Electroceramics
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Lecture - 29

So, we started with the topic on ferroelectric domains after we completed first and second order transition. So, as we discussed ferroelectric domains are actually regions of uniform polarization.

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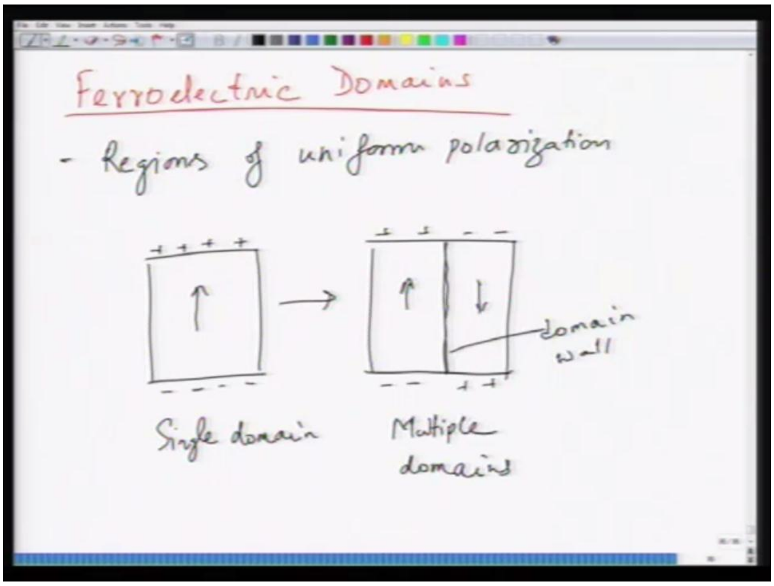

Ferroelectric Domains

- Regions of uniform polarization

So, that is one of the essential characteristics; and these domains do not translate all over the region of the crystal. Of course, it depends upon the size of the crystal, but for a normal ceramic or single crystal, you never have a state which is mono domain state means, whole material is not in single domain state. And that is, because of as we discussed last time when the domain gets bigger since you have polarization in the material. So, you have state like this. Now, this is a mono domain state, if you have a mono domain state then, you have build up charges on the phases of the crystal and this gives rise to large electro static energy which results in large depolarizing field. So, this depolarizing field wants to tilt this polarization vector in the opposite direction.

So, there is a depolarization in field or energy, electro static energy which favours reorientation of this moment or dipole moment into other direction, which means it wants to break into multi domain state. So, for instance in a state like this, so here it translates itself into 2 states, so the net charge density on the phases of the crystals goes down the as a result of formation of 2 domains. Now, you have here you have single domain and here you have multiple domains. Now, but at the same time you also see when you make a domain, it comes across it comes it with itself with the surface. So, this interface between 2 domains which is called as domain wall; this is actually a surface a physical surface. Now, as long as it is a physical surface it requires energy. So, that energy now is a positive energy it is a requirement.

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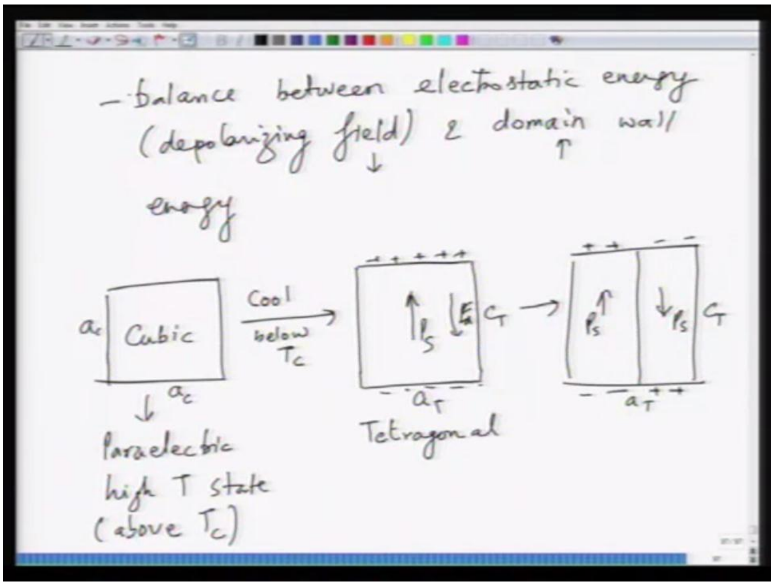

- balance between electrostatic energy (depolarizing field) & domain wall energy

So, we need to find a balance between so to basically it depends the size of the domain will depend upon balance between electro static energy which is due to depolarizing field and domain wall energy which is a surface energy. So, what we will do a little later in this lecture is we will just find a balance between these two energies in order to find the optimum domain size that we will obtain. So, this would reduce the energy of the system. So, this reduces the energy, this increases the energy. So, we need to find a balance between these two. Now, domains walls in the crystal. So, for example, you start from a cubic state of a material this is paraelectric state.

So, when you cool it so cool below T c. So, this is paraelectric high temperature state which is above the Curie temperature above T c. Now when you cool it below T c then, the material transforms into tetragonal. So, what you have is a tetragonal phase. So, here it is a c, a c here it becomes a T and C T. So, that is how tetragonal crystals are defined? Now in a tetragonal crystal this would appear as if you have formation of polarization along this direction which means build up of charges on the phases. And corresponding to this P d you will have what is called as depolarizing field, just a second let me just make a distinction here this is P s.

So, corresponding to this you will have a depolarizing field which is correspondent by P d or let us say E d. Now, this E d makes this mono domain state unstable, as a result what happens is, this crystal breaks itself into 2 parts. So, this P s in this direction this is P s in this direction and hence the surface charge density goes down. And as a result the depolarizing field gets equal to 0, but you form a interface. Now, this could also happen by application of strength stress below T c.

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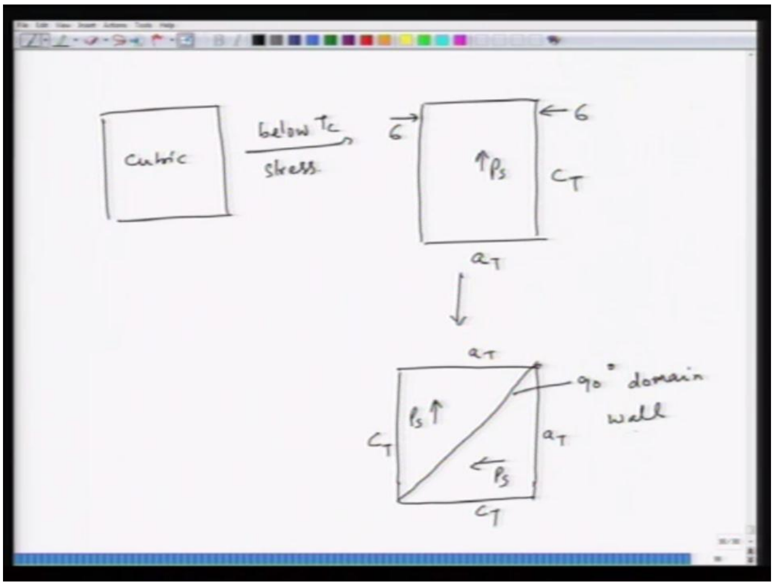

So, you take a cubic state; you take cubic state go to below T c and then, you apply stress. And when you apply stress so for instance you had a situation like this, you have a tetragonal a T and c T followed by this P s which is the polarization vector this is. So, the previous scenario it is same as saying in the, at the temperatures below T c you apply a stress sigma here. And when you apply the stress on the phases of crystal, this converts into something like this. So, you have a polarization vector in this direction, P s another polarization vector in this direction and this gives rise to. So, this would be c T this would be a T and this would be c T this would be a T. So, now, you can see the wall is not 180 degree rather you have a 90 degree domain wall and this 90 degree domain wall.

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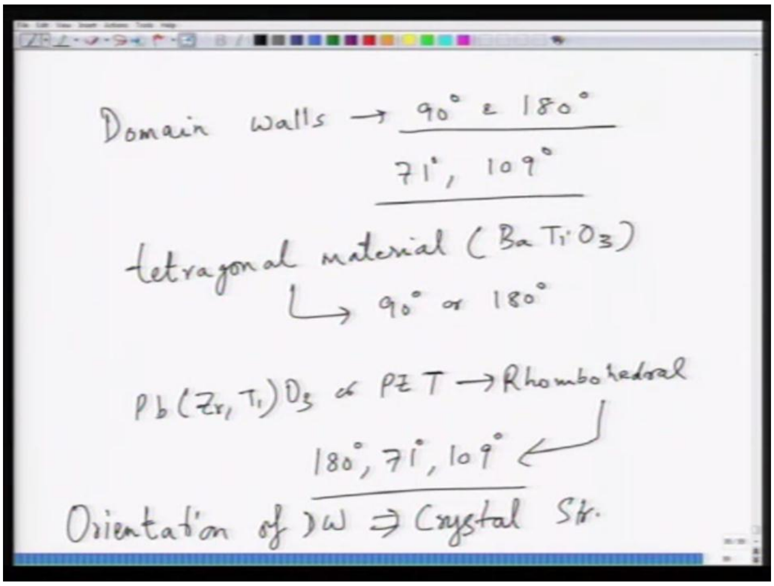

Domain walls → 90° & 180°

71°, 109°

tetragonal material ($BaTiO_3$)

↳ 90° or 180°

$Pb(Zr,Ti)O_3$ or PZT → Rhombohedral

$180^\circ, 71^\circ, 109^\circ$ ←

Orientation of DW ⇒ Crystal Str.

So, you can have variety of these domain walls you can have domain walls of 90 degree and 180 degree, you can also have the domains wall of the order of 71 degree and 109 degrees. Now, the angle of the domain wall that will that you will get in a given crystal will depend upon the crystal structure. So, for instance a tetragonal material or tetragonal structured material such as barium titanate or lead titanate in the ferroelectrics state will have 90 degree or 180 degree domain walls, whereas something like you know P b Z r T i O 3 P Z T which is commonly known as. It will have in the rhombohedral form in the ferroelectric state it will have polarization along 180 degree, it will have 70 degree, a domain walls along 180 degree domain walls, 71 domain walls and a 109 degree walls. So, the orientation of domain wall is determined by the crystal structure of the material. So, that is one of the, of domain wall is related to crystal structure of the material in the ferroelectric state. Now, that we just mentioned was do not confuse this domain wall as a grain boundary for the reasons which I will explain now.

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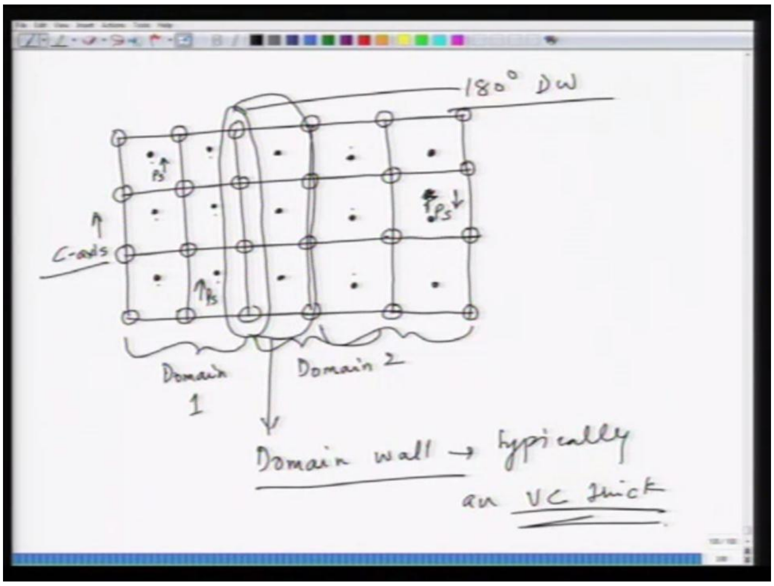

Suppose you have a crystal like this. Now, let us say in this crystal. So, this is your so these are hypothetical lattice points, now in the ferroelectric state, so this is the centre of this unit cell. So, the central atom will sit at these places in the ferroelectric state, in the non ferroelectric state. In the ferroelectric state, let us say these atoms are shifted here. So, this is the direction of P s. Now, this is the mono domain state. Now, when you form a what happens in 180 degree domain wall is simply. So, this is domain, let us say this remains as domain 1. Now, the other part of the crystal converts into domain 2 with the 180 degree domain wall. So, what essentially it will mean is that, this guy which is here will move here. And so, this would convert into domain 2 and this wall region will be 180 degree domain wall. So, you can see that there is no change in the crystal structure, there is no change in the symmetry at the domain wall, it is just that across the domain wall the orientation of polarization has changed.

So, there is little bit of shift of shift of a central, let us say titanium atom in barium titanate along the direction of along C axis. So, this would be your C axis, along C axis in case of tetragonal crystal. So, you do not so there is no discontinuity here unlike what you found in find in a grain boundary. So, this is one of the major differences in terms of grain boundary, in terms of distinguishing domain wall with a grain boundary. Similarly, you can draw the same picture for a 90 degree domain wall typically what you see is that these 180 degree domain walls would be about unit cello thick. So, this is an ideal picture, but what the picture would look like in reality is something like this.

So, you draw another unit cell across it, because here there is a abrupt change in the P s vector. Now, that is something which is which intuitively you do not expect and this does not happen mathematically as well. So, what happens physically is, essentially you have this atom in this domain, in this direction and the central region which is this region is typically you will have this atom sitting at these places approximately at the centre. So, there is a gradual transition from one domain to another, you have plus P s in this direction, you have this becomes minus P s.

So, P s changes from up to down gradually and this region is now domain 2 and this becomes domain wall. So, domain wall is typically and unit cell thick. So, this is very small number, this is you are talking in terms of angstroms, whereas domains typically of the order of few 10s of nanometers in the ferroelectric 10s or even 100s of nanometer depending upon the structure of the material. What form of materials it in whether it is in polycrystalline state whether it is in single crystal state? So, domain wall is governed by those factors as well. Similarly, you can draw this atomistic structure for a 90 degree domain wall as well which I will leave it to you to verify, to verify yourself in that how it looks like? Now, how does a the question now is how does a domain wall look like?

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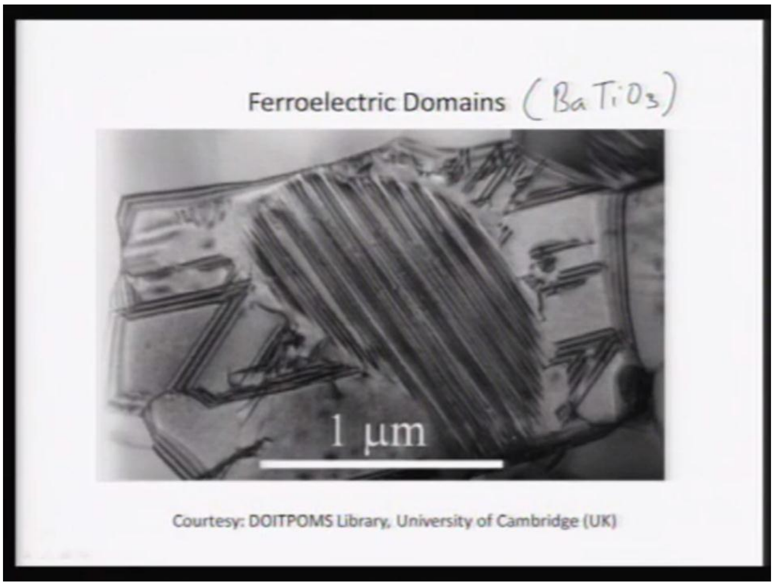

Ferroelectric Domains $(BaTiO_3)$

Courtesy: DOITPOMS Library, University of Cambridge (UK)

The domains wall looks like something like this I will show you a view graph here. So, if you go to, if you look at this slide show. So, this is a structure of domain wall in a ferroelectric material, this has been this is a picture of barium titanate. So, this is a barium titanate, single crystal and or polycrystalline material I think, and in this you see under transmission of electron microscope, so this is a T M image you can see that the error the microscope, the image bar is here about, so this much length is about 1 micron. So, this whole image is roughly 2 and half microns or 2 microns wide. And in this, these regions as you can see these stripes here, these stripes are nothing but individual domains. And these are nothing but your, so you can see, you can observe these domains under microscope you can look at single crystals and optical microscopes just by doing some polarize like microscopy.

You can do transmission electron microscopy, because you get. Some strain contrast you get this domain contrast which helps you visualising the domains of very, very fine size even under a equipment like transmission electron microscope. So, this is what is, and this image by the way was taken from DOITPOMS package of university of Cambridge UK. So, you can go to that website DOITPOMS and do the Google search DOITPOMS microscope library and just look at these images which are provided on the website. And another thing that you need to remember is.

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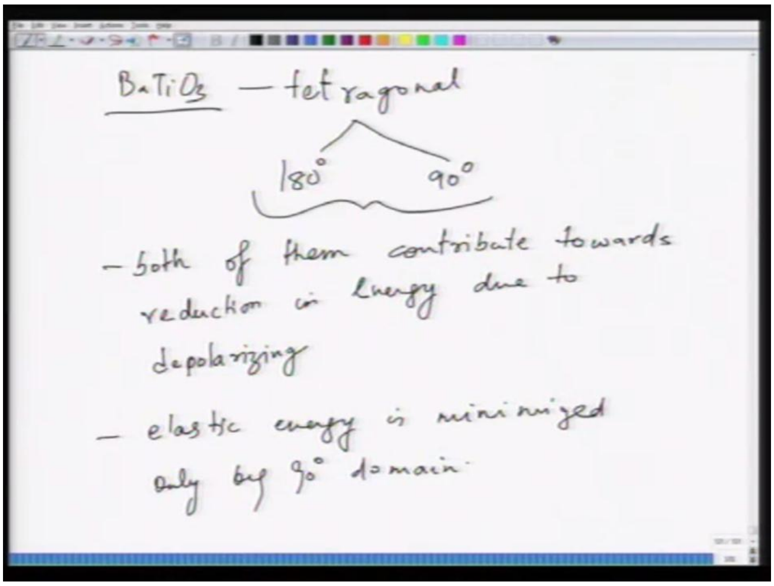

$BaTiO_3$ — tetragonal

180° 90°

- both of them contribute towards reduction in Energy due to depolarizing
- elastic energy is minimized only by 90° domain

Take the case of barium titanate or lead titanate. Now, since this is a tetragonal material, it has 180 degree domains and it has 90 degree domains. Now, these 180 degree domains, 90 degree domains, both of them are instrumental, both of them contribute towards reduction in the, in the energy which is due to depolarizing field which opposes the spontaneous polarization. However elastic energy is minimized only by 90 degree domains. So, even though you have 2 kinds of domains present here 180 degree may be more common, but although both of them are present in variety of crystals structures, both of them make different contributions to the energetics in the structure. So, basically the driving force now, now we are looking at now we are slowly moving towards the thermodynamics.

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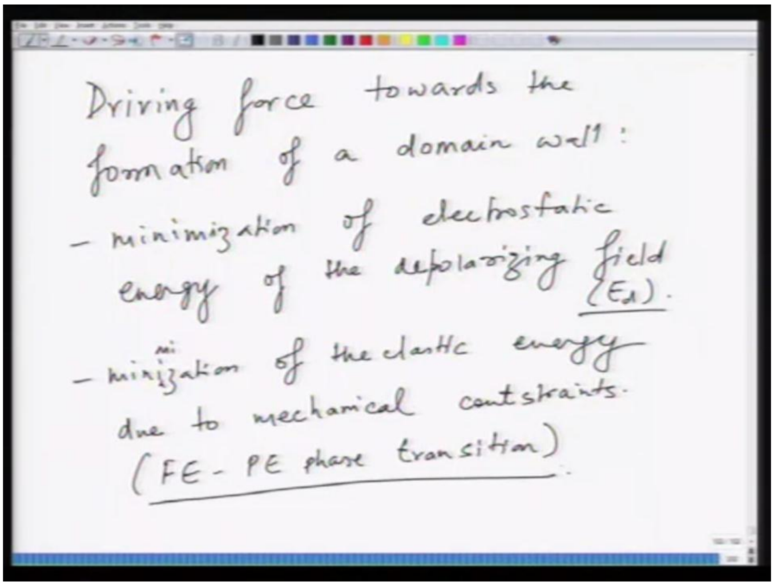

Driving force towards the formation of a domain wall :

- minimization of electrostatic energy of the depolarizing field (E_d).
- minimization of the elastic energy due to mechanical constraints. (FE - PE phase transition)

So, basically in the driving force towards the formation of domain wall of a domain, a domain wall and which is which gives rise to multiple domain states is because of minimization of electrostatic energy of the depolarizing field which is called as E d. And this is because of surface charges which are created due to a spontaneous polarization and also minimization, minimization of the elastic energy or due to mechanical constraints. And this is typically due to ferroelectric to paraelectric phase transition. So, you can and because you change the structure from cubic state to tetragonal state, there is a change in the lattice parameter. And this change in lattice parameter gives rise to stresses and these stresses or mechanical constraints lead to formation of typically 90 degree domain walls. So, elastic energy of the system is minimized by the creation of domain walls which help in minimizing this kind of energy and.

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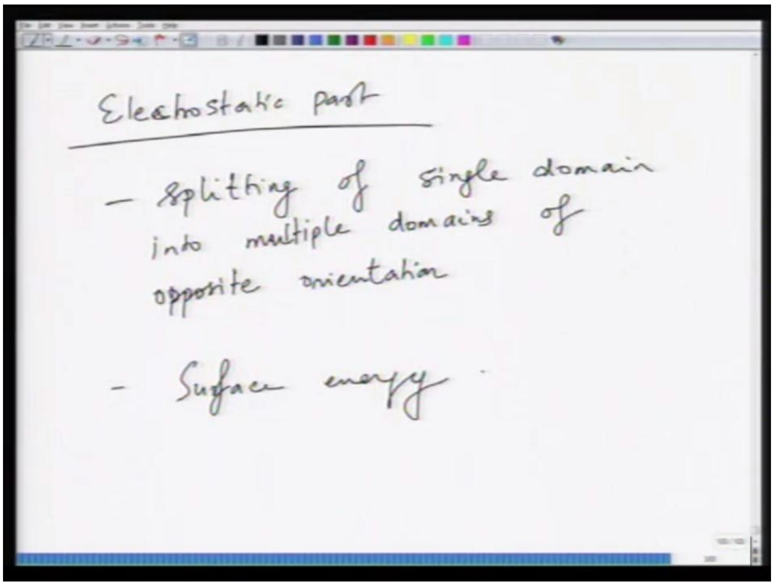

Electrostatic part

- splitting of single domain into multiple domains of opposite orientation

- Surface energy.

So, this basically your so, this electrostatic part is dealt with. So, electro static part of energy minimization is basically a splitting of a single domain into multiple domains of opposite orientation while and compensating energy is the surface energy. So, this is what you need to remember. Now what we are going to do is that we are going to do analytical treatment. In order to find out what is the optimum domain size that we get when such forces are present there. So, as we know that ferroelectric domains form because of instability of dipoles to be aligned in one direction.

Since, mono domain is not a stable state, you have a multiple domain state, as a result you have this multiple ferroelectric domain. Now, when you have such kind of situation when you have on one hand electrostatic energy, another hand you have surface energy, and other various other energies involved, overall the system will have a free energy. When you go from a single domain state to multiple domain state, this free energy must reduce in order to make this multi domain structure as a stable structure. So, this phase is the free energy change.

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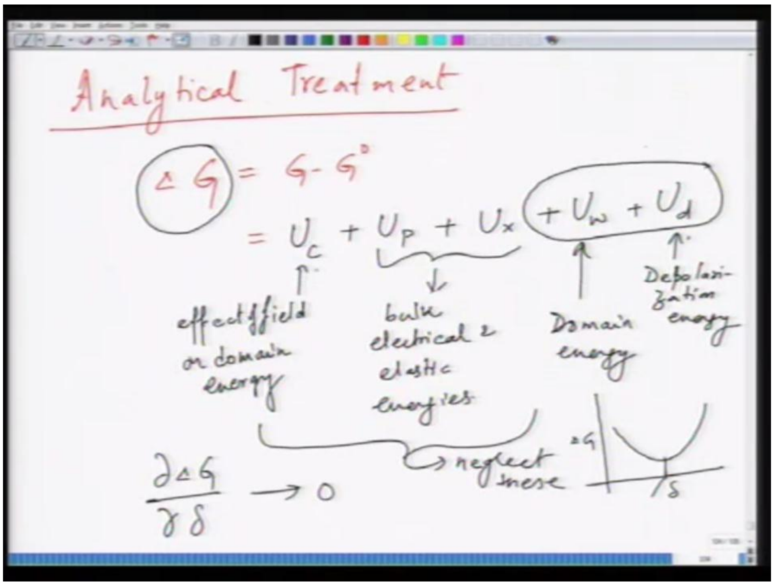

Analytical Treatment

$$\boxed{\Delta G} = G - G^0$$

$$= \underset{\uparrow}{U_c} + \underbrace{U_p + U_x}_{\downarrow} \boxed{+ \overset{\uparrow}{U_w} + \overset{\uparrow}{U_d}}$$

effect field on domain energy

bulk electrical & elastic energies

Domain energy

Depolarization energy

neglect these

$$\frac{\partial \Delta G}{\gamma \delta} \longrightarrow 0$$

So, let us just write this heading here, analytical treatment. So, this delta G which is the free energy change involved in the formation of a domain is given as or formation of domains is given as delta G which is G minus G naught. And this is nothing but sum of various kind of energies you can have U c another is U p. So, U c is nothing but the effect of applied field on domain energy. So, field there is field dependence to it as well, then you have a term called as U p and U x, and these U p and U x are bulk electrical and elastic energies. And then, you have what is called as U w and then you have another final term which is called as U d and U w is the domain energy, and U d is the depolarization energy which is basically due to depolarization field.

So, now, here the first 3 terms are effectively neglected, because in the minimization of free energy, because these 3 terms do not have significant influence on the domain size. Because elastic and electrical energies are virtually constant or they remain, they assume, they can be assumed to be constant for simplicity of treatment and if you make the effective if you make the electric field constant then, this effect also is neglected. So, we can, now what we have to do is that in order to get a stable domain energy domain structure, we need to minimize this delta G. And when you have this minimization of delta G it has to be done with respect to a given domain size. So, when you do this delta g del of delta G by del of. Let us say domain wall size is called as delta. So, del of delta G is equal to 0 and in this process we neglect these terms assuming these to be independent of domain size and which is a fairly good approximation, because it turns out that all these 3 parameters do not show an appreciable effect with respect to the domain size.

So, the first thing now we need to do is that the U d let us say and this U d is the depolarizing energy. So, what essentially it means is that, this free energy curve when you for instance, this is your delta G and this is your delta. So, this with respect to this delta this free energy curve has to show a minima somewhere. And this delta is the optimum delta that you need to find. So, basically at this point this del of delta G versus del delta has to be equal to 0. And for that we need to know which means that U w and U d have some dependence on the domain size and that is what we are going into look at.

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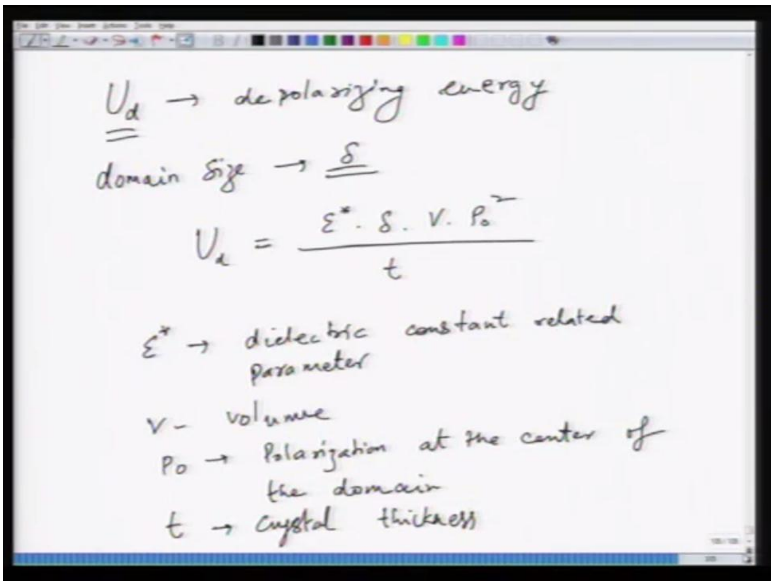

U_d → depolarizing energy

domain size → δ

$$U_d = \frac{\varepsilon^* . \delta . V . P_o^2}{t}$$

ε^* → dielectric constant related parameter

V - volume

Po → Polarization at the center of the domain

t → crystal thickness

So, let us say the domain size is delta and this U d is basically related to the internal energy which is set up by this depolarizing energy. And the, this basically internal field opposes the applied field and hence it is called as a it is called as a depolarizing field. So, this U d essentially is given as epsilon star delta V P naught square divided by t. Here epsilon star is essentially dielectric constant related parameter, V is the volume, P naught is the polarization at the centre of the domain and t is the crystal thickness. So, this is your depolarizing energy term. Now, we need to find out what is the other term?

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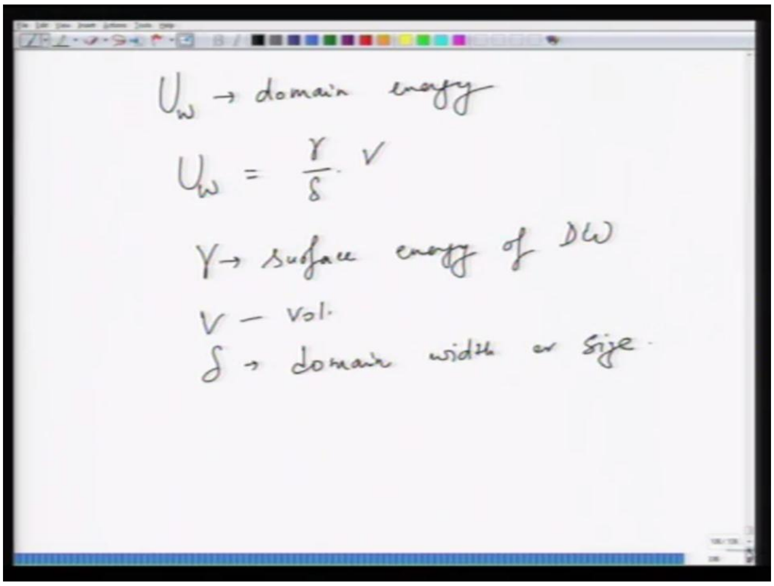

U_w → domain energy

$U_w = \frac{\gamma}{\delta} \cdot V$

γ → surface energy of DW

V — vol.

δ → domain width or size.

And this other term is U w, which is the domain energy and this domain energy U w can be expressed as gamma divided by delta into V where gamma is the surface energy of domain wall, V is the volume again and delta is the domain width or size. Now, we have taken since U p and U x as constant, because they are fairly constant in each domain. And U c is something which is also when you take constant field, and then it is the, it is again independent quantity of delta. So, we can make this whole thing equal to they remain constant. So, as a result when you differentiate delta G expression they go equal to 0. So, what you do now is that we just minimize this energy with respect to delta. So, what you need to do now is.

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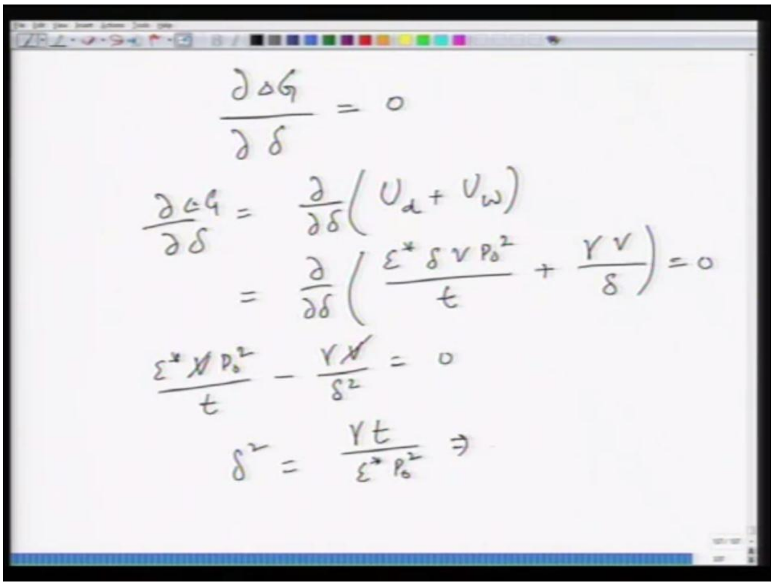

$$\frac{\partial \Delta G}{\partial \delta} = 0$$

$$\frac{\partial \Delta G}{\partial \delta} = \frac{\partial}{\partial \delta}\left(U_d + U_w\right)$$

$$= \frac{\partial}{\partial \delta}\left(\frac{\varepsilon^* \delta V P_0^2}{t} + \frac{\gamma V}{\delta}\right) = 0$$

$$\frac{\varepsilon^* \cancel{V} P_0^2}{t} - \frac{\gamma \cancel{V}}{\delta^2} = 0$$

$$\delta^2 = \frac{\gamma t}{\varepsilon^* P_0^2} \Rightarrow$$

So, now we need to we are taking del of delta G versus del of delta is equal to 0. So, as a result now, this becomes basically del of delta G del of delta is essentially of U d plus U w. And if you look at these parameters here, so what you have here is epsilon star delta V P naught square, epsilon star delta V P naught square divided by t plus you have gamma V divided by delta and this is equal to 0. So, essentially the first term becomes epsilon, epsilon star V P naught square divided by t and this other terms other term becomes minus of gamma V divided by delta naught square and this is equal to 0. So, of course, V goes out. So, what you have here is delta naught square is to be equal to gamma t divided by epsilon star P naught square and which means.

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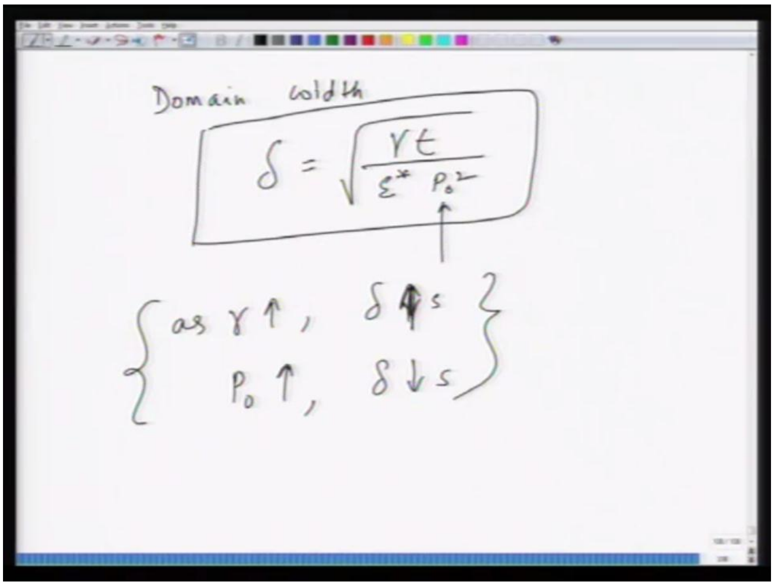

Domain width

$$\boxed{\delta = \sqrt{\frac{\gamma t}{\varepsilon^{*} P_0^{2}}}}$$

$$\left\{ \begin{array}{l} \text{as } \gamma \uparrow, \quad \delta \uparrow \text{s} \\ P_0 \uparrow, \quad \delta \downarrow \text{s} \end{array} \right\}$$

Delta domain width delta is given as root of gamma t divided by epsilon star P naught square. So, this is; what is the equilibrium domain wall width which leads to minimization of free energy? And it as you can see in this expression you have dependence up on the polarization. So, which means larger the polarization is smaller the domain size is going to be. And that kind of makes sense, because the larger the polarization is larger the depolarizing field will be, and more will be the driving force towards formation of domains. So, this increase in any increase in P naught and this goes as square as well. So, so there is pronounced effect of polarization on the domain size then there is the effect of gamma which is the surface energy on the polarization.

So, as the domain wall energy goes up delta also goes up, because you want to minimize the number of domain walls which lead to, which lead to basically increase in the requirements. So, this is the expression. So, basically as gamma increases, delta increases, which means you know and as P naught increases delta decreases. So, you can see this conflicting requirement, and that is what leads to balance of situation resulting in a equilibrium domain size and this domain. So, we have gone through the concept of domain wall. Now, this domain wall has a concept of this domain wall has a significant influence in the way we explain this ferroelectric hysteresis loop.

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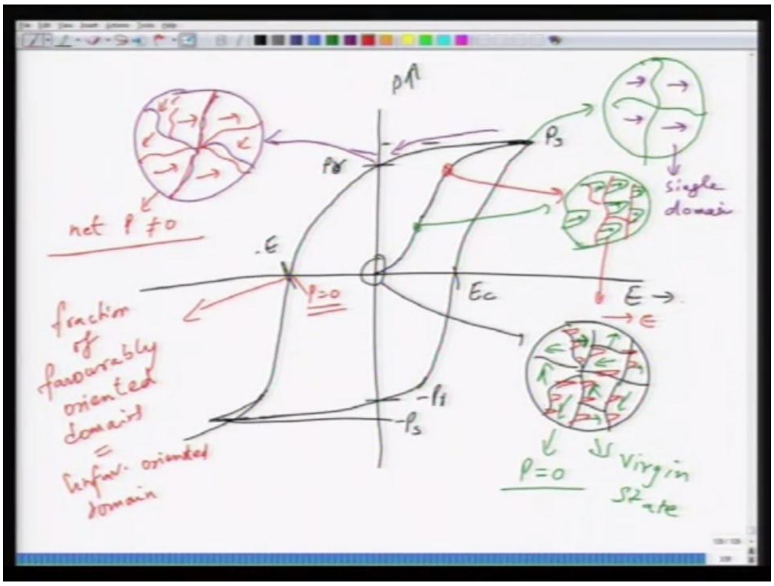

So, now when you draw a ferroelectric hysteresis loops. So, you start polarizing from this point, this is the virgin state of the material in the virgin state all the domains are randomly distributed to each other. As a result the net polarization is equal to 0, because material has never been poled and when you start polarizing it increases little bit linearly in the beginning. And then, it becomes a non-linear process and then, you reach what is called as saturation point, and when you reach saturation point and then you come back it goes back to remnant polarization and then cycle starts. So, this what it is going to be like, this is going to be your saturation polarization? This is your remnant polarization P r again minus P s minus P r and these are called as, as we know coercive fields E c, and minus E c. And this is polarization axis and this is electric field axis.

So, here in this state the domain structure of our material would be you have this is the grain size, and these are domains and in the domains you will have random distribution of domains. So, this gives rise to P equal to 0, this is called as a; this is in the virgin state which means as made materials, but the moment you start poling it, you have formation of new domains. Now, this does not happen like in as we will see in the magnetic material. In this case, here in ferroelectric materials each time when you make do the polarization it is always the nucleation in growth of new domains rather than. So, you might, you might think that, that these energies these domains which are favourably oriented with grow in the direction of applied field. But now, this process is more energy consuming in ferroelectric materials than the nucleation in growth.

So, what happens is that at the boundaries of these domains or the boundaries of grain boundaries. And various kind of surfaces which and as you know from the phase transformation fundamentals that when the nucleation in growth process happens, because of energy energetic reasons nucleation prefers to take place on foreign surfaces which minimize the energy requirement for a critical size to grow. And the critical size can also be smaller in case of foreign surfaces. So, what happens is that these domains, new domains start growing in the direction of applied field. So, what you will have for instance at this point is if you now if you look at a material.

So, you have this structure. So, what will happen if you look at here now? So, let us say the field direction is this, then new domains will start growing like this, if this is a grain boundary, the new domains will start growing. And these new domains are oriented in the direction of applied field and as they grow they consume all the domains which are unfavourably or otherwise oriented. So, what you have as it state for instance at this somewhere at this position is let us say this is the structure. So, you have these domains which have formed in the direction of applied field bigger domains. So, these are the favourably oriented domains and the other and the other domains, the basically the fraction of other domains had decreased.

And the fraction of favourably oriented domains has increased. And when you reach P s, then all the materials all the whole the across the whole volume of material you might have these are the grain boundaries and everything will be single domain. So, this is your single domain state. So, basically you have all the domains show single orientation of dipoles. When you get back to this situation what happens is that at this point? So, again this is the grain boundary and let me. So, what happens is that when you come to this point most of these domains remain in this orientation itself. But some of the domains revert back to other orientations. So, as a result there is a net P which is not equal to 0. So, because you have some domains which are favourably oriented left in the material.

In order to bring these domains back to the volume of oppositely oriented domains you need to take the material to another field in negative direction. So, that here basically the fraction of fraction of favourably oriented domains is equal to unfavourably oriented domains. So, basically all the polar vectors in all the domains cancel each other. So, this result in P is equal to 0 and then, when you go back to this when you go back to when you further decrease the field in opposite direction. Then the same thing happens which happened in the, when we increase the fill in the positive direction. And this basically gives rise to a hysteresis loop which basically the area under the hysteresis loop is the energy which is dissipated in this process or energy which is consumed in this process of domain reversal. And what you get at 0 field is 2 stable states of polarization which has plus and minus P r.

And this is what the crux of ferroelectrics, not only the ferroelectric material as we discussed earlier is a non centroelectric material has a unique polar axis, but unique polar axis can also be reversible. So, you have plus state plus P r state and minus P r state and this is what makes a ferroelectric extremely useful from the fundamental from the application point of view. I will show you one animation for this domain wall reversal how it takes place in the materials. And if you just fair with me for a couple of moment let me just find out.

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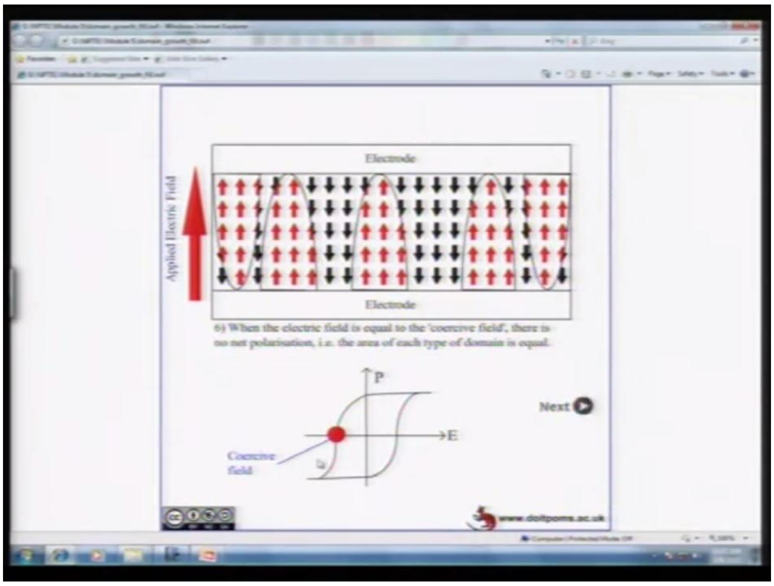

6) When the electric field is equal to the 'coercive field', there is no net polarisation, i.e. the area of each type of domain is equal.

So, essentially what you have is basically a material here which has which we start at this point which is fully polarized, and this sample is sandwiched between 2 electrodes which facilitate the application of electric field. Now, the electric field direction is shown by this red arrow. Now, we start the animation now. So, we go from this state to other state which is taking if you look at this red ball it is moving towards a left which means we are decreasing the strength of applied electric field. Now, what you see here is as a result of application of this electric field you have nucleation of these domains at the interface between the sample and the electrode. And this interface is, because it is a foreign surface and it helps the nucleation of new domains. Simply, because if you go through negation in growth fundamentals you will find that foreign surfaces assist the nucleation.

So, formation of new favourably oriented domains takes place in this direction. Now, these domains are oppositely oriented because you have, because you are decreasing the strength of applied field or which is to say that you are going taking the field in other direction. So, the new domains will have orientation in the opposite direction as to direction of applied field. So, this is just below the saturation polarization you have little bit formation of domains, and then what happens is that, this is when you reach zero electric field. So, what happen at this point is, new domains which have formed as a result of reduction in applied field they have grown larger in the extent. As a result they sweep out or they completely eliminate the overall polarization. So, what happens is basically the polarization due to these black arrows and polarization due to red arrows they cancel each other. And hence, you have they do not; they do not completely cancel each other at this point.

So, they basically so these red arrows cancel the polarization which is equivalent to this volume itself. So, but, if you can see if you can look, if you look at this image the volume of material which is occupied by black arrows is larger than the red arrows which basically shows that you still have some polarization left in the material. And this is what represents your plus P r state. And now, when you take it when you take the field further back to opposite direction which means you have gone below 0. Now, here these domains have further started growing they have become bigger the polarization is still finite, because the black arrows are the still reasonably large in number. And when you reach this point E c or minus E c here, the domains of red arrow are equal in size as in comparison to domains of black arrows. So, this is where the polarization becomes equal to 0.

And then, when you start the process again and this field is basically called as coercive of field. And when you take this field further stronger in other direction you go to. So, here look, we go basically all the way to saturation. So, here you can see that these red arrows become stronger and stronger the black arrows the area occupied by black arrows has become smaller and smaller. So, as a result when you go to this switching field which is the field at which saturation occurs, you reach the complete reversal of polarization.

So, this is the minus P s state. So, this animation sought of helps you in understanding how the domains nucleate? And how does the polarization change from plus P s to minus P s going through plus P r and 0 P r states, and the same thing will happen when you go from here to minus P s to plus P s. So, which is identical so this symmetric this hysteresis curve is symmetric with respect to the both the axis. So, as a result you have plus P r and minus P r and plus E c and minus E c, any shift in the hysteresis curve is because of extraneous regions not because the ferroelectric has that. So, ferroelectric intrinsically has this hysteresis loop which is symmetric irrespective to both the axis.

So, I hope this animation helps you understand the basically objectives of this. So, just let me go again you have a virgin state, you start nucleating new domains. Then, you get a mono domain state, when you get a mono domain state from here P s to P r not all the domains remain in that orientation. What happens is that you form the new domains with opposite orientation and these new domains with opposite orientation result in decrease in the polarization. But you still have finite polarization and then the whole process goes through P is equal to 0, because the volume or area of oppositely oriented domain is equal to volume of other orientations. So, plus and minus P s cancel each other. So and when you go to switching field which is the field at which the saturation occurs then, all the domains have oriented in other direction. So, as result you get minus P s.

So, this is what is the domain formation and domain reversal under the applied field when you switch a ferroelectric material, and these quantities you must remember P s is called as saturation polarization P r in the ferroelectric terminology is called as remnant polarization, E c is called as coercive field. And the units you can see this would be micro coulomb per centimetre square. So, this is coulomb per meter square or then, you can add whatever you want this is volt per meter. And these are the 2 quantities of these units the units which you need to remember. Now, the now next question comes is how do you measure the ferroelectric hysteresis loop?

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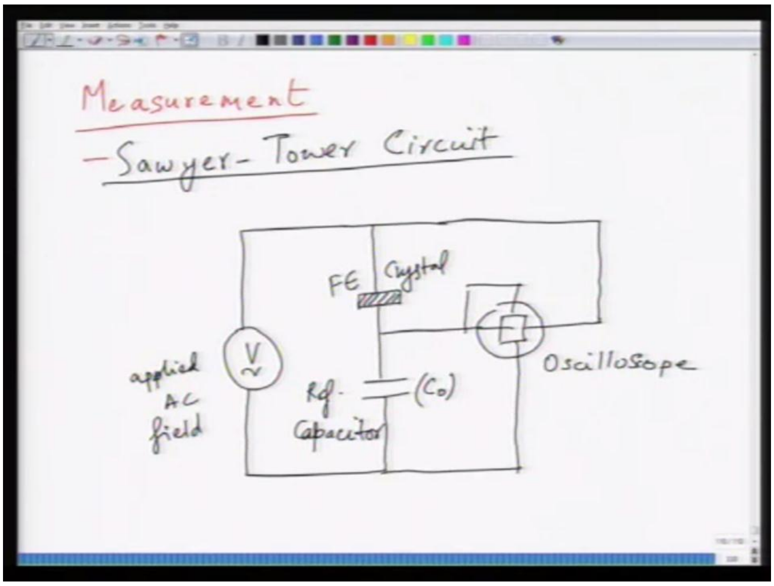

Measurement

- Sawyer- Tower Circuit

Now, measurement of hysteresis loop is essentially based upon sawyer tower circuit who basically developed this methodology to measure the ferroelectric polarization. So, basically what happens here is, this is the circuit diagram. So, basically you have oscilloscope to take the measurement on screen. This is the applied field basically A C field and what you do is that you put a ferroelectric material, ferroelectric crystal in series with a reference capacitor. And this capacitor is essentially a linear capacitor with the. So, you can say capacitance C naught. And basically in this configuration the voltage drop across C naught is proportional to the polarization of the crystal. And that is how and you measure the polarization or the charge which is accumulated in the ferroelectric crystal. And that you take with respect to a reference capacitor. This is very simple circuit it can be many people have designed equipments in the in their own labs based on this circuit. However, now a days you have variety of commercialized instruments are available which cannot only do the polarization measurements.

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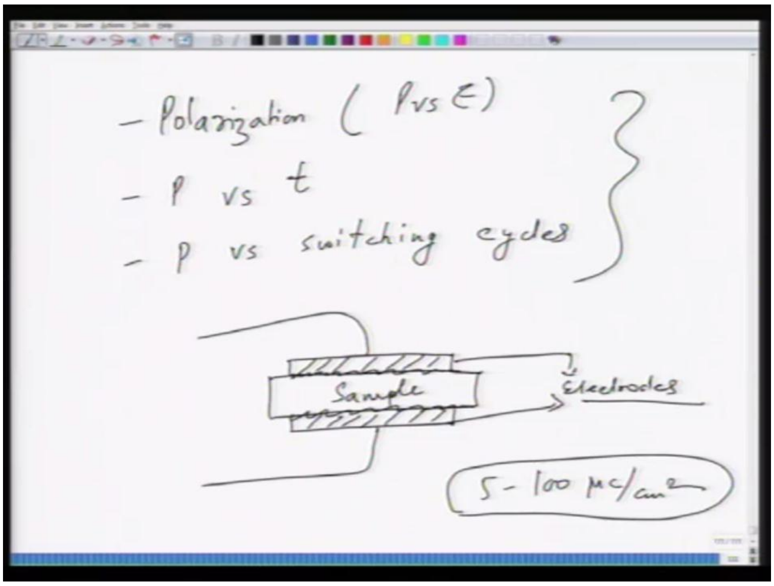

So, you can do measurements like polarization which is basically P versus E, you can also measure polarization versus time, you can also measure polarization versus switching cycles. And variety of these measures, measurements are available in order to make the measurements sample must have. So, this is your sample. So, in order to make electrical measurements sample must have contacts, these are your electrodes which are called as electrodes top and bottom electrodes.

Now, these electrodes should be of such a metal. Now, this is that the choice of electrode comes into picture and which is very important, that this electrode should not inject the charges in the ferroelectric material ferroelectric is an insulator. As a result you are only measuring the short range displacement of the material or the charges inside the material. In order to however in order to measure any response, you need to have metal contacts, but this interface between the metal contacts and the sample is very important. And this gives size to extraneous effects in the especially in the dielectric constant versus frequency measurement. And often, since metal has a different structure as compared to ferroelectric material, this interface is of significant importance. And this if you remember we discussed when we module 4, the role of this interface can be taken care by making proper impedance spectroscopy measurements.

However, in order to make ferroelectric measurements, remember that these typically these electrodes are made of high work function materials like, you make these you take platinum or gold which are basically or silver paste also in case of ceramics. So, these noble materials do not inject the charges inside this ferroelectric. As a result the measurements are much more robust, and these measurements can be done at various times and frequencies typically they are A C frequency, A C measurements depending upon the type application of course. So, you are looking at for instance a memory kind of application, you are looking at lower frequency material. But if you are looking at a microwave then, you need to go to higher frequencies.

So, which is in the range of giga Hertz and so, this is how you need to make the connection? And then of course, you apply the electric field making sure that you have a reference capacitor series with the sample. So, this is how you make the measurements? Typically, the polarization of samples range anywhere from 5 to 100 micro coulomb per centimetre square. This is a typical value solved or final answer, but typically that is where the values you see and make sure when you make the ferroelectric measurements when you get.

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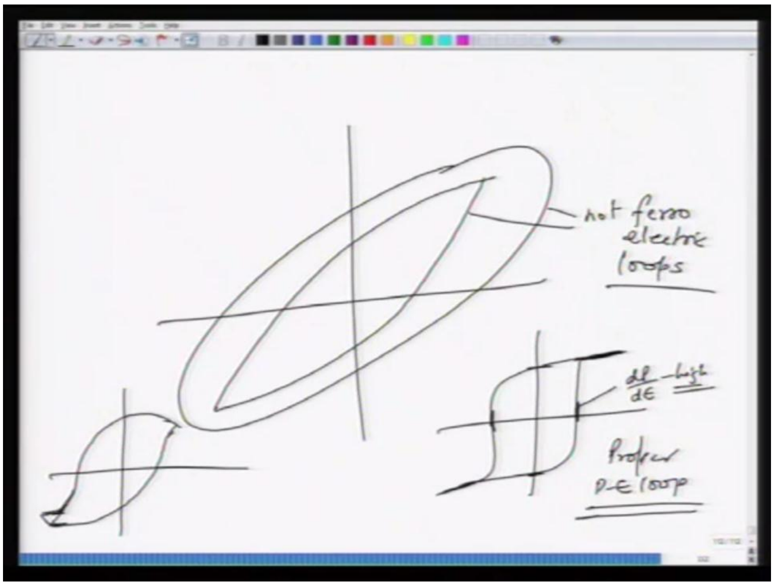

If you get any loop like this; this is not a ferroelectric loop you should not get a banana kind of loop like this, you should always. So, these are not ferroelectric loops. So, this is very important from measurements point of view, many people, many young students who do not understand this, they often confused with these two kinds of loops as ferroelectric loops. Whereas these two are not ferroelectric loops, a proper ferroelectric loop is like this is the proper ferroelectric loop a properly saturated ferroelectric loop you must get saturation here. And this should have basically the slope should be very high. So, d P by d E at these points should be high. So, this should be as vertical as possible and this should as plat as possible. And unless you have this kind of saturation, this is not a ferroelectric.

So, in many materials you see that you will have this kind of material. You have this bending of the tip and this is also because of leakiness of the sample. This is a perfect ferroelectric which is not leaky; this is the imperfect ferroelectric which has lot of leakage inside it. And these are basically not ferroelectric materials these could be lossy capacitors etcetera. So, make sure this is your proper P E loop for a. So, your bench mark is essentially this.

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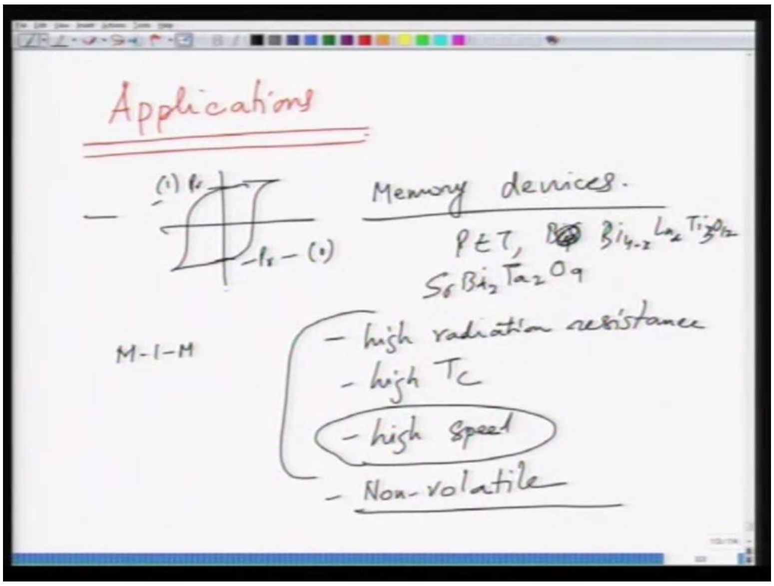

Applications

Memory devices.

PZT, $Bi_{4-x}La_xTi_3O_{12}$

$SrBi_2Ta_2O_9$

- high radiation resistance
- high T_c
- high speed
- Non-volatile

M-I-M

So, the applications of ferroelectrics they are used in variety of applications. Since you have these two states of polarization in the hysteresis loop, so you have a hysteresis loop like this, so you have plus P r and minus P r these two are often used as 0 and one state of memory binary data storage. So, they can be used in memory devices. So, materials like P z T which is lead zirconate titanate bismuth B B i 4 minus x L n x T i 3 o 12 which is lanthanide doped barium bismuth titanate, strontium barium tantalites or strontium bismuth tantalite. All these are they were have been tried for memory devices and they have been successful to some extent. The advantage of these materials is they have very high radiation resistance as well. So, they can be used in a space without damaging the polarization in the space they have large T c.

So, high radiation resistance, high T c very high T c of these materials, most of these materials have T c in that axis of 400 degree centigrade, and they have high speed. So, they are much faster than magnetic materials which are conventional memory materials there are some problems in terms of integration. But if look at if you look at the fundamental parameters they are way superior as compared to magnetic materials. So, they are used for memory devices, and basically in memory devices the configuration is M I M configuration. So, you have metal insulator metal configuration.

And then, second application can all and they can of course, be used as actuator sensor etcetera, because each ferroelectric is always a piezoelectric and pyroelectric, as I will show in case of piezoelectric and pyroelectric material. And these memories are called as non volatile memories. And you can see why non volatile, non volatile which means the data is not volatile which means when you remove the field the data is always stored. So which means this is a good point, and since they are fast they do not need a dram why you need a DRAM? Why do you need a DRAM in case of normal computer? Because magnetic memory is slow.

So, in order to speed up the operation, you need to have a buffer memory which is called as DRAM which is fast memory. But DRAM is volatile if you do not press control s, you will lose the data, because if the especially when the power goes off suddenly power goes off. So, need to be you need to have saved, you need to save the data before you switch off the power. Here you do not need to switch put control s, because the material is always stored in plus P r or minus P r state at 0 field. So, even if your power goes off data remains there. So, that is why these are called as non volatile memories.

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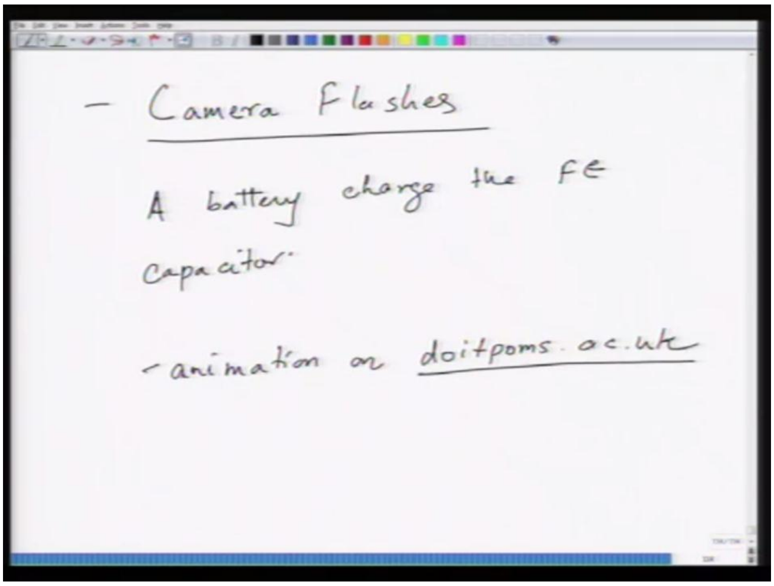

- Camera Flashes

A battery charge the FE capacitor.

- animation on doitpoms.ac.uk

And that second application could be in camera flashes and camera flashes is basically. So, you have in this application; you have a battery. So, basically a battery charges the ferroelectric capacitor. So, you charge the ferroelectric capacitor using a battery first, and when this is fully charged you connect this ferroelectric material to a bulb. And then, since this material is charged, it gives its energy to the bulb and the bulb flashes. Now once a bulb has used a material bulb has used the charge ferroelectric capacitor is discharged you need to charge it again. So, this is what is used for camera flash applications again you can see the video animation on. And there are animations on this site which you can go through how a flash bulb operates. And so, this is what basically is sought of the end of this part of this module on ferroelectric materials.

So, essentially ferroelectric materials in summary are non symmetric polar materials where direction of polarization can be reversed by reversing the direction of applied field. They undergo a transition which is called as a Curie transition, above this Curie temperature they are paraelectric. And below this Curie temperature they are in ferroelectric state and this is basically a phase transition. So, it can be it can be a first order, second order transition depending upon the material, but it characterizes a change in the phase of the material or structure of the material typically what you call it is a material goes from non centrosymmetric to centrosymmetric state to non centrosymmetric state when you cool a material below T c. And that is when it becomes ferroelectric.

And then, ferroelectric materials also have domains, these domains are regions of uniform polarization. However, because of energetics mono domain is not stable state. As a result you form multiple domains and multiple domains means you need to have a domain wall and then, the balance of energy has to govern the domain size. So, that analysis we did and we found that domain size depends upon parameters like surface energy of domain wall as well as polarization in the material. And that gives you what is called as a stable domain size? And then finally, we looked at the how the domains nucleus nucleate and grow inside a material? And in ferroelectric materials, it is not consumption of unfavourable oriented domains by favourably oriented domains they do not grow rather what you have nucleation of new domains under growth of those domains at the expense of any other domains.

So, as a result you have domain state which is always dependent upon nucleation in growth and that gives you the features of hysteresis curve. And since you have plus and P r plus P r and minus P r state, this makes this material extremely useful technologically. And one of the most favoured; one of the most fancied application is non volatile memory just been tried on a few materials, it is not been commercially that successful yet, but there are promise promises and the moment we get the fabrication integration of fabrication technology is right that should be possible. So, this is the end of this lecture. In the next few lectures, we will discuss pyroelectric and piezoelectric materials to finish this module off.

Thank you.