Electroceramics

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Lecture - 26

So, in today's class, what we will do is that first just have a look at what we did last time, and then start with the new topic. So, in the last class basically we started module 5 which was on non-linear dielectrics.

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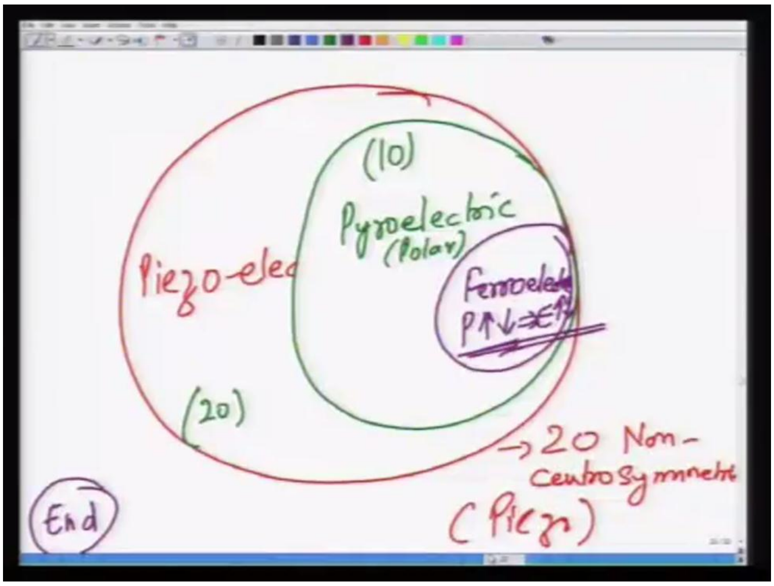

Now, these are the materials which are different from linear dielectrics in the sense that the behaviour of dielectric constant of polarization as a function of electric field is not linear. And they show some extraordinary properties like, coupling of electrical and mechanical parameters. So, such as what you see in piezoelectric materials effect of temperature on polarization such as in pyroelectric materials. And then you have when you switch, when you have a polarization electric field hysteresis loop which is which happens in ferroelectric materials. And the basis for these materials is the crystallographic basis. So, out of all the point groups your 20 are non centrosymmetric actually 21 are noncentrosymmetric. And out of 21 fourth expect 4 3 2, 20 noncentrosymmetric point groups are all piezoelectric.

So, the requirement for piezoelectricity is that the material should be noncentrosymmetric in nature. And then out of these 20 10 are pyroelectric which are polar. So, not only they are non centrosymmetric they also have a unique polar axis along which the properties are different in the ends of the polar axis. And then out of these 10 a few are ferroelectric in which the direction of polarization along the polar axis can be reversed by reversing the direction of dielectric field.

So, additional constraint imposed on the pyroelectric materials make some ferroelectric. So, naturally all the ferroelectric materials are pyroelectric and piezoelectric, but vice versa is not true. So, what we will do is in this lecture is we will take our discussion forward with the discussion on ferroelectric ceramics.

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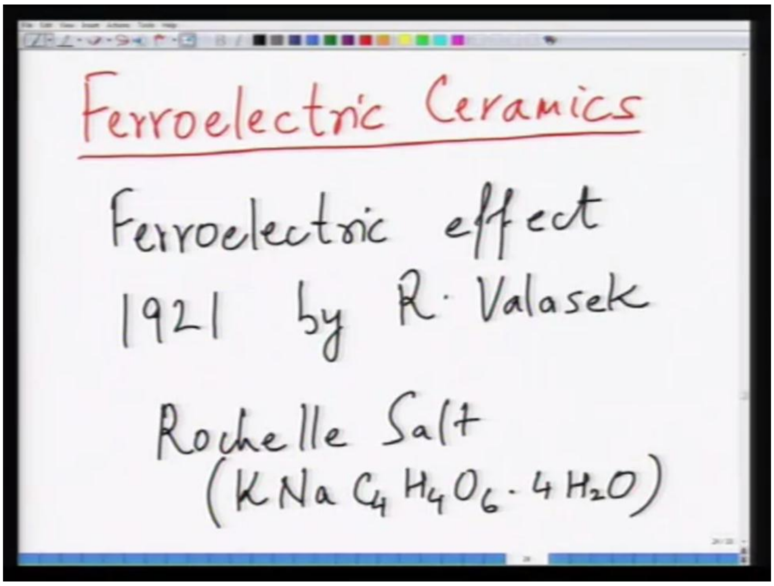

Ferroelectric Ceramics

Ferroelectric effect

1921 by R. Valasek

Rochelle Salt

($KNaC_4H_4O_6 \cdot 4H_2O$)

Now, among all these 3 classes of materials ferroelectrics have generated a lot of interest simply, because they are extraordinary they are ferroelectric, they are piezoelectric and pyroelectric at the same time. So, that naturally makes them interesting and the effect ferroelectricity, so effect of ferroelectricity or ferroelectric effect was observed in 19 21, and this was observed by a Czech scientist Roger Valasek, and he looked at what is called as Rochelle salt whose formula is K N a C 4 H 4 O 6 dot 4 H 2 O.

So, he was the first scientist to discover ferroelectricity in Rochelle salt, and this at that time did not generate enough excitement, because of variety of reasons, and however, later on after the Second World War, the research on just about the Second World War. There was a renewed technological interest in these materials, and that could have been because of variety of defence and military applications. And later the other applications also came into picture. Now, as a result in subsequent year’s variety of materials were discovered.

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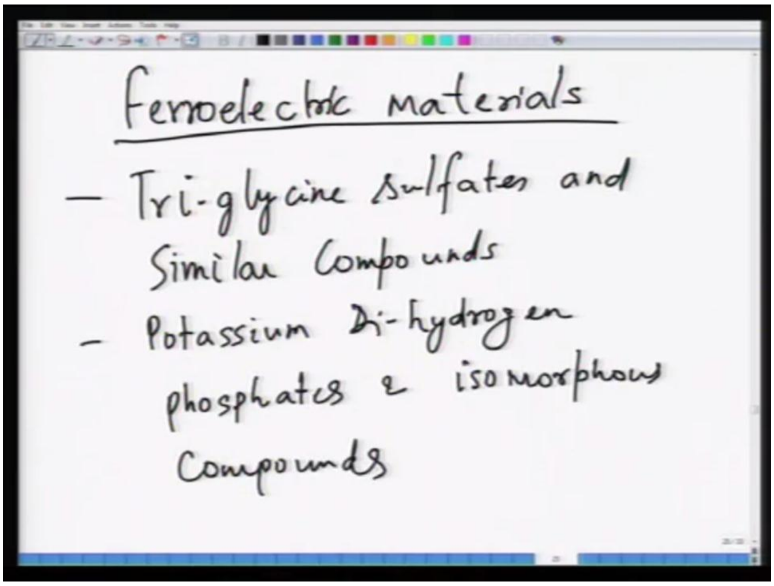

Ferroelectric materials

- Tri-glycine sulfates and Similar Compounds
- Potassium Di-hydrogen phosphates & isomorphous Compounds

And among them ferroelectric materials, that were discovered later on after the discovery by Valasek is for instance you can have tri-glycine sulphates, and similar compounds. You can have potassium di-hydrogen phosphate, and again similar compounds isomorphous. Isomorphous will mean isomorphous means same structure.

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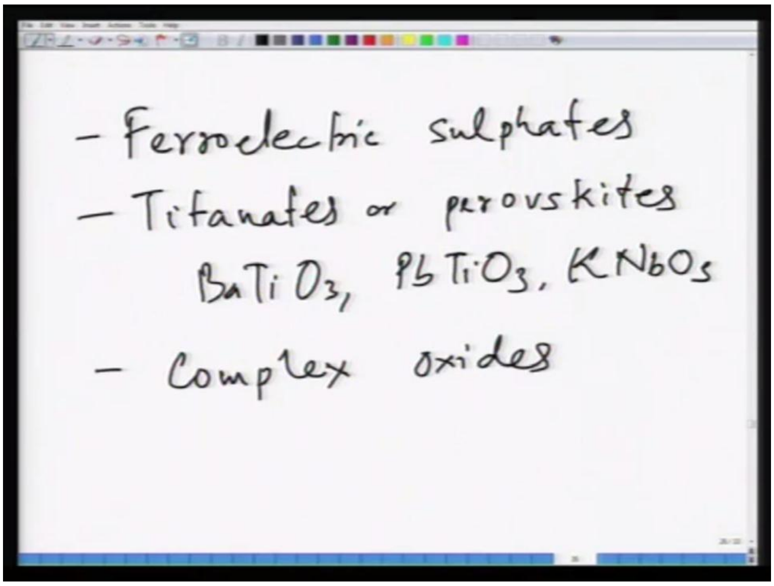

- Ferroelectric sulphates
- Titanates or perovskites
  $BaTiO_3$, $PbTiO_3$, $KNbO_3$
- Complex oxides

So, isomorphous compounds and you can also have materials like ferroelectric sulphates, plenty of sulphates are there in the literature which has been discovered. And then you have of course, Rochelle salt which was discovered earlier, and compounds similar to Rochelle salt. Then you have titanates or perovskites. And here the examples are you know barium titanate, lead titanate, and similar compounds like potassium niobates etcetera.

So, basically titanates or perovskite structure compounds. So, of course, potassium niobate is not a titanate, but it is a perovskite structured compound. And then you have complex oxides, and this would mean your material like strontium, bismuth tantalite, bismuth titanate which are you know aurivillius family family compounds. So, variety of these compounds was discovered Rochelle salt discovery was made at lower temperatures, it was ferroelectric at lower temperatures. But many more materials which are ferroelectric at room temperature, and that is what is exciting from the technological point of view. One of the important requirements for a ferroelectric material is that it should have a transition temperature which means above a certain transition temperature.

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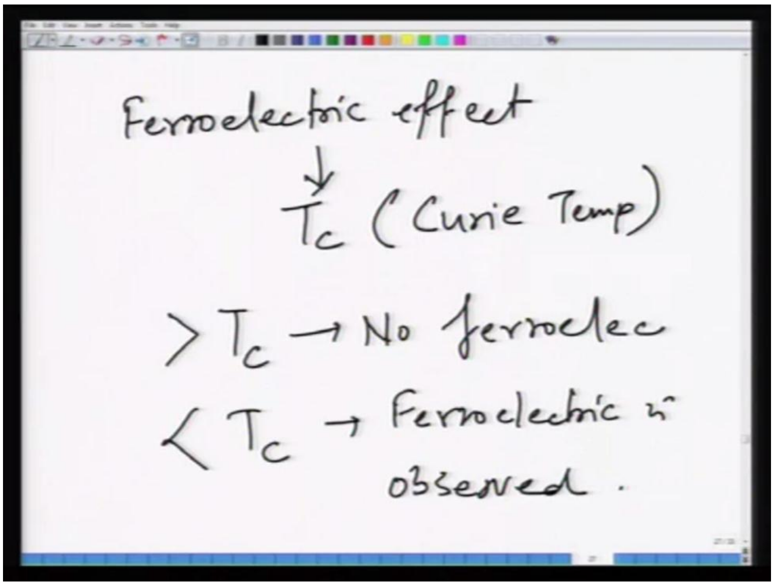

Ferroelectric effect

$\downarrow$

T_c (Curie Temp)

$> T_c \rightarrow$ No ferroelec

$< T_c \rightarrow$ Ferroelectric is observed.

So, this ferroelectric effect is associated with what is called as T c which is called as a curie’s temperature, Curie temperature and what happens is that. So, you have above T c no ferroelectricity, and below T c ferroelectric effect is observed. So, this transition temperature is quite important, we will come to the derivation of this curie’s law in a while. But this transition temperature is important, because the magnitude of this temperature make some material useful for technological applications. So, for as you can imagine for most of the technological applications this T c has to be larger than room temperature in fact as high as possible for instance. If you go for high temperature sensors etcetera this T c better it is if it is higher. So, from that point of view higher t c is better.

Now, what we will do is that although there are varieties of compounds which have been discovered most of the discussion on ferroelectrics. We will restrict totitanates which are the most studied and simplest of these compounds in order to explain the ferroelectric phenomena in variety of materials.

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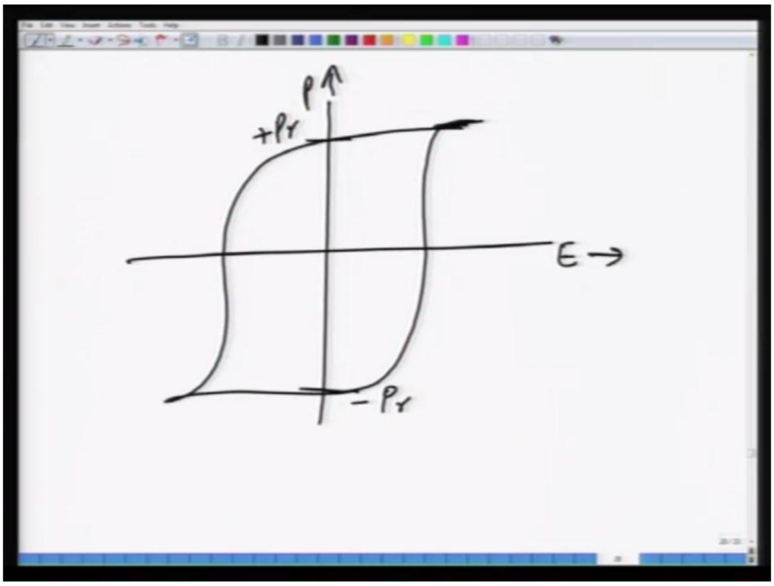

So, we will start first with the concept of in ferroelectric material given that these ferroelectric materials have, what you call as, this is the ferroelectric effect as we discussed last time. So, this is polarization; this is electric field polarization is nothing but charge stored. So, these two states which are equal and opposite called as plus P r and minus P r P r is remnant polarization. And these two states tell you that that there is a finite magnetic sorry a finite dipole moment at temperatures lower than T c in the absence of any electric field which means material can have either plus P r state or minus P r state at zero field. And this is what makes them exciting for variety of applications.

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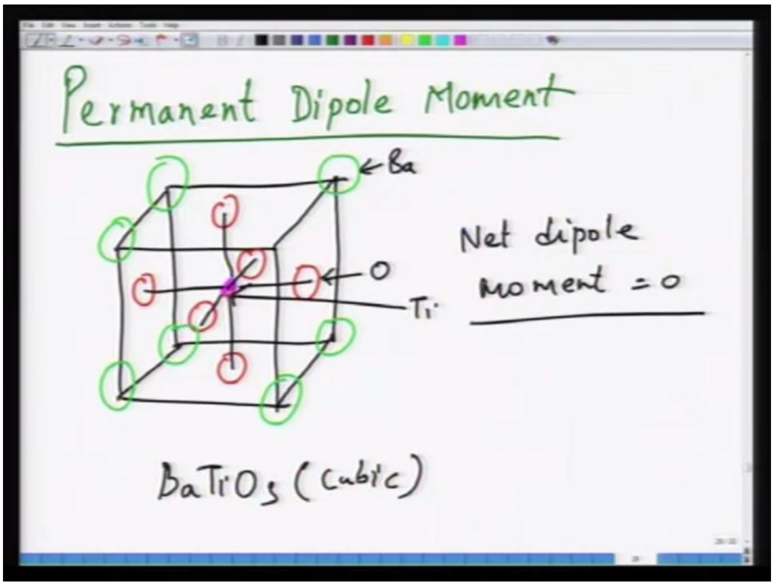

So, we will start with the concept of permanent dipole moment. So typically, what you have is a, you have a centrosymmetric material. So, a centrosymmetric material, because of symmetry will not show any polarization. So, for instance you take example of a cubic material. Now, let us say we take this form of cubic barium titanate. So, this is barium titanate cubic. Now, what we do is that we label the atoms here. So, you have oxygen sitting here, on the faces of this cube, and you have barium going here, and as you can understand titanium goes here, in the centre of a unit cell. So, this is barium, this is oxygen, and this is titanium.

Now, since this material is centrosymmetric in nature which means it does have centre symmetry. So, if you look around this point, all the other positions are symmetric around this point for instance, these 2 positions above and below or on the sides all of them are equivalent position. So, as a result this material does not show any dipole moment. So, net dipole moment for this is equal to 0, because of symmetry considerations.

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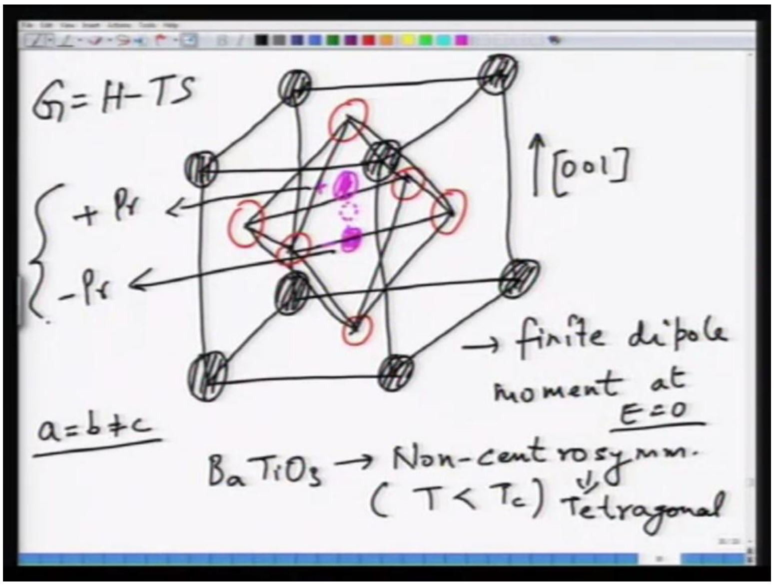

Now, when the material becomes non centrosymmetric? Now, if I draw a non centrosymmetric state, the material becomes tetragonal. So, B a T i O 3 non centrosymmetric, and this will happen at temperature T less than T c. In the previous case it was T greater than T c and it would in this case it would happen at T less than T c.

Now, in this case of course and this happens when the material is tetragonal. And in the tetragonal form what will happen is, a is equal to b is not equal to c, and alpha beta gamma remain equal to 90 degrees. So, if I draw the unit cell now, and if I just now put the atoms. So, you have barium atom sitting here, and the oxygen atom, let me see what the colour that we used last time red. So, oxygen goes at the centres here, this is oxygen and the titanium goes in the middle.

Now, what happens in this situation is, in the ferroelectric state what happens is, that this titanium atom does not sit at the centre of the unit cell rather where it sits is, because if it was sitting in the even in even for this structure. If it was sitting right in the middle of the unit cell, it will not give rise to any dipole moment again because of symmetry, now for this for the ferroelectricity to occur.

This atom which is at the centre of the unit cell will shift either up or down. So, what you will have eventually is either a position which is stable here or a position which is stable here and this is the centre. So, this is let us say plus state, this is the minus state. So, what happens here is now the centre of now what is the negative charge here? Negative charge is oxygen. So, you have oxygen octahedral. So, this is oxygen octahedral. So, this is oxygen octahedral. Now, if the titanium atom was sitting at the centre of these octahedral then centres of positive negative charges would match and they will be known at dipole moment.

However, when this titanium atom is shifted slightly towards top or towards the bottom which is along this axis which is 0 0 1 direction. So, it is shifted either along 0 0 1 direction or 0 0 bar one direction by a little margin then it gives rise to what is called as a finite dipole moment. So, this gives rise to finite dipole moment in the absence of electric field. So, it is polar in that sense and there is strong energy requirement for this. Now, this configuration is favoured for this particular kind of kind of material.

Because free energy, free energy as you know free energy is G is equal to H minus T s. And this change in free energy determines for a system to be in equilibrium or to be in the stable state, the delta G of that system must be negative. Now, what happens is that when the titanium atom is shifted in either positive z direction or minus z direction the free energy of this crystal is at a minimum as compared to when it would be at the centre.

So, there is a strong energetics behind it, and this plus state is characterized by what we call as plus P r state. This minus state is characterized by what we called as minus P r state at zero fields; remember this is at zero fields. So, finite dipole moment at E is equal to 0 and this is characterised by these two states.

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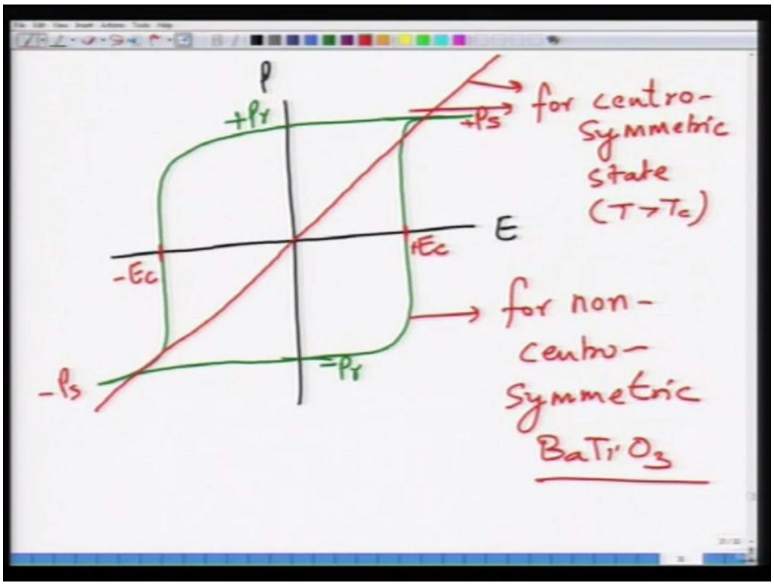

So, when you have this kind of material subjected now, when you draw a polarization versus hysteresis plot. So, if you draw such a plot for a centrosymmetric state which means it is in a cubic state then the material shows this kind of behaviour. So, this is for a at T greater than T c, when you draw the same plot in fact for this barium titanate at lower temperature, lower temperatures then the plot is something like. So, these 2 this is minus P r; this is plus P r. So, visually it is looking as if it is unequal, but it is so basically what will happen is if I just remove this line, make this line little in the middle. And I move this line is well and take this line through the middle.

So, this red would be the centrosymmetric, and this would be for non centrosymmetric barium titanate. And on the x axis and this actually this will be called as saturation polarization plus c P s. This would be called as minus P s and the zero the zero polarization fields are called as coercive fields. So, this is plus E c and this is minus E c. So, this is how it would be looking when you switch a material in the polar state, polar noncentrosymmetric state and in the centrosymmetric state. Now, this has strong implications in the terms of energy, so how it looks in terms of energy now, when you draw the free energy of such a crystal.

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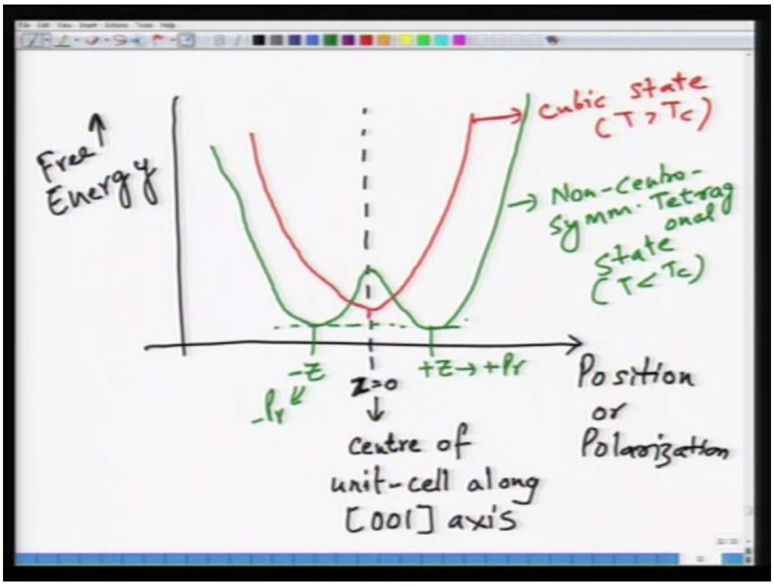

So, I am just going to do little qualitatively here, because quantitatively we will do somewhat later. So, if you draw a position or it could also be polarization, and then this is energy free energy. So, if you draw the free energy of such a crystal, now at T greater than T c. So, let us say this is the position x is equal to 0. So, x is equal to 0 would correspond to centre of the centre of unit cell along 0 0 1 axis. So, this is let us say Z is equal to 0 or I say Z is equal to 0 that is more appropriate. So, in the noncubic state in the centre of symmetric state sorry the material will show this kind of.

So, free energy minima occur at Z is equal to 0. So, this is for cubic state, but what happens at temperatures lower than T c, these free energy minima behaves like this. So, you have 2 identical states plus z minus z and this is corresponding to plus p r, this corresponds to minus P r. And this is at so you have states which are two stable states which are energetically equivalent. So, these two energies are of course, equal so depending upon how you go in the cycle, it will either be at minus z or plus z. And they would correspond to this situation. So, basically what it would mean is that if you correspond to their structure.

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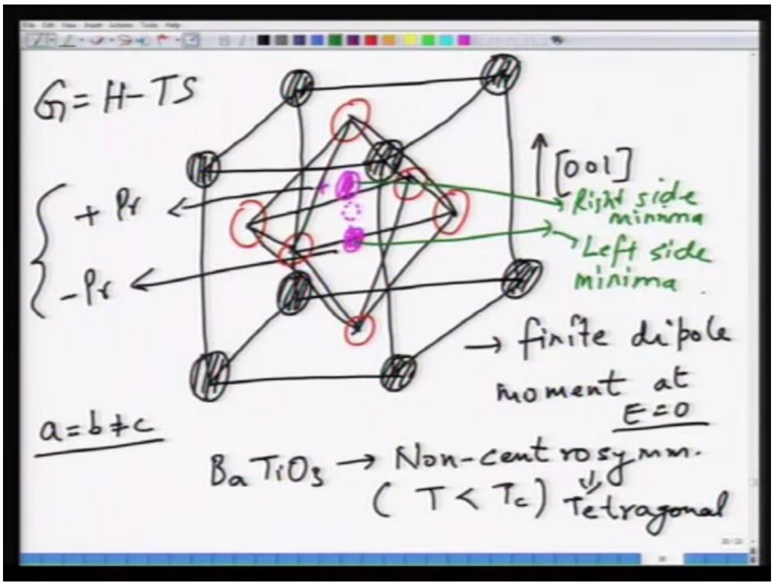

If you go back to their structure in the previous slide, in this slide, so this state will correspond to basically right side minima, and this will correspond to the left side minima. So, right side minima and this would be left side minima. And when you now, this is a situation at E is equal to 0, when you start making E finite which means when you start applying the electric field then what will happen is depending upon the direction of electric field these wells will start tilting. And as a result of tilt the atoms will move from one side to another.

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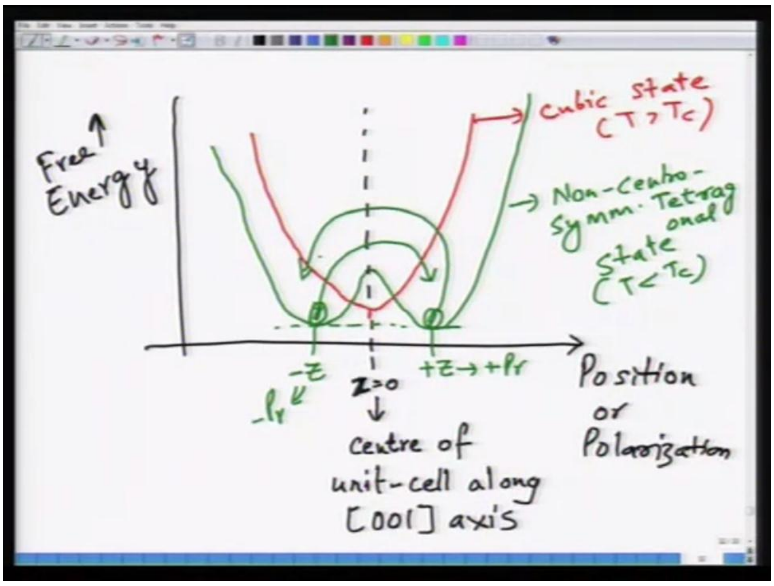

Because as you can see that either the atom is stable here or here, but not at the same time in both places, so it either goes from this to this position or from this to this position depending upon the direction of applied field. And that we will see in a little while.

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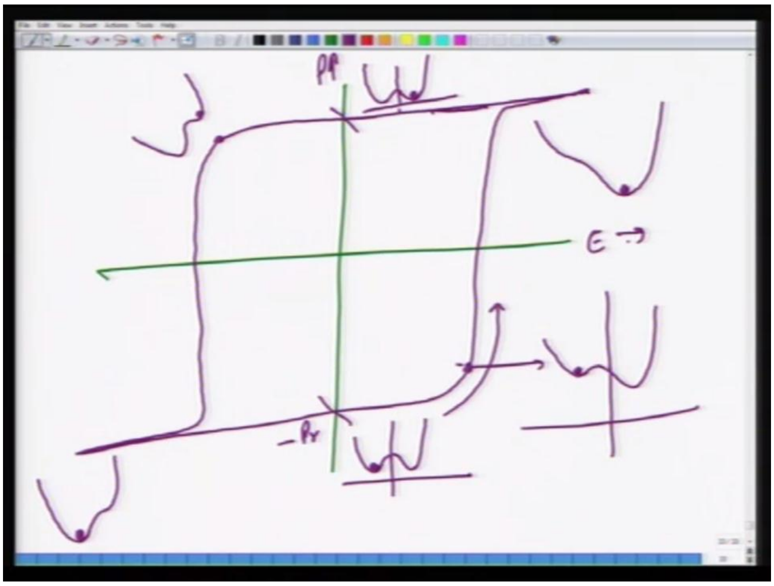

So, what will happen? So, when you draw the hysteresis loop, let us say we draw the hysteresis loop here. So, I know what the situation at these points is, at these points it is looking something like this. So, let us say this is the minus P r state. So, this is minus P r, your atom is sitting on this side, and this is your plus P r state. So, here so these two are equivalent position your atom is sitting on this side.

Now, what will happen when you start applying field. Now of course, when you go in this direction a field, then by the time you reach there, this must have come from this position to that position, which means as you go up for instance at some position here, the scenario would be, you would have a scenario like this. So, your atom is still sitting here, but the energy will it is a slightly tilted to the other side. So, as a result it has it is getting slowly the momentum to move to right side. So, when you when it reaches there then situation is like this. So, it goes completely this side, and when you go back here then the wells then you reverse the direction of applied field. So, wells again start tilting in the opposite direction. So, as a result it goes in this position.

Now, for instance in this position what will happen is that you will have now the wells will start tilting in the opposite direction. So, what you will have a scenario like this. So, your atom is still sitting here, and when you come back here, the again there is no well as such there the wells are too much tilted. So, they completely favour this direction. So, this is how it is going to look like when you switch the material from as a function of electrical field. So this is of course, is polarization and this of course, is electric field. So, these potential wells they shift they tilt as you change the direction of applied electric field determining the position of the atom on either side of the well. And so this is what energetically it is going to look like, it is a very qualitative description. We will look at the quantitative nature in a little while when we solve the when we go into landau theory, but this is how qualitatively energetics of a ferroelectric material is going to look like.

So, I hope that you understand what we mean here essentially, what it means is that a ferroelectric material is a material which is non centrosymmetric which is polar, but at zero fields, it has 2 equivalent minima’s and the centre titanium atom for instance in the case of barium titanate sits in either one of these position depending upon how you have arrived by switching the electric field. So, and this, these 2 positions because at minus P r, it has to sit in, let us say in this well at plus P r, it has to sit in this well when you go from plus P r to minus P r it has to move from right to left or left to right.

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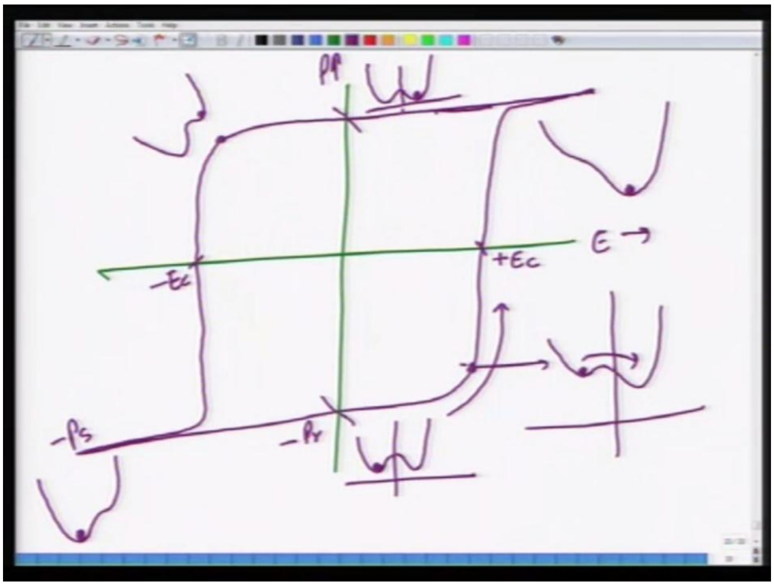

So, how would that happen, that would happen like this. So, if you are sitting, let us say on the left in this position, and when you start applying the field in the positive direction the wells will start shifting. So, they in the wells on the positive side get deeper and the on the negative side they get little higher.

So, as a result you are developing a direction of movement from this to that, but there is still a minima there. So, the atom sits here now you reach a state when you completely change the field. So, that this would be completely sitting in the right side well, because of left side well minima has is apparently lost. And when you again make the field back to 0 then both the wells become equal, but this atom is still sits there, because it has a large barrier to overcome. And when you start switching back in the reverse direction again the wells on the left start getting deeper, and well on the right start getting shallower. But not until when you reach minus P s state that is when the wells on the right become completely flat, so that the atom jumps over to the sides site on the right.

So, and this happens actually at this point. So, which is minus E c and plus E c. So, at minus E c the atoms from the right well will jump into the left well, and this would be and this would completely get stabilised when you reach minus P s state. Similarly, atoms from the left would jump into right at plus E c and the crossover would happen at plus E c. And they would be in a extremely stable state at plus P s direction. So, this is what energetics means of these ferroelectric materials.

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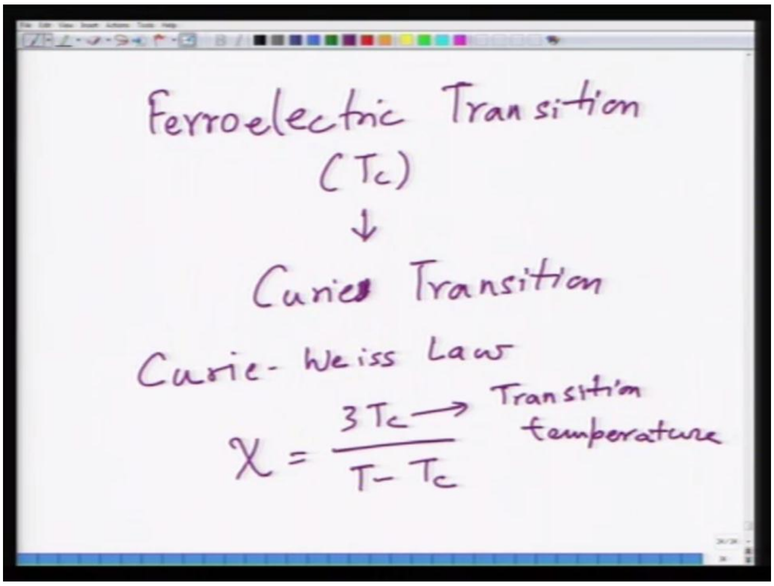

Ferroelectric Transition

(T_c)

↓

Curies Transition

Curie-Weiss Law

$$\chi = \frac{3T_c}{T - T_c}$$

$3T_c$ → Transition temperature

Another thing is as I said that these ferroelectric materials show a transition which is ferroelectric transition. And this ferroelectric transition occurs at a temperature T c, and this is often called as Curie transition, which means and which also means is that these ferroelectric materials follow what is called as Curie-Weiss law. And this Curie-Weiss law is expressed as so the susceptibility of the material you can express as 3 T c divided by T minus T c. The T c is the transition temperature, and what it means is that they are these materials are ferroelectric at temperatures lower than T c at above at temperature. Above T c they become non-ferroelectric or paraelectric in nature losing all the permanent dipole moment.

So, what we will do is that, now in the subsequent part of the lecture. We will determine basically how this expression comes up, so basically derivation of curie's law.

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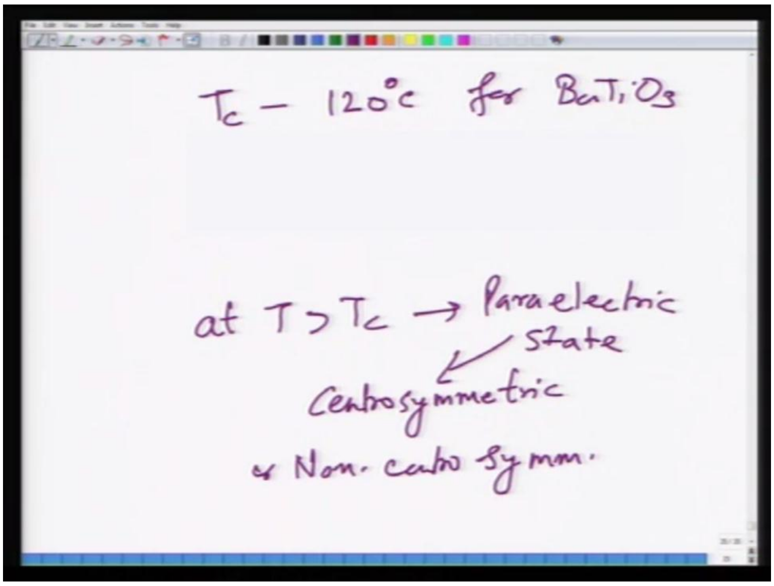

T_c – 120°C for $BaTiO_3$

at $T > T_c \rightarrow$ Paraelectric state

Centrosymmetric

or Non. centro symm.

And this T c for instance is about 120 degree centigrade for barium titanate. And so these are all useful materials because T c is higher than room temperature. So, basically below 100 and 20 degree centigrade barium titanate, it is in ferroelectric state. And at temperatures above 100 and 20 degree centigrade barium titanate would be in paraelectric or non ferroelectric state giving rise to zero polarization. And basically what it would mean is that it would mean either. So, at T greater than T c material is in paraelectric state.

Now, this would have two meaning; one meaning is either the material has gone into centrosymmetric state. So, centrosymmetric state centrosymmetric means no polarization at all in any case or what it would mean is that, it has gone into a non centrosymmetric state. But a state where all the dipole moments are randomly distributed with respect to each other which means thermal forces have taken over. And they have put or the thermal forces have taken over randomising all the dipoles giving rise to zero polarizations. So, it would mean any of these 2 scenarios, but in the end what it mean is it would mean is zero dipole moment.

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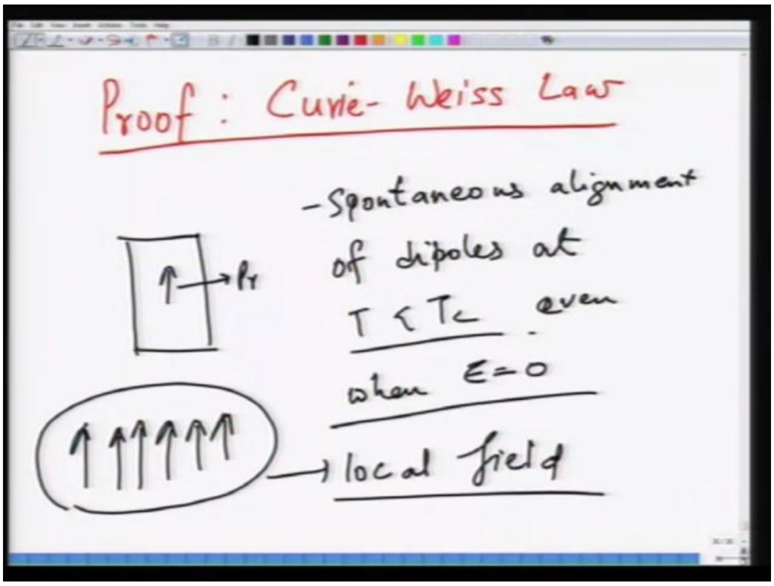

Proof : Curie- Weiss Law

- Spontaneous alignment of dipoles at $T < T_c$ even when $E = 0$

So, now, what will we, what we will do is that we will look at the proof of Curie-Weiss law. And then we will switch on to the next topic. Now, we can say that in a ferroelectric material, this we have not yet going to complete intricacies of a dielectric materials, what basically it means is that given that each of these unit cell. So, this is the barium titanate unit cell. So, all of them have a let us say each cell has P r in this direction. Now, what it has meant in the terms of ferroelectricity is that in all across the material. When you reach the very high field, all of these dipole moments aligned in the direction in a in the direction of applied field. And they give rise to maximum possible polarization, but even in the zero field state for a ferroelectric material, some of them have left oriented.

Now, how it looks like, we will look at that in a little while may be in the next lecture or so but what it means is that, there is some spontaneous alignment of dipoles which is left over when you reverse the field to zero fields. So, some you can say spontaneous alignment of dipoles at T less than T c even when E is equal to 0 and this is what gives rise to plus P r. So, there is some sort of interaction which is taking place between the dipoles and this happens. So, this is this we will also see in case of ferromagnetic material. So, basically you have one dipole vector here, but there are some other neighbouring dipole vectors which are all aligned in one direction.

And this is a state which is how should this state be created, there should be something behind this state, and this happens due to what we called as a local field. So, this theory of polarization for ferroelectrics is also called as local field theory. And this basically what it says is that, this local field is in the direction of dipoles or all dipole align themselves in the direction of this local field giving rise to a spontaneous polarization in the spontaneous or remnant polarization in the material.

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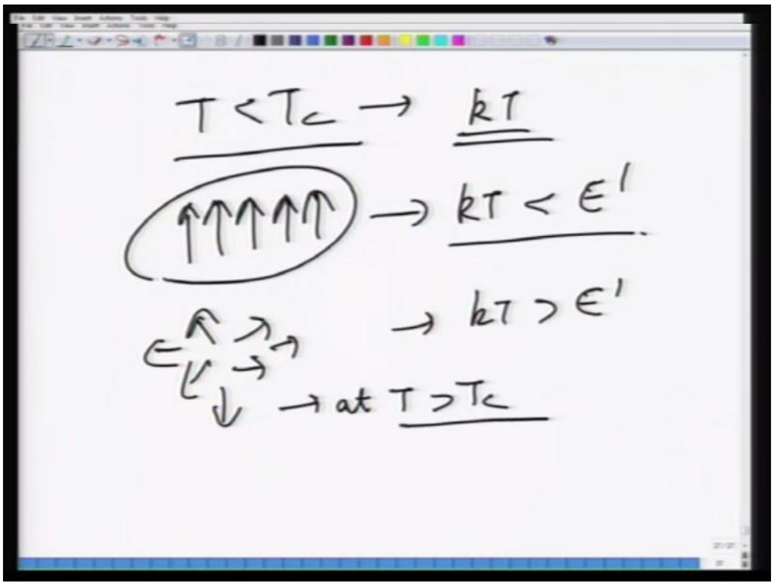

Now, this phenomenon happens at temperatures which are lower than. So, this happens at T lower than T c. And this means that, the thermal energy k T is insufficient to randomize these dipoles. So, these are the dipoles. So, if k T is a smaller than the local field then they stay together, but if k T is larger than E prime then they randomize. And this is what happens at T greater than T c if the material was still a non centrosymmetric state which means it was a still polar. Each crystal is still has dipole moment, but those dipole moments are unable to held unable to held, hold themselves together in the aligned state they become randomized simply, because thermal energy is much larger than that local field.

So, this is one theory which is given for ferroelectrics that at temperatures greater than T c. The thermal energy thermal effects take over randomizing the dipoles, but at temperatures lower than T c the local field is or the energy which is created due to local field is larger to hold these dipoles aligned in one direction giving rise to what is called as a spontaneous or remnant polarization. So, thermal effects some much less dominant at T less than T c.

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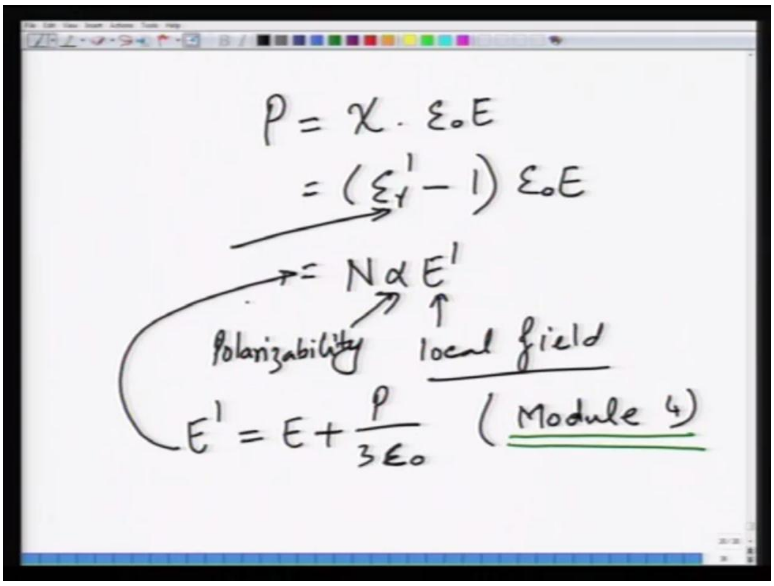

$$P = \chi \cdot \varepsilon_0 E$$

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

$$= N \alpha E'$$

$$E' = E + \frac{P}{3\varepsilon_0}$$

So, now looking back what we did in module 4. In module 4 we discussed polarization, what was polarization equal to? Polarization was equal to chi into epsilon naught E. And what was chi? Chi was a epsilon r prime minus 1 into epsilon naught E. Now, this is the macroscopic term. So, of course, we have taken what is called as a macroscopic field here, now what it means microscopically is N alpha E prime. And this E prime is local field, because now, here we are looking at microscopic quantities, because alpha is polarizability and polarizability is microscopic property. So, this local field E prime it is magnitude, as we discussed in the module 4 was equal to E plus P divided by 3 epsilon naught. So, I will just leave a link here, module 4 in the beginning of module 4 right in the beginning of module 4 may be in the first or second lecture.

So, if you go back to module 4, you will find this expression for E prime is equal to E plus P divided by 3 epsilon naught, and here alpha as you know is polarizability, epsilon r prime is nothing but relative dielectric constant. And epsilon naught is the permittivity of free space. So, what you do is that now you substitute this E prime into this expression.

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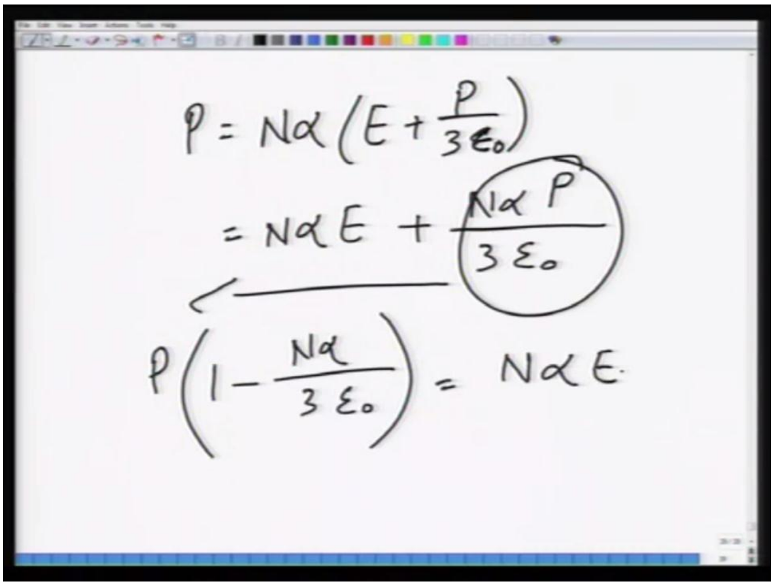

$$P = N\alpha\left(E + \frac{P}{3\varepsilon_0}\right)$$

$$= N\alpha E + \boxed{\frac{N\alpha P}{3\varepsilon_0}}$$

$$P\left(1 - \frac{N\alpha}{3\varepsilon_0}\right) = N\alpha E$$

So, what you get here is, P is equal to N alpha into E plus P divided by 3 epsilon naught, and this is equal to N alpha E plus N alpha p divided by 3 epsilon naught. And this is equal to, so what I am going to do is that I am going to shift this term to the left side. So, P. So, I am taking this here. So, this becomes P into 1 minus N alpha divided by 3 epsilon naught and this is equal to N alpha E.

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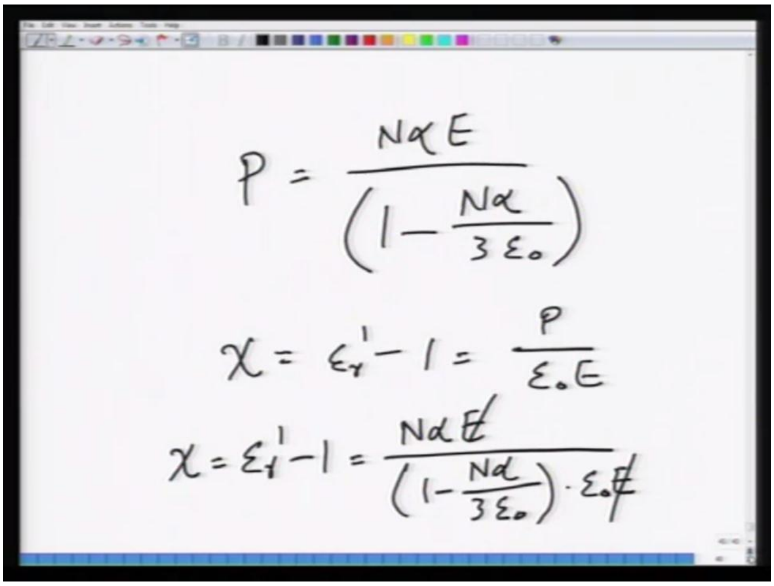

$$P = \frac{N\alpha E}{\left(1 - \frac{N\alpha}{3\varepsilon_0}\right)}$$

$$\chi = \varepsilon_r' - 1 = \frac{P}{\varepsilon_0 E}$$

$$\chi = \varepsilon_r' - 1 = \frac{N\alpha \cancel{E}}{\left(1 - \frac{N\alpha}{3\varepsilon_0}\right)\cdot \varepsilon_0 \cancel{E}}$$

This P becomes equal to N alpha E divided by 1 minus N alpha divided by 3 epsilon naught. Now, we know that chi is equal to epsilon r prime minus 1 chi is the susceptibility. And this is equal to P divided by epsilon naught E. So, chi will be equal to epsilon r, scales have shifted, let us bring them back epsilon r prime minus 1, this is equal to N alpha E divided by 1 minus N alpha divided by 3 epsilon naught into epsilon naught E. So, of course, you cancel E’s.

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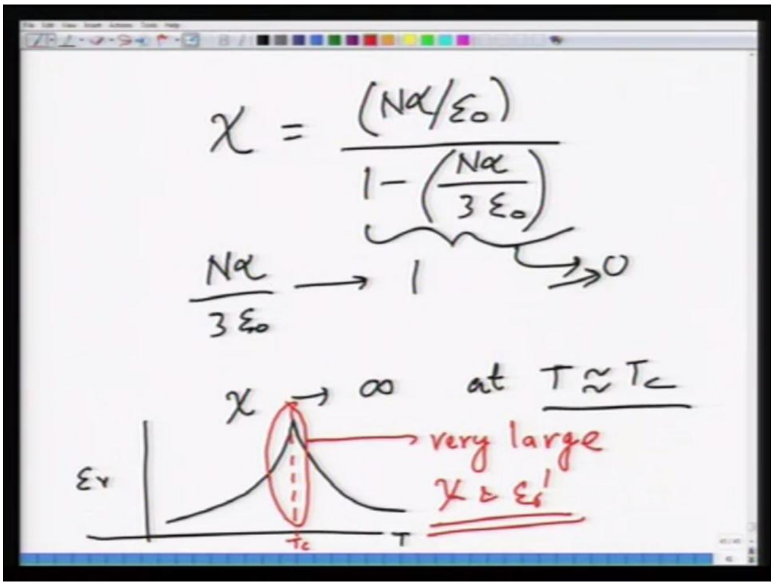

$$\chi = \frac{(N\alpha/\varepsilon_0)}{\underbrace{1 - \left(\frac{N\alpha}{3\varepsilon_0}\right)}_{\to 0}}$$

$$\frac{N\alpha}{3\varepsilon_0} \longrightarrow 1$$

$$\chi \to \infty \quad \text{at} \quad \underline{T \approx T_c}$$

And what this becomes equal to is. So, chi becomes equal to N alpha divided by epsilon naught divided by 1 minus N alpha divided by 3 epsilon naught. So, what it basically shows is that, when N alpha by three epsilon naught approaches 1 then this denominator will be approaching 0. And when the denominator approaches 0, the chi becomes infinity, and that is what is for ferroelectric materials, because ferroelectric materials have very large response to the applied field. So, which means they show very large susceptibilities and what this makes sense.

So, what it, what basically it makes sense. So, this would mean chi tending to infinity and this is what makes sense, because at T. So, near the T c this is true, because when you switch the ferroelectric material. And when you plot the dielectric constant versus temperature, they show this kind of behaviour. And these are extremely large susceptibilities there very large susceptibilities. So, this plot basically suggests that at temperatures near T c and T c is somewhere here.

So, this is T c. So, in this region near T c material shows very large susceptibility as well as dielectric constant, because epsilon r prime is nothing but related to chi plus 1. So, what basically it means is that this N alpha as it approaches N alpha by 3 epsilon naught as it approaches 1. And this happens near temperature T is equal to T c chi tends to be infinity. And this is what represents a ferroelectric behaviour near T c. So, this makes kind of a sense. And at this point given that epsilon r prime and chi is extremely large.

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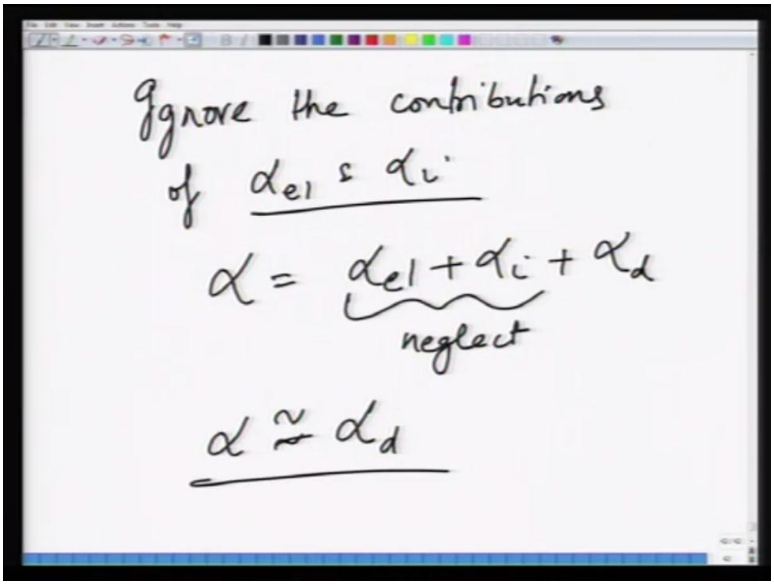

Ignore the contributions of $\underline{\alpha_{el} \text{ \& } \alpha_i}$

$$\alpha = \underbrace{\alpha_{el} + \alpha_i}_{\text{neglect}} + \alpha_d$$

$$\underline{\alpha \simeq \alpha_d}$$

You can ignore the contributions from. So, ignore the contributions of alpha electronic and alpha ionic given that these are going to be very small contributions in any sense. So, as a result you know that net alpha is equal to alpha electronic plus alpha i plus alpha dipolar. So, I am going to neglect these. So, let us say alpha is equal to alpha d at least at temperatures which are closer to T c, because susceptibilities are very large. So, as a result I can write this.

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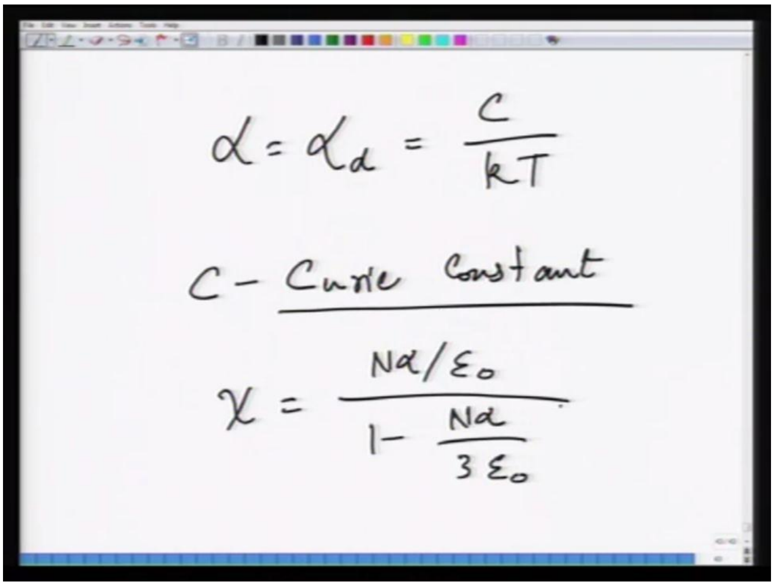

$$\alpha = \alpha_d = \frac{C}{kT}$$

C – Curie Constant

$$\chi = \frac{N\alpha/\varepsilon_0}{1-\frac{N\alpha}{3\varepsilon_0}}$$

So, let us say I define here alpha is equal to alpha d by C is equal to C divided by k T and this C is called as Curie constant. So, now the, this is kind of relation that we have similar relation we have seen in when we did module 4, when we analysed what is called as dipolar polarization. So, it is not very different from what we are doing now, but never the less it is a completely different exercise altogether.

So, the previous expression was. So, chi was equal to N alpha divided by epsilon naught divided by 1 minus N alpha divided by 3 epsilon naught. So, here what I am saying is that I will make this alpha to be equal to C by k T.

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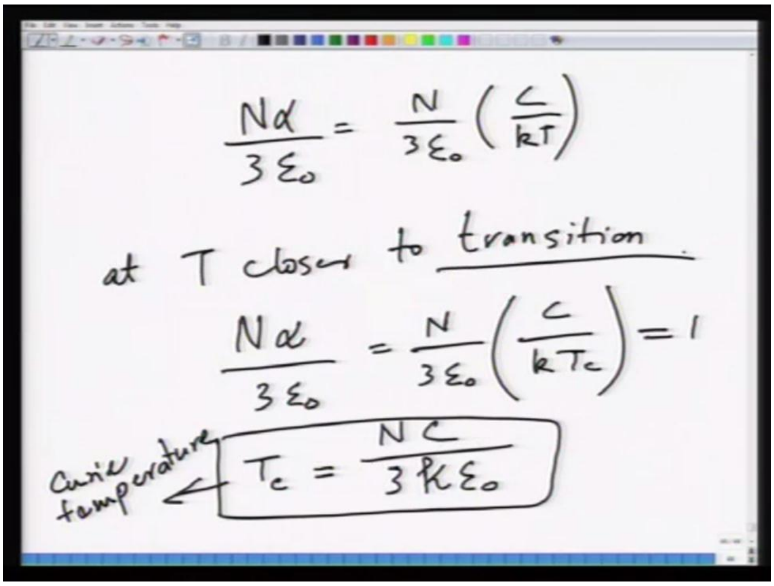

$$\frac{N\alpha}{3\varepsilon_0} = \frac{N}{3\varepsilon_0}\left(\frac{C}{kT}\right)$$

at T closer to transition

$$\frac{N\alpha}{3\varepsilon_0} = \frac{N}{3\varepsilon_0}\left(\frac{C}{kT_c}\right) = 1$$

Curie temperature ←

$$\boxed{T_c = \frac{NC}{3k\varepsilon_0}}$$

So, when I make the replacement. So, let us say N alpha, first of all let us look at N alpha itself N alpha divided by 3 epsilon naught. And this becomes N divided by 3 epsilon naught into C by k T at T closer to T c, N alpha divided by 3 epsilon naught is equal to N 3 epsilon naught c divided by k T c, and this is nothing but equal to 1 as we have seen earlier. So, if this is true then T c is equal to N c divided by 3 k epsilon naught. So, you what you do is that you take the T c there. So, this becomes N C divided by 3 k epsilon naught. So, this T c is called as Curie temperature or let us say instead of writing this here, you just write is that T closer to transition that is more appropriate, because when you talk about transition then you define transition temperature as T c.

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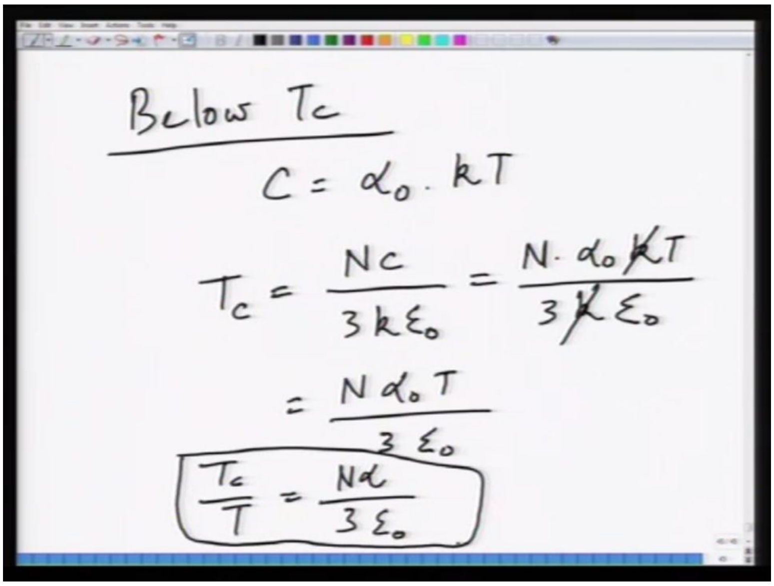

Below Tc

$$C = \alpha_0 \cdot kT$$

$$T_c = \frac{Nc}{3k\varepsilon_0} = \frac{N \cdot \alpha_0 \cancel{k} T}{3\cancel{k}\varepsilon_0}$$

$$= \frac{N\alpha_0 T}{3\varepsilon_0}$$

$$\boxed{\frac{T_c}{T} = \frac{N\alpha}{3\varepsilon_0}}$$

So, now, below this now what happens below T c, now below T c of course, you have this alignment of dipoles which takes place as a result; you have this spontaneous alignment of dipoles as spontaneous polarization. So, below T c you can define this C to be equal to alpha naught into k T. And this alpha d into k T, let us say, let us just make a distinction between the high temperature.

So, let us say alpha naught some polarizability of course, it is higher than electronic ionic in any case. So, you write this T c to be equal to now T c was equal to N C divided by 3 k epsilon naught, and what it becomes equals to is that N into alpha naught k T divided by 3 k epsilon naught, k k cancel each other. And what you get is N alpha naught T divided by 3 epsilon naught. So, that means T c by T become N alpha divided by 3 epsilon naught. So, this is an important expression which you get as a result of approximations near T is equal to T c, and this now when you substitute back.

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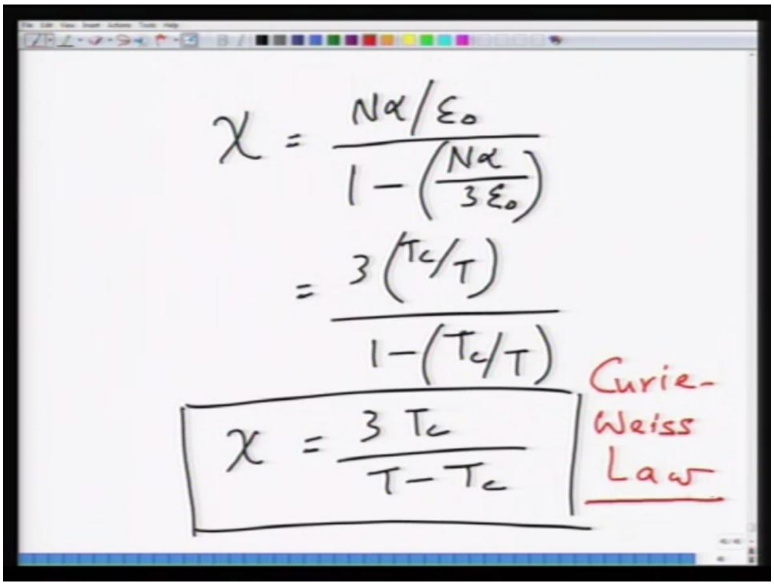

$$\chi = \frac{N\alpha/\varepsilon_0}{1-\left(\frac{N\alpha}{3\varepsilon_0}\right)}$$

$$= \frac{3\left(T_c/T\right)}{1-\left(T_c/T\right)}$$

$$\boxed{\chi = \frac{3\,T_c}{T-T_c}}$$

Curie-Weiss Law

So, your chi was equal to N alpha divided by epsilon naught divided by 1 minus N alpha 3 epsilon naught. So, in the previous slide we have N alpha divided by 3 epsilon naught is equal to T c by T. So, this would become 3 T c by T, and this would become 1 minus T c by T. And if you take T in the, if you cancel the T's here in the denominators of T c by T then this becomes three T c divided by T minus T c. And this is what is called as Curie-Weiss behaviour Curie-Weiss law.

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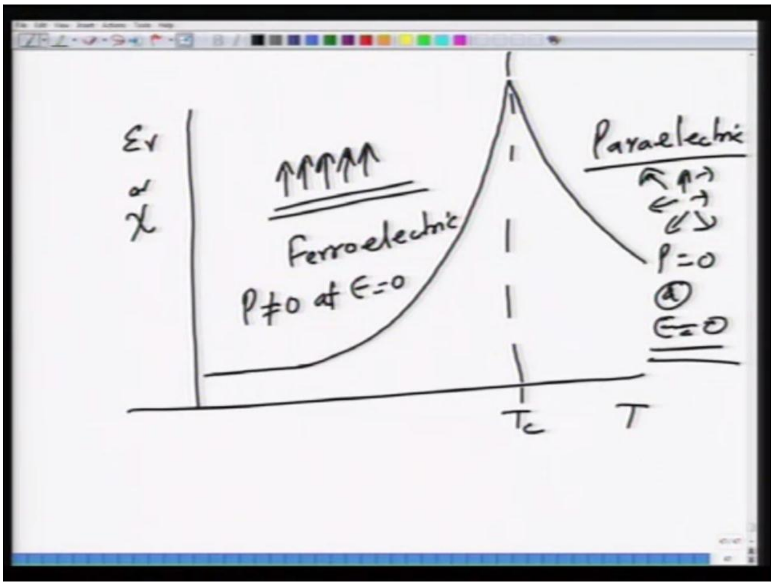

And what it means in terms in graphically is that when you plot, let us say dielectric constant or susceptibility as a function of temperature then they increase little slowly in the beginning. But they reach very high values at some temperature and then they start falling.

So, this is your T c material, in this part will be ferroelectric state and here it becomes paraelectric state. In the paraelectric state and this is a very important outcome, because this gives you not only magnitude of a temperature which is called as Curie's temperature, but also the behaviour of material near T c. And below and above T c. So what happens in ferroelectric state is dipole moments, they align with respect to each other. So, which means the thermal energy k T is less dominant thereby not interrupting the spontaneous alignment of the dipoles in the paraelectric state, you have randomization of dipoles.

And here thermal energy is large enough to make this distribution of dipoles random as a result you have P which is not equal to 0 at E is equal to 0, but here P is equal to 0 at E is equal to 0. So, as a result material behaves like as if it was a linear dielectric in the paraelectric state, and it behaves like a ferroelectric or non-linear dielectric and at temperatures lower than T c. So, this is an extremely important exercise from the point of view of behaviour of materials. I will find out some values and just to give you some of the T c's of some materials, candidate materials, let me just look at some of my notes.

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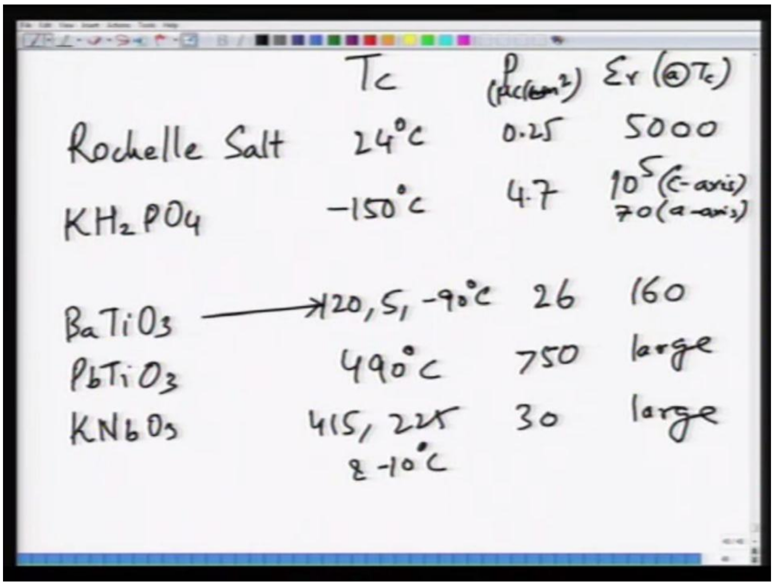

	T_c	P ($\mu C/cm^2$)	ε_r (@T_c)
Rochelle Salt	24°C	0.25	5000
KH_2PO_4	−150°C	4.7	10^5 (c-axis) 70 (a-axis)
$BaTiO_3$	120, 5, -90°C	26	160
$PbTiO_3$	490°C	750	large
$KNbO_3$	415, 225 & -10°C	30	large

So, for instance Rochelle salt, it has a Curie temperature of in degree centigrade, sorry Curie constant not Curie temperature, this should be. So, the value of C and then or let us say I just let us just write value of T c, let us not worry about C, and then polarization, and then epsilon r at T c. So, Rochelle salt shows the T c of about 24 degree centigrade, 24 degree centigrade that is why Valasek could observe in Czech republic at 24 degree centigrade, because in if it was in if he was in India, he wouldn’t be able to discover ferroelectric effect. Because in India in summer the temperature is higher than 24 degree centigrade, he has to be in winter to observe ferroelectrics in Rochelle salt.

But in Czech Republic 24 degree centigrade is the temperature which is considered as high temperature. So, as a result he could discover the ferroelectricity. So, 24 degree centigrade is the transition temperature, polarization in micro coulomb per centimetre square is about 0.25 not a very large polarization. And dielectric constant near T c is approximately 5000, if you look at potassium dihydrogen phosphate here; it is this has very low temperature minus 150 degrees centigrade polarization is approximately 4.7. And a dielectric constant is very anisotropic 10 to the power 10 to the power of 5 along C axis and 70 along a axis. So, extremely anisotropic, so the measurements were made on single crystals if you look at perovskites like barium titanate or lead titanate or potassium niobate. In this case barium titanate undergoes 3 transitions, 120 is the final transition.

There are 2 transitions at 5 and minus 90 degree centigrade, but these are the transitions which represent change in the crystal structure, but the materials still remains non centrosymmetric. And still remains ferroelectric and this has polarization of about 26 and the dielectric constant near the T c is roughly 160. This depends upon the crystal quality, and whether it is in single crystal state or poly crystalline state. So, this is in case of lead titanate; this is 490 degrees centigrade not 450 polarization again is pretty large more than 50 micro coulomb per centimetre square. And dielectric constant is large essentially, and again potassium niobate shows 3 transitions 415 225 and minus 10 degree centigrade.

This has about 30 micro coulomb per centimetre square polarization, and dielectric constants can be very large, it could be anywhere between 900 to 4000 depending upon whether you have single crystal or poly crystal etcetera. So, you can see that near the T c the dielectric constant is very high this is what we assumed in previous analysis which is the field theory or we called as local field theory of the ferroelectrics. And temperatures better than room temperature of course, are desirable, because then the material would be ferroelectric at room temperature and up to the T c, materials like K H 2 P O 4 is not very useful simply because it is T c is extremely low. And it does not really help us from any application point of view.

So, what we will do is that we will put a stop here. In the next class we will start discussing about the energetics of ferroelectric material what happens at the transition. Because this transition temperature extremely important not only the material goes from ferroelectric to non ferroelectric state, it is also associated with the phase transition. So, we need to understand what is the nature of that phase transition? And that is very essential in order to understand the ferroelectrics well and so on and so forth.