Fundamentals and Applications of Dielectric Ceramics
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Module No # 08
Lecture No # 36
Domain Walls in Ferroelectric Materials

Welcome again to the new lecture of the course fundamentals and application of electric ceramics just let us just briefly recaps the precious lecture.

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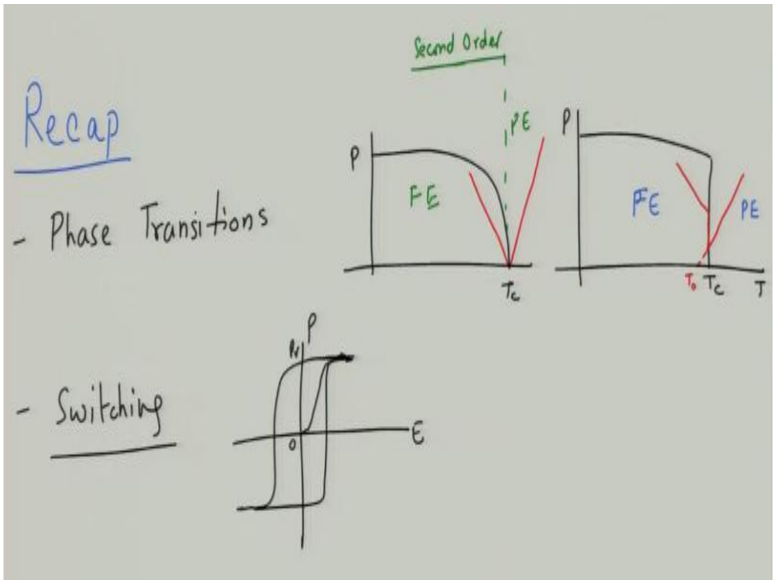

So in the previous lecture we finished our discussion on phase transitions and ferroelectric materials. So basically the message for that is that the in the second order phase transition the polarization drops gradually until T_c and susceptibility shows a $1/\chi$ shows a decreasing behavior as it approaches from paraelectric to ferroelectric region. So this region is ferroelectric and this region is paraelectric and this is basically you can say it is the boundary between the two.

And this is for second order and this is because and this is also manifested the free energy show second derivative of free energies showing a discontinuity whereas first derivative is continuous as a result there is no latent involved in this transition. If you look at the first order the first order shows a different behavior in the first order when you plot P versus T the polarization suddenly drops to zero at T_c. So this abrupt change in polarization and the susceptibility change is manifested in this fashion. So this is a change in susceptibility with susceptibility of high temperature region extrapolating back to a temperature T_0 and between T_0 and T_c.

We have the three more subsidiary minimize energy landscape between these two temperatures. And this is manifested in the first energy of first derivative of energy being discontinuous or entropy being discontinuous. We also started our discussion little bit on and switching in ferroelectrics where we looked at the ferroelectric hysteresis loop.

And now we are going talk about the microscopic mechanisms of why do we get such a behavior in ferroelectric switching. So we saw such a switching behavior because in the beginning you change your ferroelectric hysteresis like this. And then once it is achieves saturation when you bring it back to lower fields then the polarization does not come back to initial state rather it goes through a P_r state.

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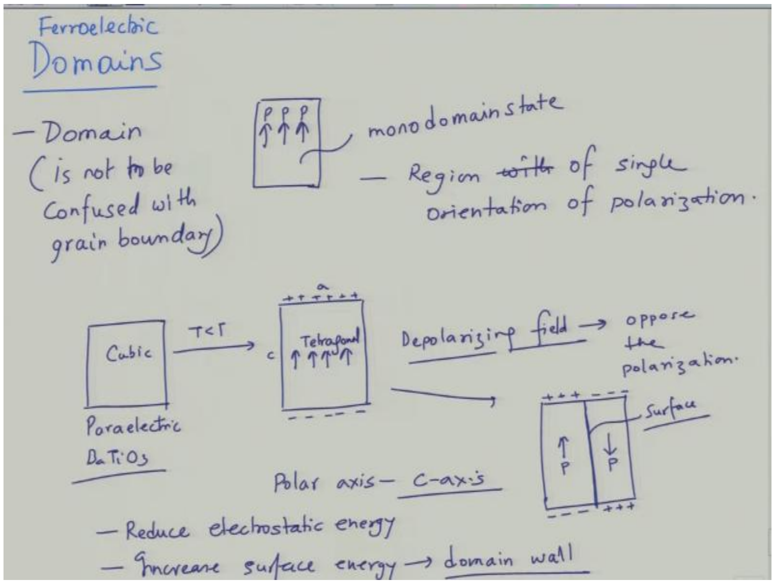

Ferroelectric Domains

- Domain (is not to be Confused with grain boundary)

monodomain state

- Region ~~with~~ of single orientation of polarization.

Depolarising field → oppose the polarization.

Polar axis – c-axis

- Reduce electrostatic energy
- Increase surface energy → domain wall

So question is what is the reason? The reason for these as we said lies in domains. So we will start our discussion on domains or rather ferroelectric domains. So as we said ferroelectric domain is basically if you take a crystal small crystal and if all the polarization vectors are aligned in one direction. Then this will be called as mono domain state so all the polarization vector.

So basically a domain is a region in which all the polarization vectors of the dipoles are aligned in one direction. So that is called as a domain. And domain is not a grain boundary is not to be confused with the grain boundary. Grain boundary is a crystal orientation the differences and difference in the crystal orientations of neighboring grains where domain is about the polarization orientation with respect to applied field and polarization orientation within a particular region.

So it is possible that you know within a grain you can have multiple domains it is also possible that several when you apply large electric field despite having several grains the whole material becomes in mono domain state. So it is not to be confused with the grain boundaries. So domain is basically a region of single orientation of polarization. Now let us say you have cubic material so you cool it below T_c. So this paraelectric state.

Paraelectric state when you cool it below Tc the system transforms let us say it becomes tetragonal. So your ‘c’ parameter becomes little larger than the ‘a’ parameter as a result you have some distortion. Now what may happen in this system is that since if you have a mono domain let us say you convert in this fashion and you think that all the dipoles are now aligned in this direction.

Because the polar axis in such a material let us say if it is a case of barium titanate then the polar axis in such a material will be along the C axis which is 001 axis. So polar axis is in ferroelectric state is C axis. So you would say that you would assume that all the polarization vectors will be aligned in one direction. Now all these polarization vectors will allow are aligned in one direction you will have massive surface charge density.

So you will have all the negative charges aligned here and all the positive charges aligned here. So you will have massive surface charge density on the surfaces of crystal suppose this crystal is of the order of you know 1cm x 1cm in terms of dimension this means massive charge density. This massive charge density leads to creation of what we call as a depolarization field.

So depolarization field is something which would like to minimize the surface charge density. So this single orientation of polarization sets up what we call as depolarizing field and this depolarizing field will oppose the polarization. So all the dipoles would like to align in one direction there will be massive surface charge density as a result electrostatic energy will increase and this will lead to depolarization of charges.

So these two act in competition with each other eventually what will happen because of competition of polarization energy and depolarization energy the system will transform into a situation something like this let us say if we now create a situation in which we have two regions within the same crystal one with orientation P upwards another with orientation P downwards. Then this will have surface charge density in this fashion.

So now the net surface charge density has gone down but while the net surface charge density has gone down we have created an interface between the two. So this is the surface extra surface surfaces all the cost energy. So it is a competition between also the depolarizing and so depolarizing energy has to reduction in the electrostatic energy due to depolarizing field has to compete with the surface energy.

So reduction so on one hand we have to reduce electrostatic energy by having depolarizing field which will prevent charges buildup on the other hand we will increase surface energy which is in the form of domain wall which is basically the interface the interface between the two just like a grain boundary you will have a domain wall energy. So these domains are created now the type of domains which are created will depend upon the type of material.

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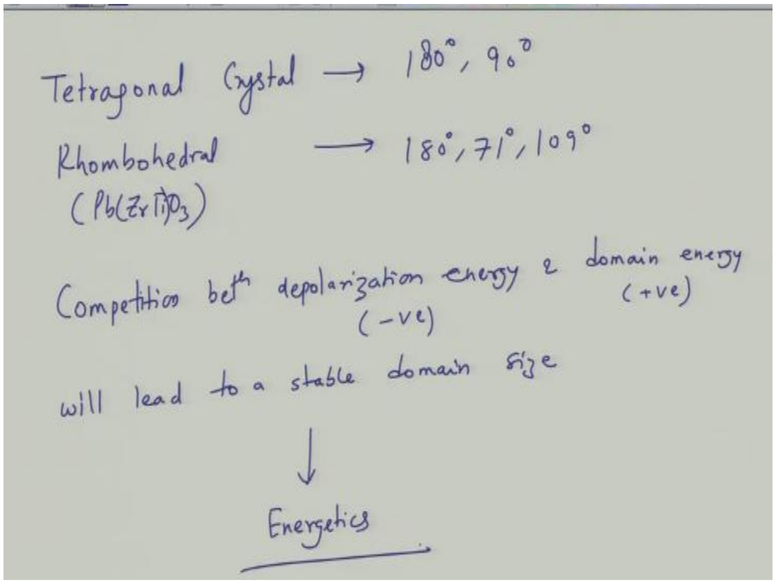

Tetragonal Crystal → $180^\circ, 90^\circ$

Rhombohedral → $180^\circ, 71^\circ, 109^\circ$

($Pb(ZrTi)O_3$)

Competition betn depolarization energy (−ve) & domain energy (+ve)

will lead to a stable domain size

↓

Energetics

So for example if you have a tetragonal crystal you will create 180^0 domain walls and you will create 90^0 domain walls. But if you have for example rhombohedral crystal such as lead zirconate, titanate this is rhombohedral this will give rise to 180^0 domains also 71^0 domains and

109^0 domains. So depending upon the type of crystal system that we have you will have different types of domains in the system.

So as we said it is a competition between depolarization energy which minimizes the electrostatic energy and the domain wall energy or the domain energy will so one is negative another one is positive will lead to a stable domain size which means we need to deal with the energetics of the process.

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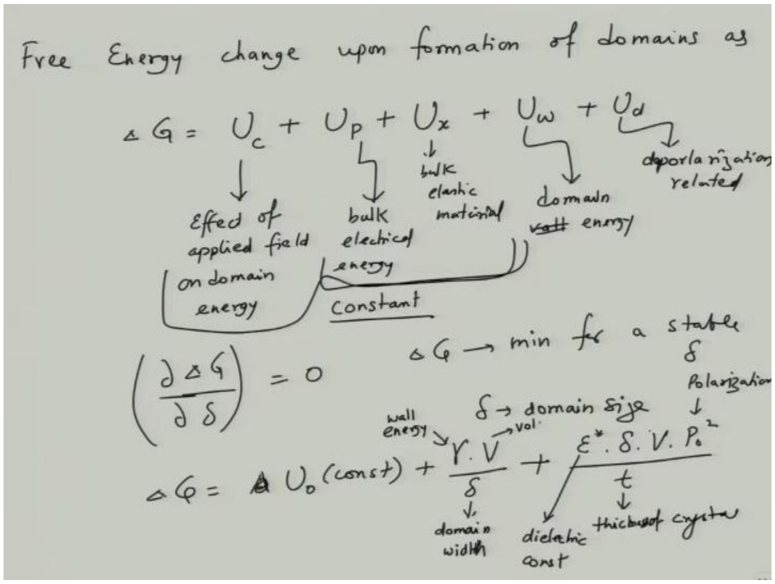

Free Energy change upon formation of domains as

$$\Delta G = U_c + U_p + U_x + U_w + U_d$$

U_c → Effect of applied field on domain energy

U_p → bulk electrical energy

U_x → bulk elastic material

U_p, U_x → constant

U_w → domain ~~wall~~ energy

U_d → depolarization related

ΔG → min for a stable δ

$$\left(\frac{\partial \Delta G}{\partial \delta}\right) = 0$$

δ → domain size

$$\Delta G = \Delta U_0 \text{(const)} + \frac{\gamma . V}{\delta} + \frac{\varepsilon^* . \delta . V . P_0^2}{t}$$

γ → wall energy

V → vol.

δ → domain width

ε^* → dielectric const

P_0 → Polarization

t → thickness of crystal

So for a ferroelectric crystal we express the energy as so the free energy change that is a we can write the free energy change upon formation of domains as so if you write ΔG which is:

$$\Delta G = G - G_0$$

which will be it is composed of few energies like:

$$\Delta G = U_c + U_p + U_x + U_w + U_d$$

So let us say U_c is the energy which is effect of applied field on domain energy. Up is basically bulk let us say electrical energy and this is bulk elastic energy. So this is basically material dependent parameter for a given material you will have certain electrical energy and elastic energy. Then U_w is what we call as domain wall energy. And U_d is nothing but depolarizing energy related to depolarization.

To get a stable domain structure:

$$\left(\frac{\partial \Delta G}{\partial \delta}\right)=0$$

where δ is the domain size. So basically these U_x,U_p they are material parameters they are same in each domain.

And U_c is effect of applied field these energies can be treated as constant. So we will so these energies do not vary much depending upon the domain size. So these we can treat as constant. So we can write this ΔG as a constant let us say:

$$\Delta G = U_d(const.)+\frac{\gamma.V}{\delta}+\frac{\varepsilon^*.\delta.V.P_0^2}{t}$$

U_w is the expression is γ which is the surface energy domain one energy multiplied by the volume divided by the δ which is the domain wall domain thickness or domain width.

In U_d,$P^2{}_0$ is the polarization at the center of the domain and then divided by thickness 't' which is the crystal thickness of crystal. This is polarization in the middle of the crystal in the middle of the domain this is dielectric constant and so this is dielectric constant V is the volume delta is the domain width.

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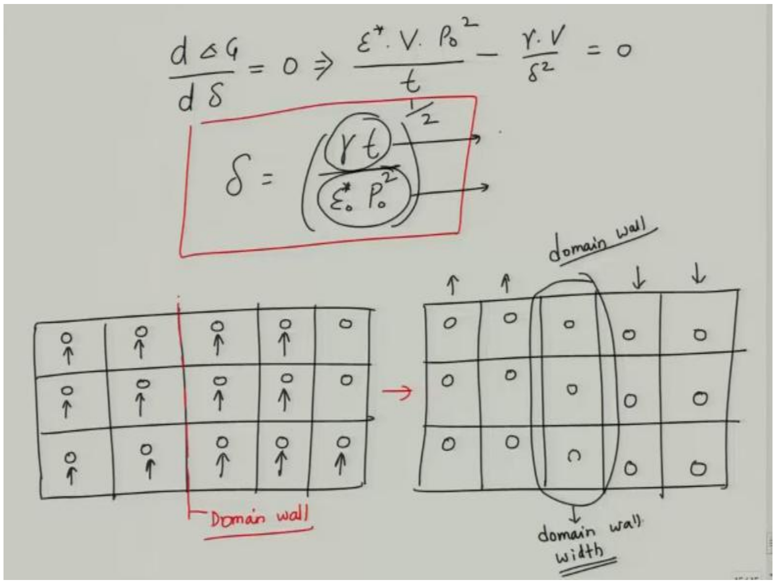

Now what we are going to do is that we are going to take a derivative of this ΔG with respect to to δ and this must be equal to zero. So when we do that what we get is:

$$\frac{d\Delta G}{d\delta}=0 \ \Rightarrow \frac{\varepsilon^{*}.V.P_0^2}{t}-\frac{\gamma.V}{\delta^2}=0$$

So from this we determine δ as:

$$\delta=\left(\frac{\gamma.t}{\varepsilon_0^{*}.P_0^2}\right)^{1/2}$$

This is the stable domain wall width that you get in ferroelectric material. So you can see here this δ is proportional to γ so which means higher the interfacial energy is smaller will be bigger will be the domain size that makes sense higher the interfacial energy is so this like grain boundaries higher the grain boundary energy is larger the grain sizes because you would like to minimize the surface energy.

So any increase in gamma will prefer bigger domains similarly if you make the crystal thicker which means the net so this means like charge density. The charge density the charge density per unit of the crystal also goes down which means you can manage with bigger domains the electric constant if you increase that electric constant of the material.

So if increase ε_0^*, we have to constant the material which means you will have more depolarizing energy which means you would have smaller domains higher the polarization and higher the polarization again you will have more polarize more separation of the charges as a result you will have more charge density which will create more depolarizing energy.

So basically these two factors lead to larger δ and these two factors lead to smaller delta and this is the surface energy term and this is the term which is related to polarization or depolarization of the material. So this is the stable domain size that you get in a material essentially now a different type of crystals will give you how does it look microscopically.

So suppose you have a crystal in which you have these multiple regions. So crystal at the center the central atom in this case all of them have this orientation. It is moved up from the central position so this is all pointing up. Creation of a domain wall let us say at this point so if you create domain wall here then this leads to formation of a slightly different.

So what will happen is that in these two regions the atom will remain shifted up and these regions we will have atom shifted down because the polarization is now shifted. So these regions will have up and these regions it will be down and somewhere in these two in the regions in the middle there will be a change in the domain wall. So these regions will have some variation so you might have a little bit of sort of intermediate positions somewhere here.

So this region will be the domain wall the region of disturbance along which the orientation changes. Because you have this change in orientation from here to here these changes will not be abrupt there will be little random. So as a result each domain wall will also have domain wall width which is sort of the order of a unit cell or they are little they are much more sharper than magnetic domain walls but there will be a region in which they will have to go transition from up to down.

So there could be about a unit cell across which the transition occurs so this is basically a domain wall as we said domain walls are of multiple types. So you can have in this case we have shown you 180^0 domain walls that but there is a possibility that you might create something like this.

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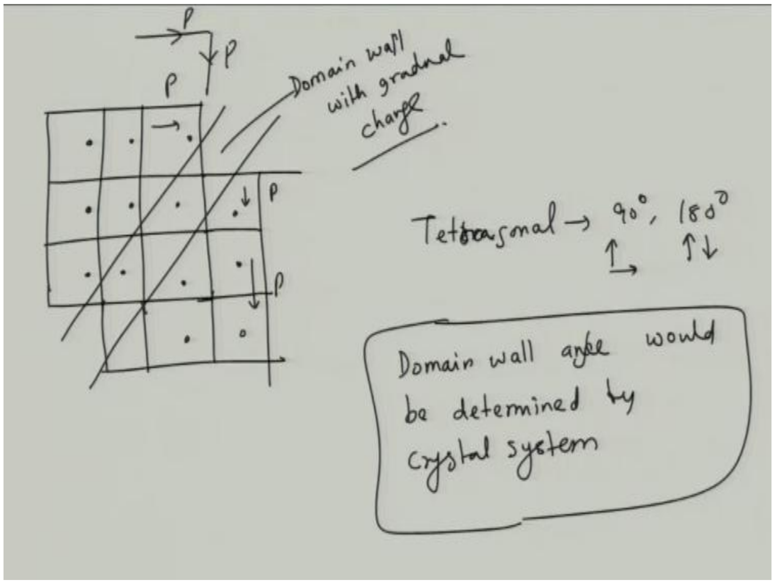

You might have a crystal in which let us say something with 90 degree domain walls. So let us say the orientation in this case is like this and this is a domain wall that you create in between in this case that this atom may be sitting right at the center whereas in these regions that domain that the polarization may be in this direction.

So here the P is different in different domains. So there will be a gradual transition within this region. So this will be domain wall width gradual change. So as I said there are multiple domain walls in tetragonal crystals generally we observe 90^0 domain walls. So this is 90^0 domain wall because polarization changes by 90^0 from one to the other.

You can also have 180^0 domain walls in around which polarization flips in opposite directions. But depending upon the crystal orientation you may have multiple orientations and there are some nice papers available on which you can see that different crystals will show different orientations. So domain wall type domain wall angle would be determined by crystal system. But generally when we talk of tetragonal crystal we talk of 90^0 180^0 domains.

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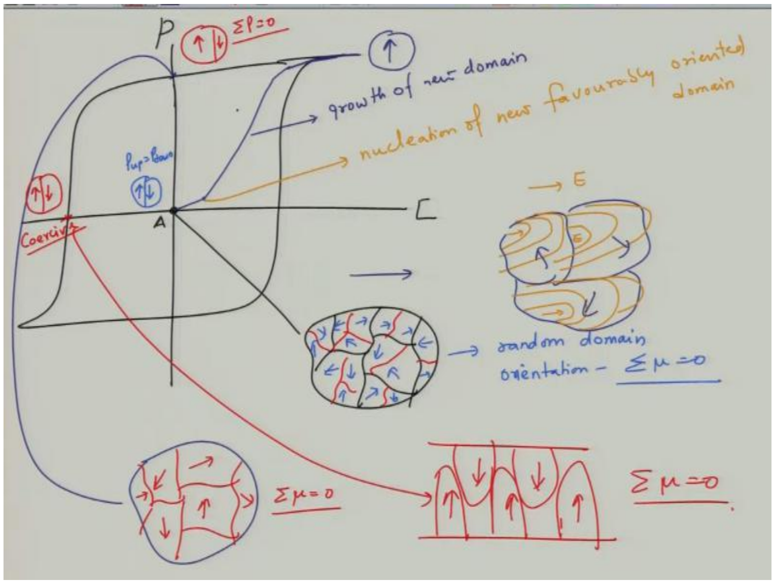

So now let us see once we know how the domains from basically what happens in case of free energy in case of switching is essentially when you start switching. So you start at this point in P-E loop, in this material at this point A although material has domains but in it is in the poly crystalline state. So you might have a material these are the grains. Now these grains will have domains distribution is something like this assuming that domain sizes.

So red ones are domain boundaries now it might happen that the polarization vectors are rotated randomly so we have random domain orientation as a result:

$$\sum \mu = 0$$

So you have zero polarization so in this state you can say that number of opposite polarization states are equal. So P↓ = P↑. Zero polarization as you start switching it in the linear region you just create polarization because of electric field associated polarization.

So this the linear region when you increase the electric field what you do is that and these crystals let us say we apply the electric field in this direction we start nucleating new domains of the which are oriented along the direction of electric field. So what will happen is that let us say this is the these are the few domains we will start nucleating new domains in this direction which are oriented in this direction and they are generally created at the interfaces.

So at this point we will have nucleation of new favorably oriented domains. And up to this point up to which all of them are oriented they will keep increasing in size at the expense of old domains. So domain will keep growing as you increase the strength of electric field in this direction irrespective of the orientation of previous domain. Previous domain could have been like this.

But the new domains are all oriented along the electric field. So basically this domain is the region in which growth of new domains which will consume old domain something like Ostwald ripening once all the domains are oriented again you will have a change in linear region. So this is where we will have a state in which whole material will be in this a state mono domain state.

So what might happen is that initially you might form a domain which is slightly tilted to E which starts new creating finally the domain will also orient towards the electric field. So once you each a mono domain state when you switch off the electric field at zero that domains do not get back. So only some of the domains get back to previous different orientations but or not all domains come back.

So what might happen at this point is you will have a crystal in which electric field is now zero most of domains remain oriented in one direction very few domains come other direction.

So as a result your net $\mu \neq 0$ and you have basically more polarization in one direction than in other direction. So basically:

$$\sum P \neq 0$$

So that is where you cause remnant polarization now to bring all the domains back to zero back to this orientation you need to apply a field which is called as coercive field then if you now look at the bigger picture number of domains which are oriented in one direction and number of domains which are oriented in other direction, is the sort of state you want to achieve when:

$$\sum \mu = 0$$

So opposite oriented domains are equal in fraction and then again the same process repeats as you go in the negative cycle. So this is how the switching occurs in ferroelectrics by formation of new favorably oriented domains to the direction of applied electric field and their growth and then saturation when all the domains get aligned there is nothing more to be aligned you basically saturate the polarization.

But when we come back to zero electric field the domains do not revert back to original position. You can say it is because of friction in the lattice or whatever but they do not get back to the original situation and to bring them back to original configuration of equal domain proportion of opposite types. You will have to apply an extra electric field which is called as coercive field. Coercive means coercion.

You are forcing the material back to zero polarization by applying in a extra electric field and these states are by the way equal and opposite so $+E_C$ and $-E_C$ are equal in magnitude similarly $+ P_R$ and $-P_R$ are equal, $+P_S$ and $-P_S$ are equal and opposite because material for a given material for a limited volume. So in this lecture what we have done is we have looked at the domains in ferroelectric materials and they are their origin and how they play an important role is switching.

And that is why they give rise to a hysteresis that view observe so we will stop here and in the next lecture we will finish our discussion on ferroelectrics and we will of piezoelectric from hydroelectric and ferroelectric materials.