Fundamentals and Applications of Dielectric Ceramics
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Lecture – 32
Ferroelectric Phase Transitions

So, welcome again to the new lecture of the course, fundamental and application of dielectric ceramics, let us just briefly recap what we did in the last lecture.

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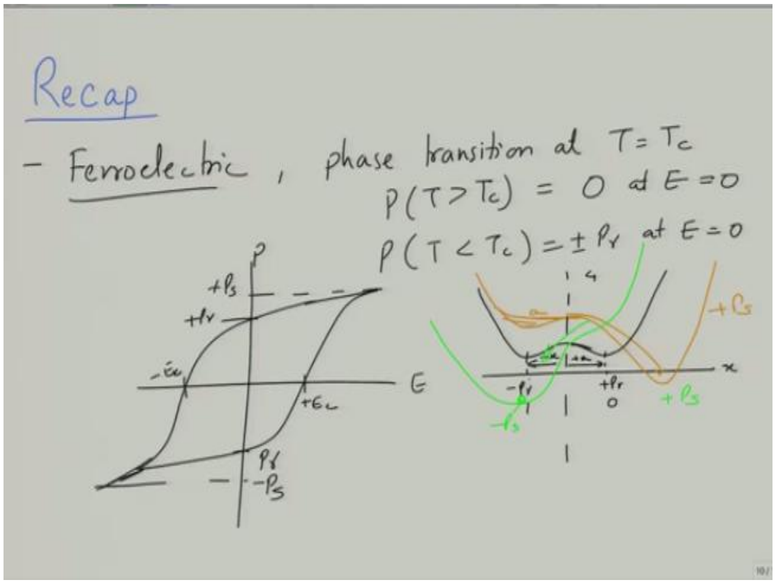

Recap

- Ferroelectric, phase transition at $T = T_c$

$P(T > T_c) = 0$ at $E = 0$

$P(T < T_c) = \pm P_r$ at $E = 0$

So, in the last lecture, we started our discussions on ferroelectrics; ferroelectric materials are those materials which are non-centro symmetric which have a polar axis; unique polar axis and the polarisation along that polar axis is reversible by reversing the direction of electric field. In addition, they have a phase transition at the temperature T_c, below which they are ferroelectric and above which they are paraelectric and then basically, you can say that the polarisation above T_c is 0 at E = 0.

And polarisation at less than T_c is $\pm P_r$ at E = 0 and they show a characteristic hysteresis loop which is something like symmetric hysteresis loop and so this is polarisation electric field.

$$P(T > T_c) = 0$$
$$P(T < T_c) = \pm P_r$$

we have a remnant polarisation at zero field and you have a saturation polarisation at maximum field and then you have an electric field which is coercive electric field.

So, you are forcing the material to come to zero polarisation state that is the coercive field, so this is ± E_c and this is manifested in the form of energy wells, so at ferroelectric show a sort of energy, so this is G as a function of X let us say, so the in the ferroelectric state, you have either of one state available, this is $+P_r$ or $-P_r$, so atom goes to either of these two positions and in terms of applications, it is also denoted as zero in one state.

So, one state is zero state so, basically you show binary data storage that is why it is called a zero or one state but nevertheless, it is basically, the position which is either +x or -x position at which the titanium central atom, so basically anion is shifted with respect; and cation is shifted with respect to anion polyhedra centre by a small amount given rise to a net dipole moment.

And this switching behaviour of ferroelectric can be explained in terms of change of free energy wells, so at very high field, the wells will become like this, so your all the items will basically, in fact it will become like this, so all the atoms from here will jump into this, so this is; this will give rise to $+P_s$ and at $-P_s$, you will have reverse situation.

So, all the atoms will shift here and the intermediate situations will happen as per the movement of the atom in the wells and then correspondingly, you will have zero or ± P_r. So, this is what we looked at last time now, let us look at little bit more details of ferroelectric materials.

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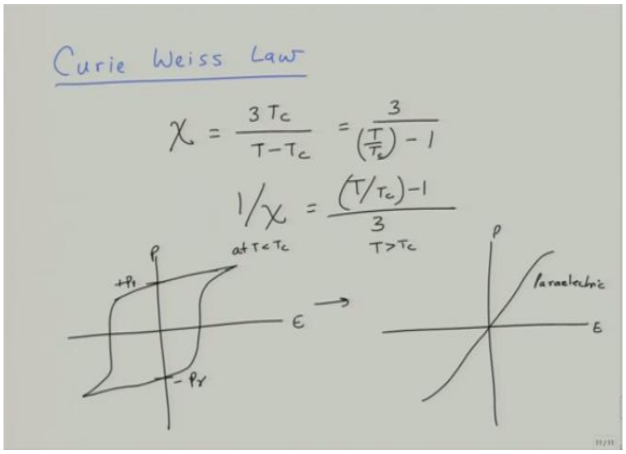

Curie Weiss Law

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

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

So, ferroelectric materials follow what we call as Curie-Weiss law, so basically this law is depicted as the susceptibility of ferroelectric follows this behaviour:

$$\chi = \frac{3T_c}{T - T_c} = \frac{3}{T/T_c - 1}$$

$$\frac{1}{\chi} = \frac{T/T_c - 1}{3}$$

This is manifested in change in polarisation, at T < Tc, a ferroelectric material will show you a hysteresis loop and it will have ± Pr at zero field. When you go to a temperature T >Tc, the material will show behaviour of a paraelectric. So, you will not observe any sort of finite polarisation at zero field.

When you are at a temperature above T_c and this is a typical ferroelectric condition that you should see, this is also manifested in what we call as dielectric constant.

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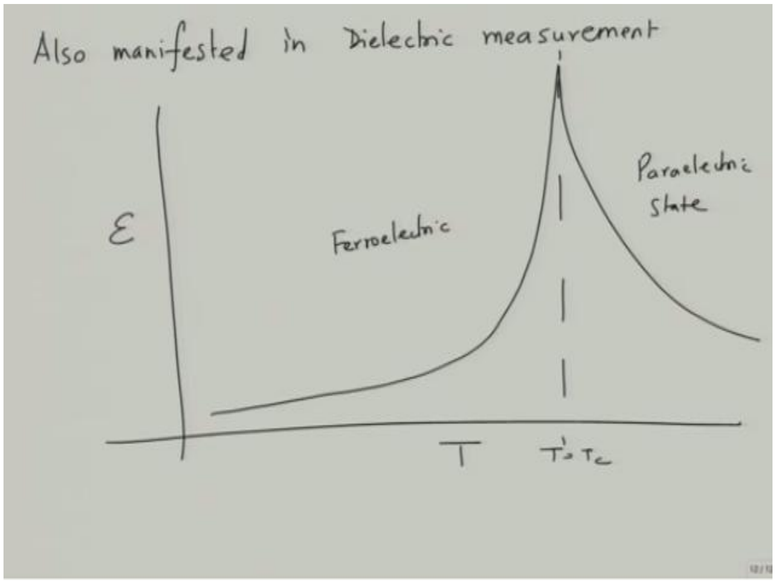

When you measure; so what you do is that when you measure dielectric constant as the function of temperature, that electric constant increases, reaches mostly very high values and then slowly decrease, so this is your ferro electric state and this is your paraelectric state and at T_c, it undergoes abnormally high values.

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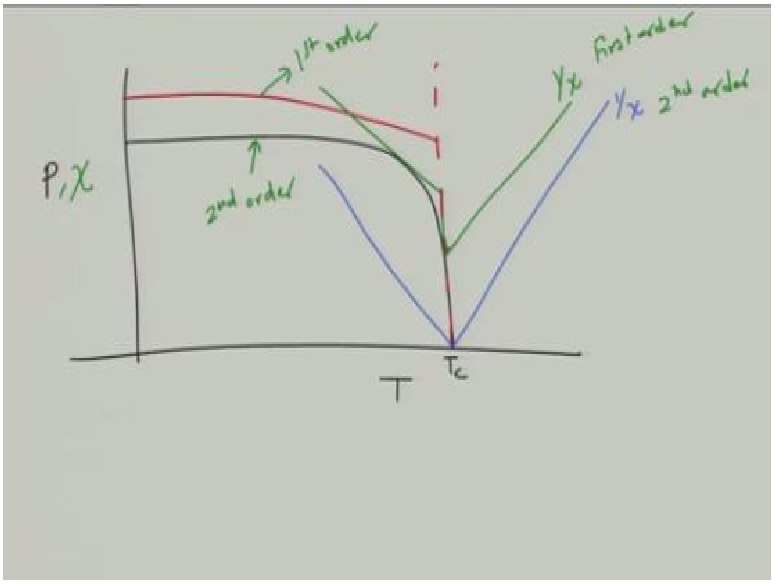

And this is because of change in properties such as when you measure polarisation, the polarisation drops at T = T_c and the susceptibility, the $1/\chi$ goes in the fashion shown, but this is not the only way it happens, the polarisation may drop in this fashion, polarisation may also drop in this fashion, so you may have what you called line at T_c,
the polarisation will decrease and then suddenly go boom.

So, you can have different ways in which polarisation will drop, this is a gradual drop in polarisation at T_c, there is a sudden drop in polarisation at T_c and that depends upon the nature of this transition. So, if you have gradual drop in polarisation at T_c, it is mainly when the materials have second order phase transition but when it is a sudden drop, then you have first order phase transition.

Second order phase transition is generally more gentle in nature whereas, first order phase transition is more destructive in nature or more radical in nature, similarly if you see; if you measure the susceptibility in the second order susceptibility, shows a depth but it does not show a discontinuity. In the case of second order phase transition, the susceptibility will show a discontinuity.

So, the susceptibility in the first order will have behaviour like shown, so that is a behaviour of susceptibility in case of first order phase transition, so this is second order and this is first order, so this is P, χ , this is first order and this is second order, so basically, these the temperature dependence of polarisation is what the nature of temperature dependence of polarisation susceptibility are determined by the type of phase transition that is present in the material.

So, we will look at that in thermodynamic aspects of these materials but basically, no matter what the ferroelectric is; ferroelectric undergoes a curie transition of phase transition at temperature T_c, above T_c, the and ferroelectric nature disappears, material becomes paraelectric and the susceptibility dependence is given as:

$$\frac{1}{\chi} = \frac{T/T_c - 1}{3}$$

and this equation is valid only in the para electric state, it is not valid in the ferro electric state.

And it undergoes a curie transition, where epsilon value of dielectric constant reaches a maxima before it starts decreasing further and then the polarisation and susceptibility also show a transition at; so, let us first look at the derivation of the proof of Curie-Weiss law, the equation that we have written, before we get into the thermodynamics of phase transition of ferroelectrics.

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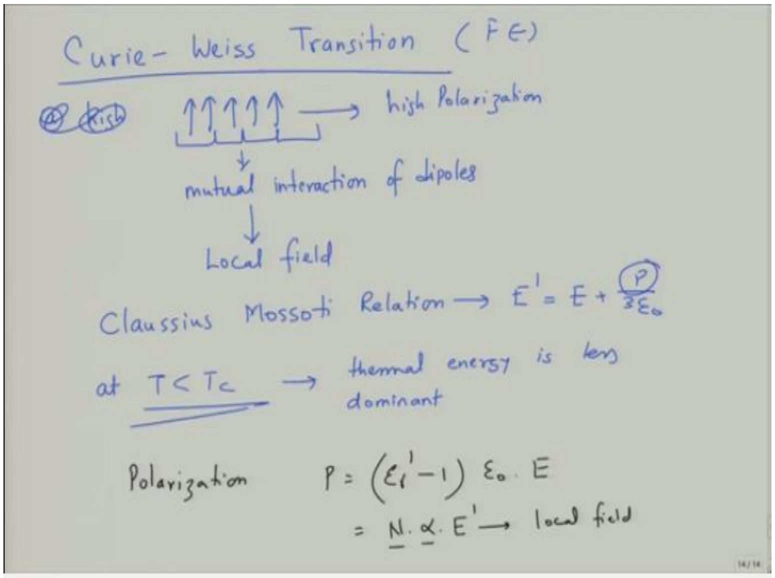

Curie- Weiss Transition (FE)

$\uparrow\uparrow\uparrow\uparrow\uparrow \longrightarrow$ high Polarization

$\downarrow$

mutual interaction of dipoles

$\downarrow$

Local field

Claussius Mossoti Relation $\longrightarrow E' = E + \frac{P}{3\varepsilon_0}$

at $T < T_c$ $\longrightarrow$ thermal energy is less dominant

Polarization $P = (\varepsilon_r' - 1)\,\varepsilon_0 \cdot E$

$= N \cdot \alpha \cdot E' \longrightarrow$ local field

So, let us first look at the Curie-Weiss behaviour in ferroelectrics, so now basically what is happening is that in ferroelectric at when you have zero, so we are saying that you have dipole moments like this, when you apply a electric field, these dipole moment get aligned in one direction and this gives rise to what we call as high polarisation but this can happen in any material.

In ferro electrics what also happens is the interaction between these dipoles, so these dipoles are not; non interacting rather they are interacting the dipole, so we can say there is a mutual interaction of dipoles and this mutual interaction of dipoles is due to what we call as the local field, so far we have not talked of local field, we have only talked of a macroscopic field and this local field tends to be higher than the applied electric field.

And the interaction between the dipoles leads to higher local field, it turns out using, we have not done the derivation and we probably would not have time to do the derivation but they something called as Claussius Mossoti relation which gives you, local field value as:

$$E^{|} = E + \frac{P}{3\varepsilon_0}$$

so the local field when the dipoles and interacting, when there is a mutual interaction between the dipole, it is little bit higher than the applied electric field.

And as higher the value of P in the system is more will be the local field, so especially in ferro electric systems, the polarisation tends to be very high, this electric field is also quite high. So, and this is this happens only when we consider this at temperatures, T > Tc, where thermal energy is less dominant, right that is going to interactions can happen if it is thermal energy is dominant, it breaks over the dipole interactions.

As a result, then it leads to dipole randomisations and you will not have any dipole moments, so it happens at T < Tc, where thermal energy is less dominant. So, we can write the expression for let us say polarisation, the polarisation can be expressed as:

$$P = (\varepsilon_r' - 1)\varepsilon_0 E = N\alpha E'$$

where E now is taken as local field.

And we are taking for all the N number of dipoles of polarisibility α and a field which is something different which is not the applied field, which is the local field.

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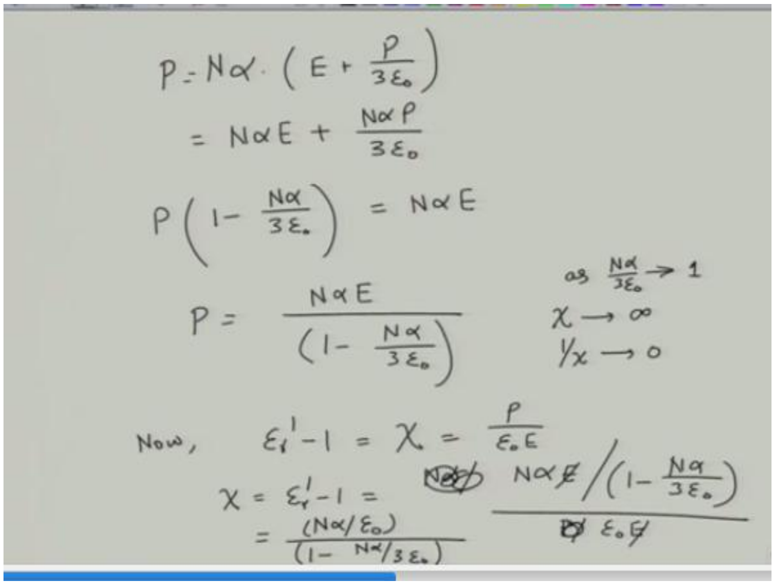

$$P = N\alpha \cdot \left(E + \frac{P}{3\varepsilon_0}\right)$$

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

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

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

as $\frac{N\alpha}{3\varepsilon_0} \to 1$

$\chi \to \infty$

$1/\chi \to 0$

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

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

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

Let us say this local field is, so we replaced this local field as:

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

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

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

And this is purely in the linear region, right and if you do that, we get:

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

Now, what this shows you is that, as Nα/3ε0 tends to reach 1, what happens, the χ tends to reach infinity or we can say that $1/\chi$ will become zero and that is what we have seen that at the phase transition; near the phase transition, near the ferroelectric transition, the ferro electrics show very large susceptibility.

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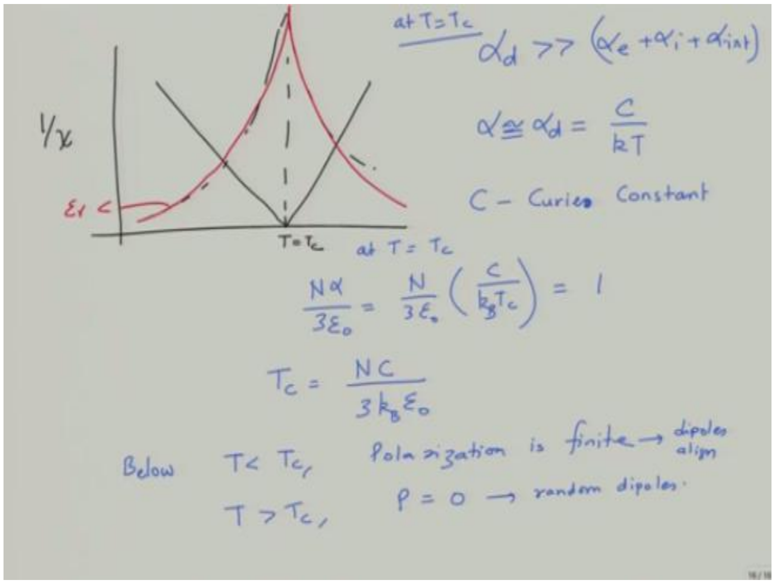

at T=Tc $\alpha_d >> (\alpha_e + \alpha_i + \alpha_{int})$

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

C – Curies Constant

at T = Tc

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

$T_c = \frac{NC}{3k_B\varepsilon_0}$

Below T< Tc, Polarization is finite → dipoles align

T > Tc, P = 0 → random dipoles.

So, when you look at $1/\chi$ as a function of T, this is what you see that χ will become very large, it will diverge at that point right, so when you measure dielectric constant, the dielectric constant goes as in this, so this is let us say, dielectric constant and dielectric constant is nothing but 1 + χ, so this tends to diverge at T = T_c that is very large susceptibility.

Or $1/\chi$ will show a depth, so at this point we basically have to ignore all other contributions such as electronic and ionic contributions as well as interfacial polarisation, we assumed that:

$$\alpha_d >> (\alpha_e + \alpha_i + \alpha_{\text{int}})$$

So, at T = T_c, this α_d is extremely high and hence we can write this as:

$$\alpha \cong \alpha_d = \frac{C}{k_B T}$$

where c is the Curie constant.

We saw that you know ɑ to be some number divided by kT and so that is why we are saying that alpha is equal to C/kT, where C is Curie constant and hence we can write now:

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

$$T_c = \frac{NC}{3k_B\varepsilon_0}$$

So, below this T_c, we can say the polarisation is there, so we can say that below T < Tc, polarisation is finite and T > Tc, polarisation is zero, so, this means the dipoles will align and this means the dipoles will be random dipoles. So, what is then T_c? So,

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

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

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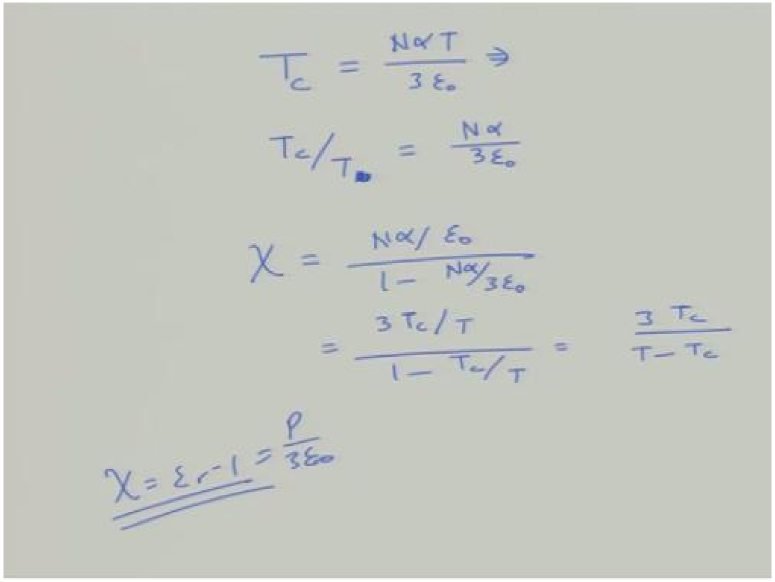

$$T_c = \frac{N\alpha T}{3\varepsilon_0} \Rightarrow$$

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

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

$$\underline{\underline{\chi = \varepsilon_r - 1}} = \frac{P}{3\varepsilon_0}$$

So, this is the general expression right, so we have said that using this at T = T_c.

Now, if you modify this and put in the expression of susceptibility; susceptibility we worked out as:

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

So, this is what basically, is the expression that is to revise law which is applicable only near T_c.

When we consider the linear relationships so on and so forth, when the relationships are non-linear, it is not valid because we have relied on the expression $\chi = \varepsilon_r - 1 = P/3\varepsilon_0$, so we have assumed that it is working in the linear regions, so basically this expression is valid near T_c only, nowhere else.

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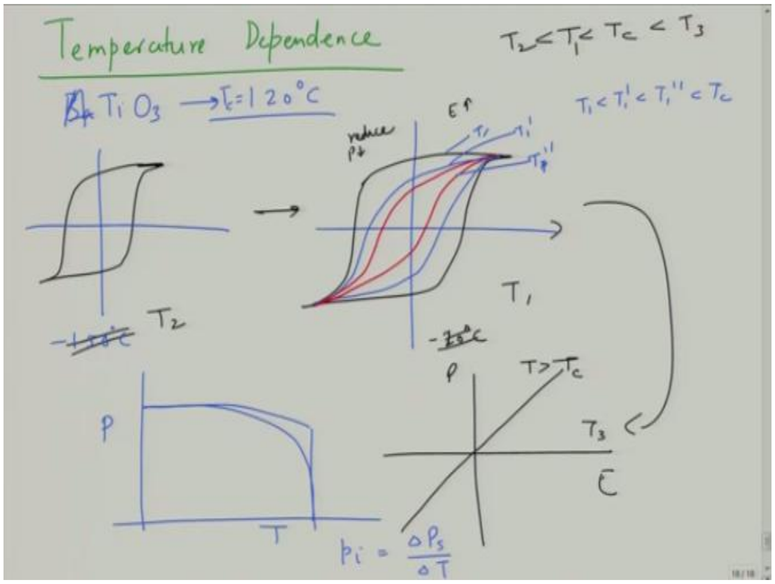

So, if you now look at the temperature dependence in totality, so let us say we have barium titinate example, which has a transition at nearly 120^0C. So, or some material $ATiO_3$, so T_c is this term, as you start from very low temperature let us say you start from -150^0C, you will obtain certain ferroelectric hysteresis loop.

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So, this is certain hysteresis loop as you go to little higher temperature, what will happen; a little higher temperature will lead to slight change in the polarisation loop but nothing significant will happen, so you might have some reduction in P because you have gone to little higher temperatures, so thermal interactions will reduce the P, so they will reduce some P and as a result, the voltage that we need to apply to align them also increase.

So, as a result your E will increase to achieve the same polarisation and you keep doing that process, until you reach T_3, this is P-E, somewhere in between T_1 and T_c, what will happen is that the polarisation will keep decreasing, so as you plot this for other temperatures, the polarisation will keep decreasing a little bit so, for example it will become like this, then it will also become so, let us say these are the temperatures; intermediate temperatures, these are all, so this is let us say for a temperature T_1, let us say this is $T^{|}_{1}$.

This is $T^{|}_{2}$ prime, so $T^{||}_{1}$ and this $T_1 < T^{|}_{1} < T^{||}_{1} < T_c$, this is how the behaviour will evolve and then, eventually you will need a para electric state, so this is how you can see the polarisation as you plot as a function of temperature, it will show a decrease before it goes low or it might show a behaviour in which it will be a little bit gradual, something like this, both the behaviours are possible.

So, form this you can also determine what we call as from the change of polarisation as the function of temperature, we can determine what is pyroelectric coefficient, that is:

$$p_i = \frac{\Delta P_s}{\Delta T}$$

you can also determine what is polarisation pyro electric constant for a given material because we know that every ferroelectric is a pyroelectric in nature.

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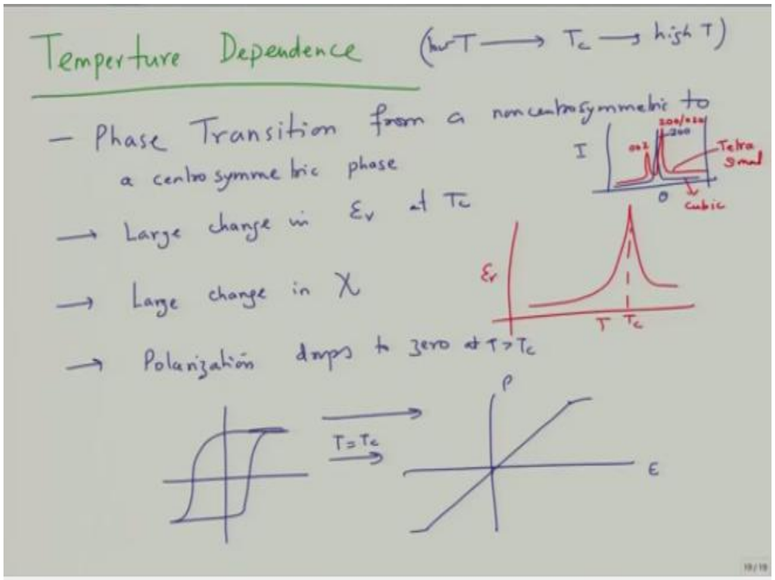

Temperture Dependence (low T $\longrightarrow$ T_c $\longrightarrow$ high T)

- Phase Transition from a noncentrosymmetric to a centrosymmetric phase

$\rightarrow$ Large change in ε_r at T_c

$\rightarrow$ Lage change in χ

$\rightarrow$ Polarization drops to zero at $T > T_c$

So, basically what will happen is that; so what will happen, what are the key takeaway is; one, you will have a phase transition from a temperature dependence so, as you go from the T to T_c to high T, so this is low T, this is T_c to high T, so we are looking at the heating process, so phase transition from a non-centro symmetric to a centro symmetric phase. So, basically large change in the electric constant at T_c, so this will be change in; so when you take the x-ray diffraction pattern of such a material let us say, so this is intensity versus θ.

So, in the cubic state if you look at for example, 100 peak; in the cubic state, 100 peak will be let us say 200 peak, you will have single 200 peak, when you take a temperature dependent x or d, this will show a splitting, so you will have a zero to zero and then you will have a 200, so this cubic and this is tetra, this is how you see the study the phase transition. So, this will be 200/020 and this will be 002.

So, you will see a clear peak splitting, you will have a change in the x or d peak profile because of phase transition and this phase transition is because of subtle change in the crystalline structure which goes from noncentro symmetric to centro symmetric that is from the tetragonal to cubic. So, this is what you will see in the height temperature region, the cubic region and this is what you see in the low temperature region that is tetragonal.

So, this is a and when you make the electric constant measurements ε_r versus T, you will see a large change in the electric constant, this is at T = Tc, these are experimental verification which are done easily and then we have, we can say large change in the susceptibility also, so susceptibility that is similar to and then polarisation drops to zero at T > Tc. How it will drop to 0? It will depend upon the nature of this transition but it will drop.

So, you have a phase transition, you have a large at electric constant, you have large in the susceptibility and you have a polarisation change, these are few signatures of ferroelectric conditions in ferro electric material that you see when and material which was like this, it will convert into sort of a linear electric, it is not a very good straight line but okay, so this is at T = Tc.

So, these are signatures of phase transitions in ferro electrics, these are certain thing to and remember this P loop is not a transit; transitory phenomena, it is a permanent phenomena, so if you measure the polarisation hysteresis loop again and again and again and again, several cycles, several months, several years it should remain the same at the same temperature of course. So, it means that is why temperature materials which have T_c is near room temperature, they are difficult to established.

Because of you know, in a country like you know in colder countries, the summer temperature may be 30^0C and winter may be -10^0C and if you do not have heating in the houses, in winter something will be ferroelectric and in summer it will be paraelectric, so that is why there were lot of conclusions in the early stages especially, in places like England and America where lot of people who are working on these materials, they could not determine materials.

But then when they made the measurement at constant temperature, they found now, they did have T_c's close to room temperature and these are the observation that one makes when you make measurements close to across the T_c. So, this is what a brief information about ferro electrics is, in the next lecture we will discuss the thermodynamics of the phase transition of two types and how the susceptibility and polarisation vary across the condition temperature.