Fundamentals and Applications of Dielectric Ceramics

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Lecture – 31

Basics of Ferroelectric Materials

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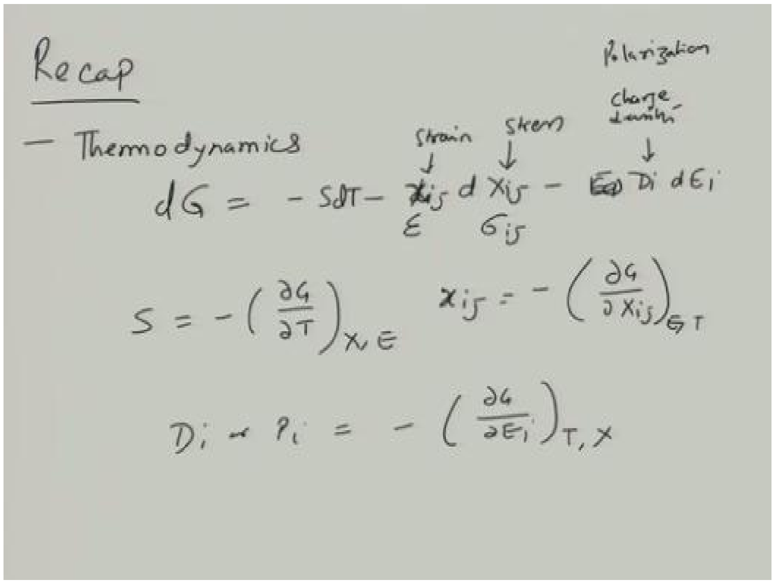

Recap

— Thermodynamics

Strain, Stress, Polarization / Charge density

$$dG = -SdT - \underset{\varepsilon}{x_{ij}}\, d\underset{\sigma_{ij}}{X_{ij}} - D_i\, dE_i$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{X,E} \qquad x_{ij} = -\left(\frac{\partial G}{\partial X_{ij}}\right)_{E,T}$$

$$D_i \sim P_i = -\left(\frac{\partial G}{\partial E_i}\right)_{T,X}$$

So, welcome again to the new lecture of the course fundamentals and applications of dielectric ceramics, so let us just briefly recap what we have been doing until last lecture, so in the last lecture we finished on thermodynamics of these materials basically, looking into how these properties are related to each other. So, to begin with we wrote this thermodynamics expression, we calculated the free energy change that is:

$$dG = -SdT - x_{ij}dX_{ij} - D_i dE_i$$

And we can also write x as ε but we introduce ε because we are using what electric permittivity and then, you write this as negative of D_i.dEi, you can say charge density or you can say polarisation and E is the electric fields, so from this we determine what are the properties such as entropy that was equal to:

$$S = -\left(\frac{\partial G}{\partial T}\right)_{X,E}$$

And then we also determine what is D_i or we can also say Pi as:

$$D_i \;\; or \;\; P_i = -\left(\frac{\partial G}{\partial E_i}\right)_{T,X}$$

from these we determined various, so if you write the full form of these total differential forms, you can see that entropy is for example consists of terms such as heat capacity, piezo calorific effect and electric caloric effect, whereas if you write the same expression for example, for strain you can see that it consists of terms like thermal expansion, piezo calorific effect.

And that is converse piezo calorific effect as well as compliance; elastic compliance and if you write the same expression for things like for polarisation, you can see consists of terms because of temperature that is pyroelectricity and then because of stress that is direct piezo electricity and then because of the change in electric field that is the electric permittivity and you can combine these together and look at the equivalence of various parameters such as you can establish the equivalence between direct and indirect piezo electric effect.

Thermodynamically speaking, both are similar. Similarly, if you establish equivalence between piezo calorific effect; piezo calorific effect connects mechanical to temperature, so it is equivalent to thermal expansion that is also related to expansion with respect to temperature, so these sort of properties are inter related to each other and then we wrote the constitutive equations for piezoelectricity.

So, this sort of provides a little bit of mathematical thermodynamic basis for writing these expressions in reality, we use much simpler forms because of symmetry and thermodynamic arguments and for poly-crystalline materials we can take them to the scalar or isotopic, as a result many of the properties becomes simplified in poly crystalline materials but nevertheless, it is important from the sake of complete understanding to understand the exact forms of these properties.

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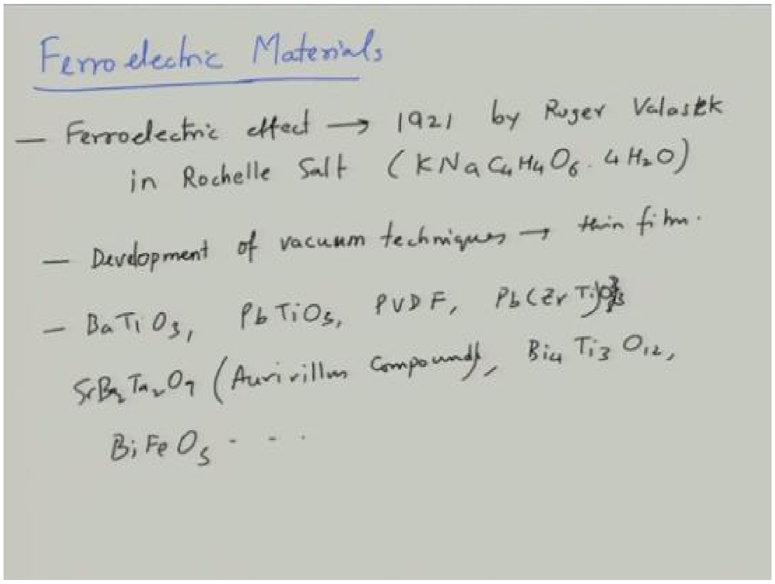

Ferroelectric Materials

- Ferroelectric effect → 1921 by Roger Valasek in Rochelle Salt ($KNaC_4H_4O_6 \cdot 4H_2O$)
- Development of vacuum techniques → thin film.
- $BaTiO_3$, $PbTiO_3$, PVDF, $Pb(Zr\,Ti)O_3$, $SrBi_2Ta_2O_9$ (Aurivillus Compound), $Bi_4Ti_3O_{12}$, $BiFeO_3$ . . .

So, now what we will do is that; we will begin in this lecture with our discussion on ferroelectric materials, so we have looked at the equations related to piezoelectrics and we also looked at what piezoelectric phenomena is now, we will look at the phenomena related to ferroelectric materials. So, ferroelectric materials let us just go into bit of history of it, we know that ferro electricity from the basics if you remember every ferroelectric is by default a pyroelectric and a piezoelectric.

And many of the pyroelectrics and piezoelectrics that we use in practical application they are nothing but ferroelectric. So, ferroelectric effect was first discovered in 1921 by Roger Valast, he was a Czech scientist and he discovered this in Rochelle Salt which is nothing but $KNaC_4H_4O_6.4H_2O$. Basically, a potassium sodium based salt that shows ferroelectricity, now we do not have much research earlier on but later on after the Second World War, there was a renewed interest in these materials.

And especially Russians and East Europeans carried out a lot of work on these materials, lot of work was carried out in US as well; and as a result there was renewed interest in ferroelectrics after Second World War and lot of discoveries were made, lot of devices were made, so it became really popular after the development of vacuum technologies.

Because one could make thin film of these materials and these thin films are far more exciting as compared to bulk materials. For example, for ferroelectric memories and data storage devices they were of great potential, they were very important candidates or very interesting candidates once upon a time in 90s and 2000's, so lot of work was there, so development of vacuum techniques lead to lot of thin film work.

So, ferroelectrics; typical ferroelectrics or you can say Rochelle salt other than that you have barium titanate, we have lead titanate, you have PVDF, then we have $PbZrTiO_3$ and then we have $SrBa_2Ta_2O_9$, which is basically, Aurivillius kind of compound then, we have Bismuth titanate, now we have compounds such as $BiFe_3O_3$, they are all ferro electric materials, so there is a huge variety of materials are which are ferroelectrics.

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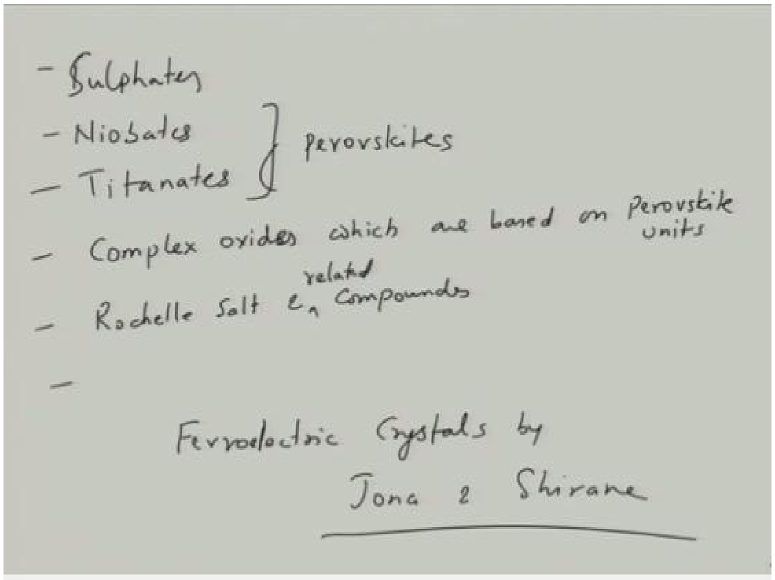

- Sulphates
- Niobates } perovskites
- Titanates
- Complex oxides which are based on Perovskite units
- Rochelle Salt & related compounds
-

Ferroelectric Crystals by
Jona & Shirane

So, for example they can be divided into certain categories, you can have sulphates, various sulphates which are ferroelectrics, then we have niobates, then we have titanate. Titanes, niobates many of them found to be perovskites and then we have many of the complex oxides based on perovskite units, so things like bismuth titanate and strontium bismuth tantalite, they are all based on series of perovskite stacked together along a certain axis.

And then of course as said Rochelle salt, parent compound and its related compounds and then, you have sulphates, niobates, complex oxides, titanates etc., there are huge series of materials, if you really wanted to know about the materials, I would recommend you go to through a book *Ferroelectric crystals by Jona and Shirane*, these 2 gentlemen are pioneers of ferroelectrics and they have written this beautiful book ferroelectric crystals.

It is a book which goes through a variety of materials and gives you a good insight into ferro electricity in different materials, their structure, their properties and so on and so forth and also it treats whether bit of thermodynamics of ferroelectric materials.

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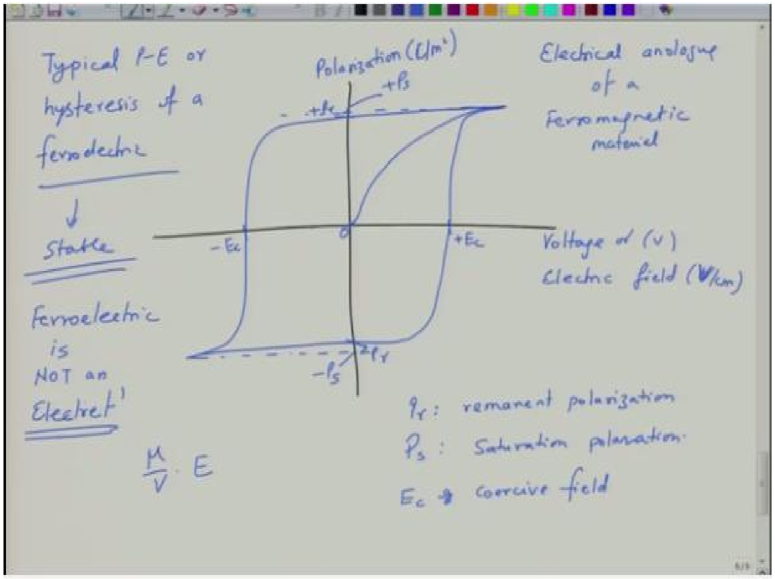

Typical P-E or hysteresis of a ferroelectric
↓
Stable

Ferroelectric is NOT an Electret

$\frac{M}{V} \cdot E$

Electrical analogue of a Ferromagnetic material

P_r : remanent polarization
P_s : Saturation polarisation
E_c → coercive field

Now, ferroelectric materials, so we will see what ferro electric materials is a gem, a ferroelectric materials by nature it is a non-linear dielectric, when you switch a ferro electric and electric field, a ferroelectric shows a hysteresis curve like this, so just like a magnetic material, a ferro magnetic material, the ferroelectric material also exhibits what we call as the hysteresis of this is polarisation which is in typically, C/m^2 and the x-axis is voltage or electric field.

So what it shows is the hysteresis loop to essentially add zero field, you have two states which are positive and negative, so we call it $+P_r$ and $-P_r$, P_r is called as remnant polarisation and then this remnant polarisation saturates to polarisation which is called as $+P_s$ and here you will have this is $+P_r$, $-P_r$, this is $-P_s$.

So, P_s is called as saturation polarisation and then polarisation is zero not at the zero field but at a non-zero field which is called as $+E_c$ and $-E_c$, where E_c is called as coercive filed, and so basically, what happens is for a virgin ferroelectric, you start in this fashion and then when you keep repeating the loop, it just keeps making the loop again and again and again and again, you do it for many cycles, it will produce the same loop again and again.

So, this is basically because of as we will see later on formation of domains in these materials, so the switching processes somewhat similar to what we see in ferromagnetic materials, in some sense you can call it as a electrical analogue of a ferromagnetic material; in ferromagnetic material this loop will exist between magnetic field and induced moment or flux density whereas, in this case, this is a loop between voltage or electric field versus polarisation.

So, polarisation is a charge density and this is the electric fields, so basically you are measuring the charge density on a capacitor and this is what you see, the area under the curve is essentially the energy, the product of P and E which is the; product of P and E is nothing but:

$$P.E = \frac{\mu}{V}.E$$

and this is nothing but the energy density, so energy that is spent in the process of switching.

So, we will see mechanisms of why this happened but this is a typical you can say P-E or as we say hysteresis curve of a ferro electric material, so if a material is ferroelectric, a material will show a nonzero polarisation at zero field and the polarisation is zero at some finite field and this is a stable effect, so most important thing is this is a stable effect, it remains a stable for long time, so these are another class of materials called as electrets, in which this phenomena is transient, so temporary phenomena.

So, you will see in electret also similar sort of loop but that is not a stable as a function of time, so do not confuse ferroelectric is not an electret, so lot of electrets are also tend to show similar loops may be of lot of very good quality loops but they show hysteresis between polarisation and electric field but that is not a permanent behaviour, this is a permanent behaviour, as long as your temperature is below certain temperatures.

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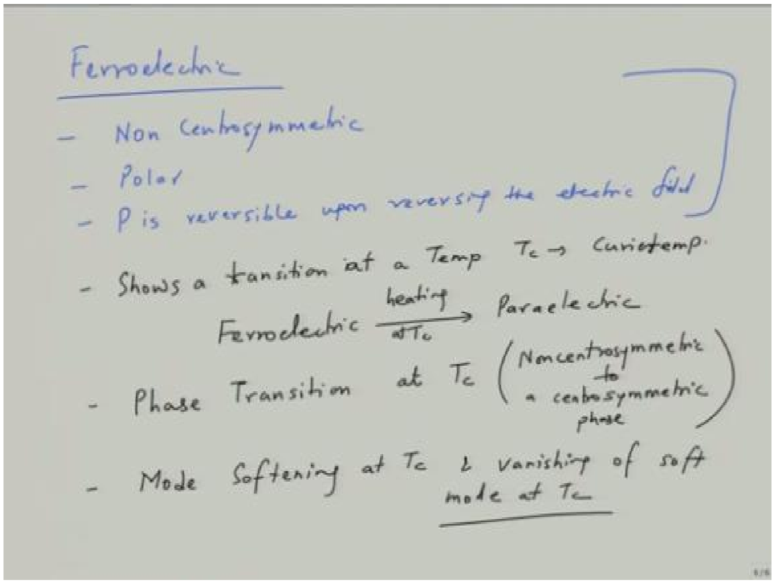

Ferroelectric

- Non Centrosymmetric
- Polar
- P is reversible upon reversing the electric field
- Shows a transition at a Temp $T_c \rightarrow$ Curie temp.

$$\text{Ferroelectric} \xrightarrow[\text{at } T_c]{\text{heating}} \text{Paraelectric}$$

- Phase Transition at T_c (Noncentrosymmetric to a centrosymmetric phase)
- Mode Softening at T_c & vanishing of soft mode at T_c

So, what are the characteristics of a ferroelectric; ferroelectric material is:

1: It is non-centro symmetric.

2: It is polar secondly

3: P is reversible upon reversing the electric field

These are must have requirements additionally, ferroelectric material shows a transition at a temperature called as T_c which is called a curie temperature, above which when you heat it, it becomes paraelectric.

So, ferroelectric will become paraelectric upon heating at T_c and there it shows a phase transition so generally, this transition will be from or non-centro symmetric to a centro symmetric, so you can see the terms are similar just like the magnetism, we have paramagnetic, we have para electric here, just like we have ferromagnetic, we have ferroelectric here, so there is a transition from a non-centro symmetric phase to a centro symmetric phase at a temperature T_c and this T_c is called as curie temperature.

And then in physics language, we also call it there is a mode softening at T_c and the soft mode vanishes that T_c that is in terms of when you do Raman measurement on these materials, you will see a disappearance of the soft mode at T_c and this is the signature of ferroelectric and vanishing of soft mode. These are certain characteristics of ferroelectric material.

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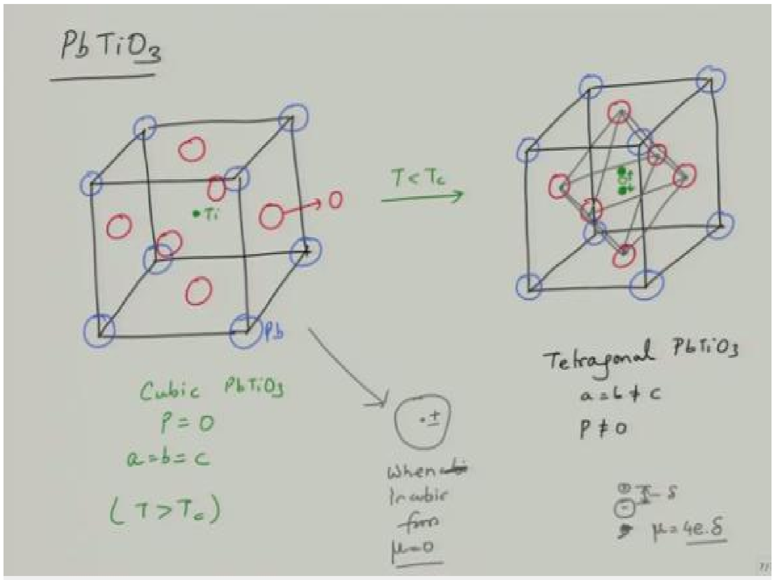

So, essentially what happens, so if you take a model example of let us say $PbTiO_3$, it has a perovskite structure, drawing the structure of $PbTiO_3$, which is, center of faces are all the Pb ions, let us draw the oxygen ions, all corners are occupied by oxygen ions, then we have somewhere in between we have a titanium ion, this is cubic $PbTiO_3$ with P being equal to zero, this is a centro-symmetric material, it does not have a polarisation, it has $a = b = c$.

So, as you cool it below T_c , this will transform into a tetragonal structures, so what will happen is that this a, b will be parameters will be different now, so it will be slightly will be a the lattice distortion leading to the formation of a tetragonal structure, where so this will become tetragonal where $a = b \neq c$ and the overall P is not equal to zero.

So, in this case what will happen is that you have similar atoms sitting at various positions, this is oxygen, do not worry about the sizes, the sizes and this will be titanium now, the titanium in this case will be slightly of centred, so this is the central position, so titanium will either be here or it will be here, so this is the downward or upward movement of titanium. So, titanium is little bit shifted with respect to the dipole with respect to the; so you can see that oxygen here makes an octahedron, this is oxygen octahedron.

And when so oxygen octahedron will have certain charge, it will have net charge of -4, titanium has +4 charge, so let us say if we do a dipole movement calculation, then the centre of negative charge and centre of positive charge when they match with each other, when it is in cubic form, so these pluses and minuses match each other as a result, $\mu = 0$. Now, when you cool it below T_c, a central titanium atoms move up and down as a result, now the centre of negative charge is somewhere here, this is my negative.

And the positive charge is either here or here, so let us say we take one of them, there is a distance δ let us say, δ is in a few pico metres. Now, what we have is we have a dipole moment of 4 electrons multiplied by δ, so this is a nonzero dipole movement that is developed and as a result, you have a permanent dipole movement which is called as and that is why ferroelectric material show nonzero dipole moment of polarisation at room temperature in the absence of electric field.

Because, they have a nonzero dipole moment, so these are polar non centro symmetric phases which forms and this is manifested in what we call as free energy.

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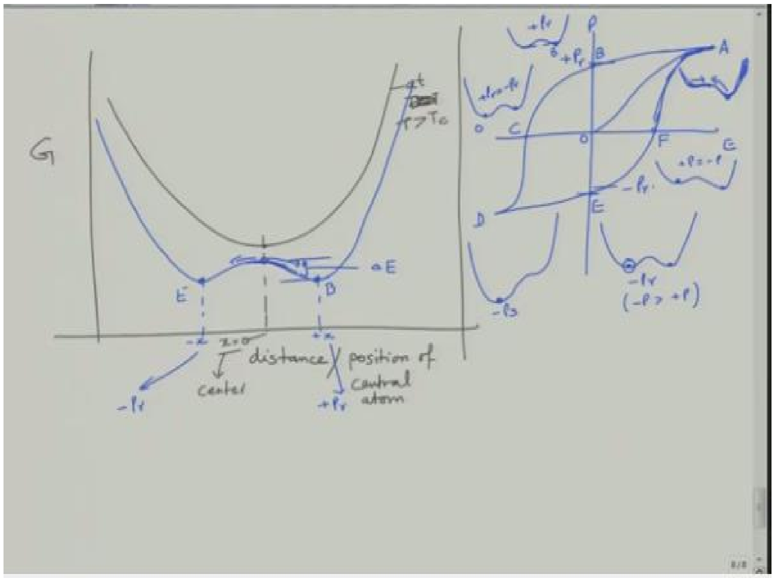

So, when you plot a free energy of such a solid as a function of distance, a position of atom, let us say position of central atom, now when it is about T_c, then free energy shows a minima, this is at $x = 0$; $x = 0$ remains centre, the titanium atom sits right here, however so this is at $T > T_c$, when the temperature changes, then what happens is that the free energy shows the double well kind of structure.

So, there are two minimum positions, these correspond to +x or -x, they correspond to $-P_r$ or $+P_r$, so these are both equal energy position, so this is the maxima now, so x is equal to zero, you can see there is a local maxima, so which means, $x = 0$ is not a stable position, atom cannot sit here, atom has to fall either one side or other, so depending upon the local perturbations, it will either fall into right one or left one.

So, as a result you have two states; one of the two states which has stable as $+P_r$ or P_r and this is because the titanium atom now sits either here or it sits here. Now, this is what happens in terms of free energy, we will do the free energy discussion a little bit in detail, so this is basically, you can see this energy is ΔE and this energy when you do the switching for example, when you go from $+P_r$ to -Pr, you are saying you need to overcome this energy.

So, if you look at the hysteresis for instance here, now try to relate these two hysteresis, this is your hysteresis curve, so this is P-E, so you are at this state $+P_r$, so when you switch it completely, so the loop is not very symmetric, so this is $-P_r$ and this is $+P_r$, ao this is zero. So, as you switch it, so you from zero field to here, let us say this is A, you come to B then you come to C, then you come to D, you come to E and you go to F.

And then this whole cycle continues so, as you switch it, you go from 0 to A for a new material, from A, you go to B, from B you go to C, you need to apply a extra field to bring it back to zero polarisation, then you go to D, then you go to E again. So, what is happening in terms of energetics let us say at B, you are in this position, so for a given region for it to come from $+P_r$ to $-P_r$, atom must shift from B to E, so this position will correspond E position.

So, looking at the free energy diagram what you see is that as you go from B to E, you need to overcome energy barrier of ΔE and this ΔE is nothing but what we call as switching energy barrier or switching barrier. So, basically how the free energy will change as you do switching, so for example at A, we are in saturation polarisation state, so which means all the atoms are shifted at A within.

So, we can say that the free energy curve will look like this, we have applied an extra electric field, so the wells are tilted in this direction, so all the atoms sit here, energy to go to this direction is very high but all of them can fall here, so which means, my energy wells are tilted extremely in this direction and all the atom sits here, this is the situation at A. What is the situation at B? Situation at B will be like this, so both of the wells are at equal height.

When you come to C, what will happen at C? You applied an electric field but still there are some atoms here, there are some atoms here and both of them are equal, in amount, so as a result, polarisation is equal to zero, when you go to D, it will all be like this, so all the atoms come here. When you go to E, it again goes to sort of equilibrium, so there are more atoms sitting on E than here.

So, we can see that there is a $-P_r$, this is $-P_r$, this is $-P_s$, this is zero, so you have all that so basically, you can say $+P_r = +P_r$ in this case. So, what $-P_r$ will mean is that your $-P > +P$ and then when you go to F again, you are applying positive field but then your wells are becoming like this but then you can see $+P = -P$.

But this is how as you apply the electric field in one direction, the wells get tilted to one direction and when you apply very large field, they tilt such a manner, so that all the atoms hop to one direction that is when you reach $-P_s$ or $+P_s$, but when you are at zero field, the wells are symmetric, so but there is an uneven distribution because of switching process and some, so although there is an equal probability.

But because of the ways switching that happened, not all the atoms of negative position move to positive position, not all the positive atoms moved to negative position atoms, so, this is how the switching happens in these materials, we will look at the microscopic aspects of switching and the free energy well and thermodynamics, a little later on.