ve charges residing within } \delta)}{4\pi\epsilon_0 \cdot \delta^2}$$

$$= Ze \cdot Ze\left(\frac{\cancel{\frac{4}{3}\pi}\,\delta^3}{\cancel{\frac{4}{3}\pi}\,R^3}\right) \Big/ 4\pi\epsilon_0\delta^2$$

$$= \frac{z^2e^2\delta}{4\pi\epsilon_0 \cdot R^3}$$

At equilibrium, $\delta = \delta_0$

$F_a = F_b$

So, let us say first a treatment of polarizability of electronic polarization okay. So let us say we will see what kind of parameter does it depend upon so let us first bring a let us make a simple picture so we will we have a nucleus which is of some charge and then center of the nucleus charge let us say so these are variety of orbitals and let us say we apply a electric field so that this positive charge and negative so this is the sort of electron cloud this gets shifted little bit in this direction and as a result the center of this charge is now.

So, this is your can say center of electron cloud and this is center of positive charge this is basically nucleus right. So this is +q and this is –q so when electric field is not equal to 0 then we separate these two by a delta (δ) and you have a corresponding dipole moment right there is a dipole moment this created between the two entities. So, upon application of electric field E so obviously when E is 0 the μ is also 0 right because the centers of charges coincide okay because of coincidence of coinciding of centers of positive and negative charges.

However, when we apply electric field E on the charges so let say this when you charge about is when you will create a force. This force $F_a = z \cdot eE$ okay so as a result you will have forces on the two charges you will separate them by a distance let us say δ *or* d whatever you may call it but this force that you apply by applying electric pole there is a coulomb force of attraction as well because they have to be held together it is not that you cannot you can rib them apart you cannot, there is a coulombic force of attraction.

So, this force is balanced by what we call as so balancing forces is then so this is the applied upon application of a pole this is F_a this is an applied force. The balancing force let us say we write as F_b balance force is because of coulombic attraction between the positive and negative charges and what will that be? That will be

$$F_b = \frac{q(nucleus) \times q(charges\ residing\ within\ \delta)}{4\pi\varepsilon_0 \cdot \delta^2}$$

and what will this be?

This will be basically let us say if this is Ze okay this will be since we are taking, we can take the ratio of again this will be total charges Ze. But we are taking how much it has been because it depends upon the extent of force right so depending upon the size of that bigger sphere let us say or small is sphere so it will be $4/3\pi\delta^3$ divided by $4/3\pi R^3$ is the complete radius of the whole electron cloud but δ is basically the distance that we have created by separation.

So, the moment they are equal both the forces will be equal so this is basically you can say is equal to $Z^2e^2\delta$ sorry and this is divided by $4\pi\varepsilon_0\delta^2$. So, if you do the maths you will have Z^2e^2 4/3π this will cancel each other you will have δ divided by $4\pi\varepsilon_0 \cdot R^3$ this is the expression that we will get.

$$F_b = \frac{Z^2e^2\delta}{4\pi\varepsilon_0 \cdot R^3}$$

So, let us say there is a equilibrium separation so at equilibrium $\delta = \delta_0$ okay so when we do that and equilibrium delta is equal to delta naught and $F_a = F_b$ right.

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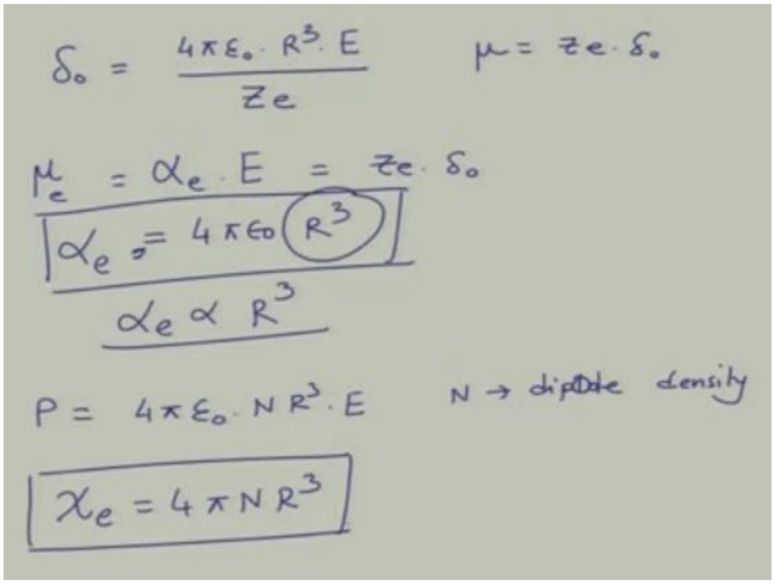

$$\delta_o = \frac{4\pi\varepsilon_o \cdot R^3 \cdot E}{Ze} \qquad \mu = Ze \cdot \delta_o$$

$$\mu_e = \alpha_e \cdot E = Ze \cdot \delta_o$$

$$\boxed{\alpha_e = 4\pi\varepsilon_0 R^3}$$

$$\alpha_e \propto R^3$$

$$P = 4\pi\varepsilon_o \cdot N R^3 \cdot E \qquad N \rightarrow \text{dipole density}$$

$$\boxed{\chi_e = 4\pi N R^3}$$

So, when we do that together applied forces equal to balancing force by balancing the two forces, we can find out we can determine

$$\delta_0 = \frac{4\pi\varepsilon_0 \cdot R^3 \cdot E}{Ze}$$

So, we can calculate now the dipole moment is equal to basically we said it is equal to basically

$$\mu_e = \alpha_e \cdot E = Ze \cdot \delta_0$$

So now when you balance it you will get,

$$\alpha_e = 4\pi\varepsilon_0 \cdot R^3$$

what it tells you is that for a given atom the atomic polarizability depends only on the radius of atom.

So $\alpha_e \propto R^3$ this is the constant, this is the constant only R is the variable.

So bigger the atom is more polarizable atom is which make sense because for smaller atom electron cloud is closer with respect to nucleus whereas for the bigger atoms the coulombic force of balancing coulombic forces is smaller as a result they are polarizable the electrons can shift or can get polarized to longer distances as compared to easily as compared to for a smaller atoms and correspondingly if you say the dipole density was N then

$$P = 4\pi\varepsilon_0 \cdot NR^3 \cdot E$$

if N is equal to dipolar dipole density which is number of dipoles per unit volume okay.

So basically, we are saying so we can get from this we can get so $\alpha_e = 4\pi\varepsilon_0 \cdot R^3$ we can also determine $\chi_e = 4\pi N \cdot R^3$. So, bigger the atom is higher the polarizability of an atom is so this is the take home message from this.

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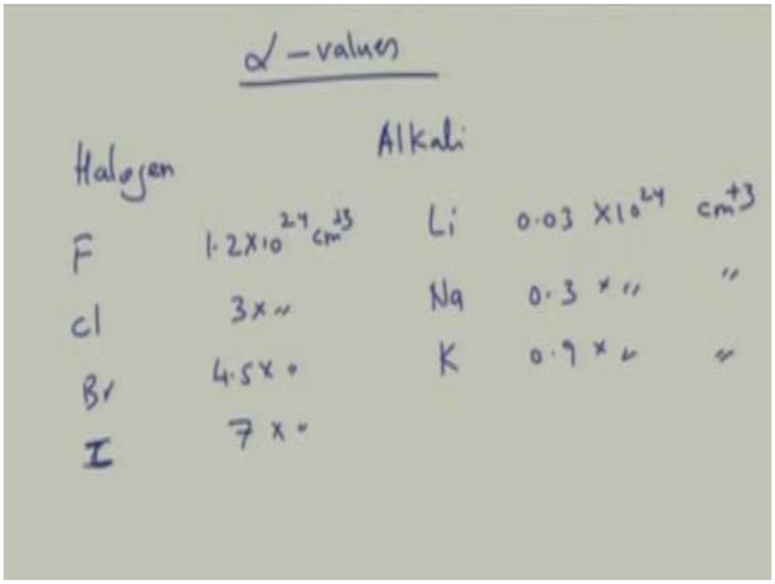

α – values

Halogen		Alkali		
F	$1{\cdot}2\times10^{24}\ cm^{+3}$	Li	$0{\cdot}03\times10^{24}$	cm^{+3}
cl	3× "	Na	0·3 × "	"
Br	4·5× "	K	0·9 × "	"
I	7× "			

And then we can now see the few values for example if you look at Halogens you look at Alkali metals so for Halogen, fluorine 1.2 $*10^{24}$ centimeter cube chlorine is 3 into similar value Bromine is 4.5 into and sorry iodine is 7 into similar one we can see that it goes as size of the atom fluorine is the smallest atom chlorine iodine is the biggest atom and it scales with similarly for Alkaline metals if you go from Lithium to let us say sodium to potassium Lithium as value of $0.03*10^{24}$ same unit.

And then 0.3 and then 0.9 okay polarizability alpha sorry alpha is per centimeter cube 4 pi epsilon naught centimeter cube okay alright. So now let us move to the analytical treatment of ionic polarizabilities.

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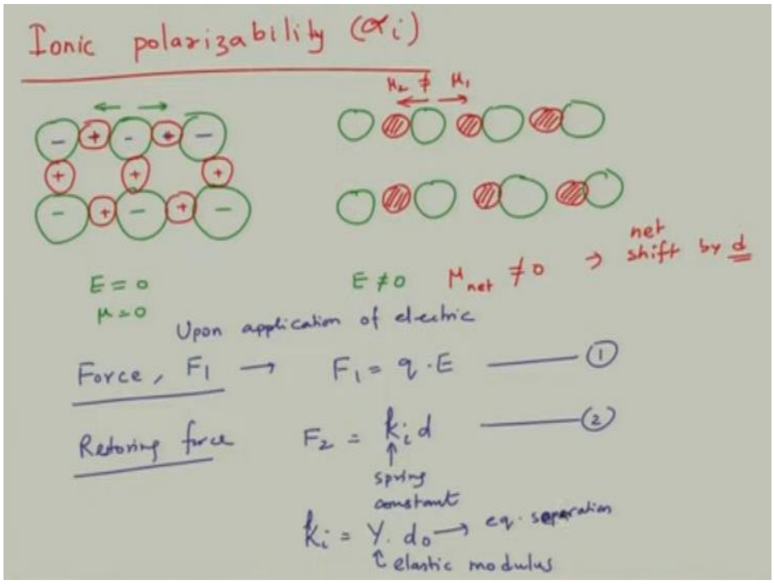

Ionic polarizability (α_i)

$E = 0$

$\mu = 0$

$E \neq 0$ $\mu_{net} \neq 0$ → net shift by $\underline{\underline{d}}$

Upon application of electric

Force, F_1 → $F_1 = q \cdot E$ —— ①

Restoring force $F_2 = k_i d$ —— ②

↑ spring constant

$k_i = Y \cdot d_0 \rightarrow$ eq. separation

↑ elastic modulus

Now in case of ionic polarizabilities we are also have slightly different picture. So the first picture is that when we have these in ensemble of atoms so let us say and in between we have these smaller atoms sitting okay and so if you look at value of μ so this is let us say negative this is positive this is negative this is positive negative and in between we will have these ions negative.

So, this will be essentially positive this is positive, this is positive, positive and then we have negative, negative, negative. So, the dipole moments essentially will cancel out you will have 1 in this direction another in this direction so when $E = 0$ then $\mu = 0$ okay. Now you change the picture little bit so you let us say is not equal to 0 if $E \neq 0$ that means you will polarize some parts more with respect to another so there is a possibility you might create the scenario something like that.

So, what will happen is that this red ion will shift more towards let us say this green ion as a result you can see that this is you know red is positive essentially there is a dipole moment in this direction the dipole moment in this direction. So, μ_1 and μ_2 they are not equal to each other okay because of separation differences. As a result, you can say the $\mu \neq 0$ so this is what we will create so we are like equilibrium separation and then we have a chain separation.

So, it decreases so the basically you can say the distance between the ions increases by an amount delta in one direction and decreases by the same amount δ in another direction okay. So as a result, you have this difference of δD the D difference that is called the $\delta\mu$ difference that will come and that too. So, we need to calculate this we can say accordingly you have a shift net shift by some value *D* okay. So, we need to calculate this so let us say the force F_1 which increases the distance between two ions is basically.

So when apply electric field so you create a force F_1 so upon application of electric field we separate these irons as a result you will have $F_1 = q*E$ so this is the force that is caused which causes the separation but as at the same time the if imagine that these ions are connectivity to each other by spring right there will be storing force so the storing force will be F_2 this will be equal to

$$F_2 = k_i d$$

where k is the spring constant and d is the distance.

So let us say *i* represent this as k_i okay this is the second equation that we have so this is basically assuming that at ions are connecting each other just like springs so just like their harmonic oscillators this kind of model and this spring constant can be represented in terms of so this small k_i can be represented in terms of elastic modulus this is given by $K_i = Y \cdot d_0$,this Y is elastic modulus and d_0 is the equilibrium separation okay.

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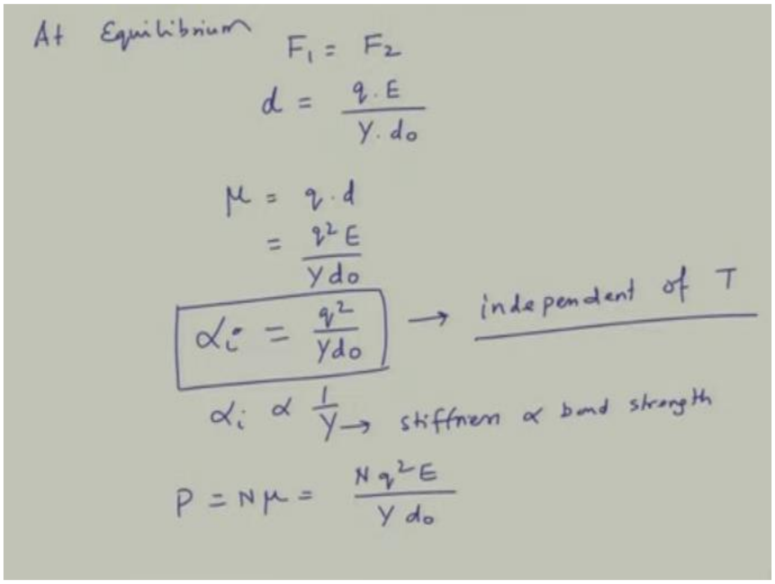

At Equilibrium $F_1 = F_2$

$$d = \frac{q.E}{Y.d_o}$$

$$\mu = q.d = \frac{q^2 E}{Y d_o}$$

$$\boxed{\alpha_i = \frac{q^2}{Y d_o}} \rightarrow \text{independent of } T$$

$$\alpha_i \propto \frac{1}{Y} \rightarrow \text{stiffness} \propto \text{bond strength}$$

$$P = N\mu = \frac{N q^2 E}{Y d_o}$$

So now seems to straight forward now so at equilibrium what will happen at equilibrium these two forces have $F_1 = F_2$ will balance each other and you combines these equations what we will get d will be equal

$$d = \frac{q \cdot E}{Y \cdot d_0}$$

$$\mu = q \cdot d$$

$$\mu = \frac{q^2 \cdot E}{Y \cdot d_0}$$

so what is

$$\alpha_i = \frac{q^2}{Y \cdot d_0}$$

this is equal to this is what is α_i= ironic polarizability what is it depend upon it depends upon what is the equilibrium separation and what is the elastic modulus which means more stiff the bond is or in some sense more stronger the bond is more difficult it is to polarize it and that makes sense right stronger the bond is.

So basically, you can see that

$$\alpha_i \propto \frac{1}{Y}$$

which is stiffness which is proportional to bond strength. So, something which as more melting point it will be difficult to polarize something which are lower melting point it will be easy to polarize and accordingly you can also calculate the polarization. Polarization will be equal

$$P = N\mu = \frac{Nq^2E}{Yd_0}$$

one thing that you might note here is there is no temperature dependence here it is independent of temperature.

So this α_i is independent of temperature similarly in the previous case we saw this is also independent of I mean you might have some changes in R that is happening with respect to but there is no strong dependence upon temperature except that the size will change as the function of temperature. So, there is no temperature terms as such okay so this is basically a very rough guide to calculation of ionic and electronic polarizabilities.

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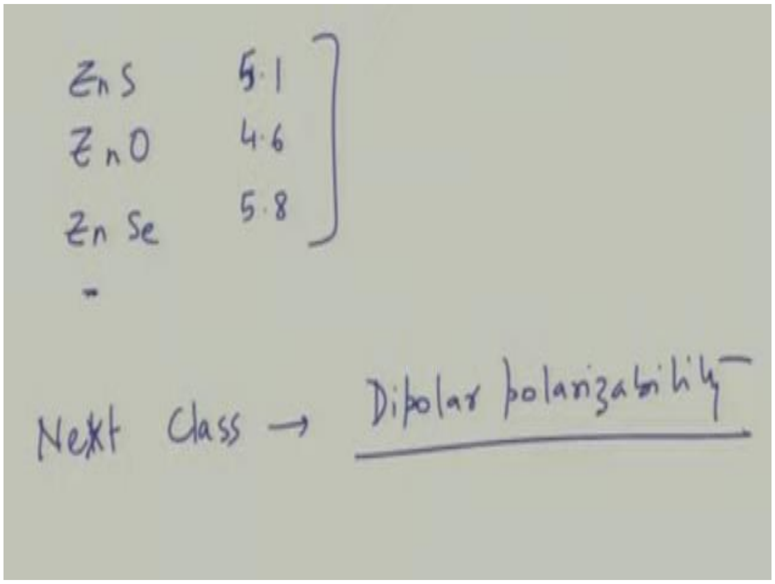

ZnS	5.1
ZnO	4.6
ZnSe	5.8

Next Class → Dipolar polarizability

So if you consider now for these if you compare the value of different materials for instance you take for ZnO, ZnSe let say and so ZnO, ZnS, ZnO as a value of dielectric constant of ZnS is 5.1, ZnO is 4.6, ZnSe is 5.8 and these differences are basically because of changes in the bonding characteristics and these materials. So basically, stronger the material is higher the electric constant will be for a given material sorry stronger the material lower the dielectric constant because this smaller the polarizability it will be.

So, we can say strong bonds meaning lower ionic polarizability bigger atoms are easy to polarize electronic polarizability stronger materials are difficult to polarize that is ionic polarizability in case of ionic polar ability. So, these are the two treatments that we have done in the next class we will look at the treatment of dipolar polarizability which is an interesting case to look at okay thank you very much.