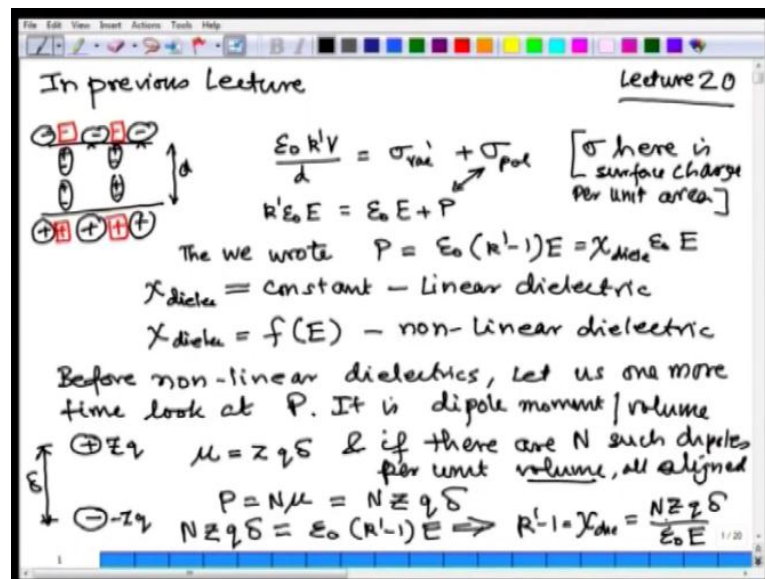


Optoelectronic Materials and Devices
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Module - 2
Electrical Properties of Materials
Lecture - 20
Non-linear dielectric behaviour

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Welcome to lecture number twenty. This is, I have written down some summary of what we did in the previous lecture. In this previous lecture let us see what did we do? We, I had built a capacitor, parallel plate capacitor. I had shown in vacuum you would, if there were no dielectric material inside, then I had said, that there will be, if you apply a voltage V across these parallel plate capacitor. Then you would get these black coloured charges and there will be σ_{vac} , and there will be σ_{vac} , which is σ here stands for surface charge per unit area on the electrode plate, so that would be, that would be the charge you would generate. But if you put a dielectric material inside, then there will be some polarization consequence of that would be, that additional charges, the red coloured ones would appear and there would be σ_{pol} .

And in that case, the total charge per unit area would have been written like this, and that had led to this kind of equation where we had related this σ_{vac} to $\epsilon_0 E$ and we have related this σ_{pol} with P . Further, we had written,

that this polarization P is related to dielectric constant, is proportional to electric field E and through that we had defined a macroscopic dielectric constant k' or susceptibility χ is a same thing, P is proportional to E and then in that proportionality, either you define k' or this susceptibility and this electric permeability.

So, this susceptibility, not permeability, susceptibility, permeability comes in magnetic, so this χ , the dielectric, the permeability, if it is a constant, then we say this would be a linear material and we have assumed this to be proportional and if you treat this as a constant. However, this, this is, P is not exactly proportional to E though we are trying to make it proportional. In those cases it is traditional to make this quantity itself, though write it as if it is proportional, but make this quantity itself a function of the electric field; it is a function of electric field.

So, if this dielectric, this susceptibility, dielectric susceptibility is function of electric field itself, then it is non-linear dielectric, that is what we are we are going to do in this lecture, that is what, that is where we had learnt last time. However, before I start I would like to do little bit more on, for continuing from past itself if there is, before we discuss this non-linear, non-linear dielectrics let us one more time look at this polarization, this quantity polarization. It is, it is, it can also be defined as dipole moment in this μ quantity, which I had already defined last time, dipole moment per unit volume.

Now, if I take this dipole, for example, there is a dipole, plus charges, minus charges and this is written as z , which is the, it represents the valency and q is the fundamental charge of an electron. Then plus zq and minus zq are these two charges separated by distance δ . Then this dipole moment is defined as $zq\delta$, by the way this dipole moment is a vector quantity, it has a direction; it has a direction. I am just writing it as scalar, but otherwise you could make this, all these quantities, polarization and this electric field, all, all are really vector quantities. So, if you write this dipole moment and if there are N such dipoles per unit volume because you remember, we are interested in polarization, which is per dipole moment per unit volume.

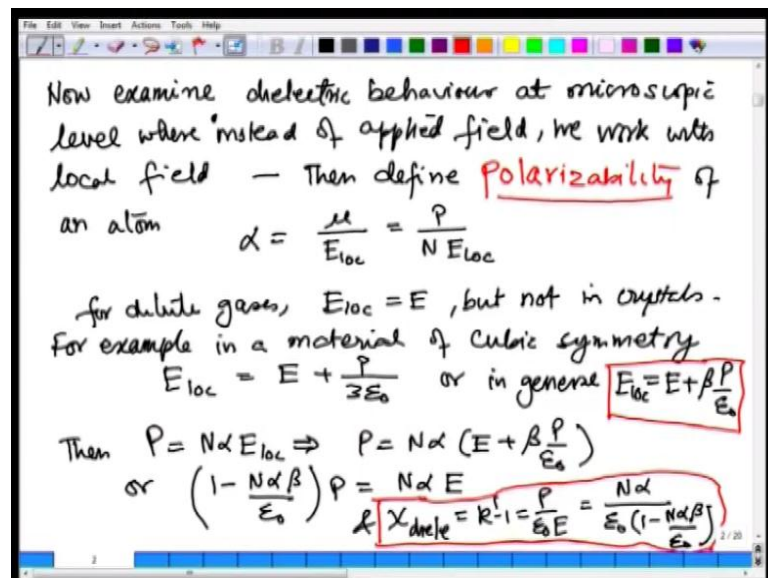
So, I am looking at, if N , this is dipole moment because of one dipole and if there are N such dipoles per unit volume and I am writing all of them are aligned, the reason I am writing all of them are aligned are, so that I can simply add them up vectorially. Also,

since I am not putting a vector symbol here and otherwise, in principle issue do vectorial addition, but I am just trying to look at the scalar values. So, I must make sure, that they are all aligned, so that I can, it can be added in a scalar way.

So, if that is the case, then this polarization, by this definition, that it is dipole moment per unit volume, then polarization would be equal to N times mu. Of course, again, vector mu and vector P will be in same direction. So, if that is the case, then given the value of mu I can write this expression, N times this z q delta, z q delta, and that is the polarization and if this is the polarization, then remember, we can write polarization as epsilon naught k minus 1, like this quantity here, which is what I have done.

So, this polarization I have written as epsilon naught k prime minus 1 times E, electric field, which implies, that dielectric constant minus 1, which is dielectric susceptibility is equal to N z q delta, N z q delta divided by epsilon naught E, epsilon naught E, basically that is what this dielectric constant, then would be defined as in terms of dipole moments.

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Continuing further, now what part I wanted to do, also talk about today was, we looked at the bulk, that means, a collection of dipoles and that is how, so when we say dielectric properties we are really talking of that of material, that means, collection of many dipoles. However, before we even, we, whatever the value is in collection, as a collection of dipole, one must look at individual dipoles also or we should look at, at microscopic

level also. So, if you were to look, that is a part additional I wanted to add, if you wanted to examine dielectric behaviour at microscopic level where instead of, instead of applied fields we work with local fields, fields in a material, if you apply a little field, that is the applied field, but inside the material there would be a field, which will be different from the from the electric field, that one applies and hence that field is being called the local field.

So, if you deal with the local fields, then we define this quantity polarizability, this quantity polarizability as of an atom, that means, we are now dealing with microscopic level as this quantity alpha, which is same thing as, which is written as μ by μ divided by E . But this time electric field is local instead of electric field that is applied, which then I can write as P divided by E N E local. Remember, N is, this is dipole moment per unit volume and this is number of dipoles per unit volume, of course, all aligned and hence we are able to do this exercise in a scalar way. So, the same expression we have written.

And now, if you look at the local field, what local field is, if you were to take dilute gases, then this local field will be same thing as (()) far apart. You have gas, we have gas atoms, atoms, atoms in a gas fall apart because it is dilute and hence, overall, overall you can treat it like, you know, sort of vacuum in, in between and therefore, while saying that it is vacuum, it will be inappropriate. But the point is, that local field will be same as the applied field E , but that is not true in crystals.

For example, if you were to take materials of cubic symmetry, if you took materials, crystalline materials, which had cubic symmetry, in that case, the local, if you had E as the applied field, then this E field will produce a polarization P such that the local field inside the material at a point would become equal to E plus P by $3 \epsilon_0$. It is relatively easy to prove, but I am not going to go through it in this class here. Often students do this in physics class when they are first introduced to, when, effect of electric field on materials in general. However, the way we will treat it is because we do not necessarily going to be dealing with materials of cubic symmetry.

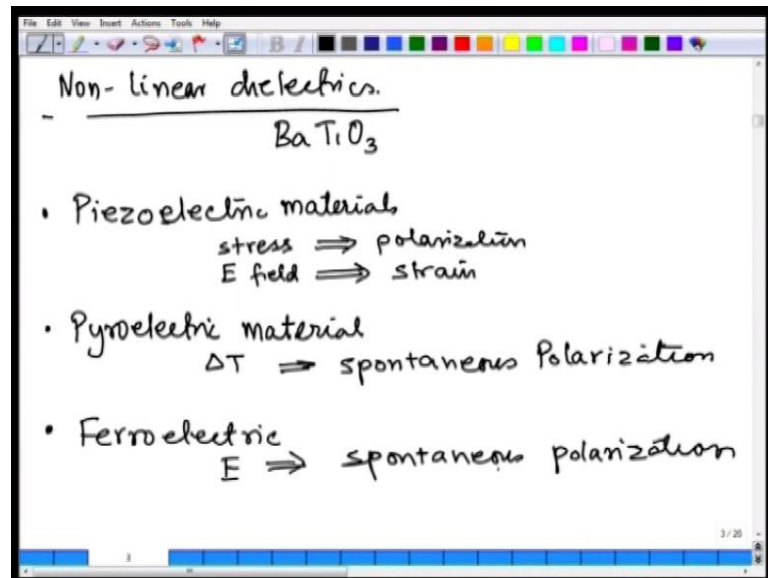
We will say, that in general, the form of local field is something like E plus a factor beta, which is $N P$ by ϵ_0 . Basically, I am drawing from the fact, therefore cubic symmetry, this factor was beta was $1/3$ and in some other materials, in (()) this could

change to a more complex expression, but that some number, which you are going to show up here, we are going to write that number as beta in general, in a general form. If that is the case, then we can write it from here, P as equal to alpha times N times E_{local} , which is what I have done. P equal to N times alpha times E_{local} , which now I am trying to bring in to expand, P is equal to N alpha and this E_{local} we have written out here.

So, this is the E_{local} we are going to use, this E_{local} we are going to use and substitute in here E_{local} , then you are going to get, what, what you are going to get is, we are going to separate P , N , E . So, you will take this on left hand side. So, I am going to write 1, which is for, because of this $P = 1 - N \alpha \beta$, $N \alpha \beta \epsilon_0$. We are taking this on this side, is equal to $N \alpha E$ and now again I can write, remember definition of susceptibility, dielectric susceptibility is or dielectric constant $k' - 1$, rather is P divided by $\epsilon_0 E$, which is, which is what this expression right here was, which is what this expression right here was.

So, we will use this expression and therefore, right from here, P divided by E , which I have get from this equation and I will write this as $N \alpha$, $N \alpha$ divided by this quantity in the bracket. I am going to write this as, this quantity is E and ϵ_0 is there, so I get my susceptibility right here. So, this is a expression I am going to use and I have derived this before when I am doing this non, non-linear dielectrics. We are going to reuse this and hence I have derived this part... Now, with this I am going to start with today's lecture in earnest on non-linear dielectrics and I will come back to this equation, I will point this out and we will use this in this context.

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So, let us get going on this non-linear dielectrics. Remember, one example yesterday we took was Ba Ti O 3, barium titanate. You use this as an example of a non-linear dielectric. And remember this, I had shown this, the dielectric constant of this material as something like 3000, a very, very high dielectric constant material and this is the material, which when I said this is a non-linear dielectric.

So, today let us look at this particular material to explain what non-linear dielectrics are and as we do, we will then generalize our ideas using this as a, as a material and mathematically, we will connect this behaviour of this material, dielectric behaviour of this material with this expression, which we have derived right here. So, I am going to connect back to this. So, let us start with this, but even before we start talking about non-linear dielectrics, let me just give a quick rundown of certain facts, which I am not going to prove, but they are just fact.

Let us first start with what is a piezoelectric material. You may be wondering why I am talking about piezoelectric materials when I was talking about dielectric properties, but this will become apparent to you in a minute. What are piezoelectric materials? These are, if you apply stress, if you apply stress they produce, then they produce polarization and stress means, mechanical stress, if you apply they produce polarization. This is the power charges, they produce charges or if you apply electric field, then they produce strain.

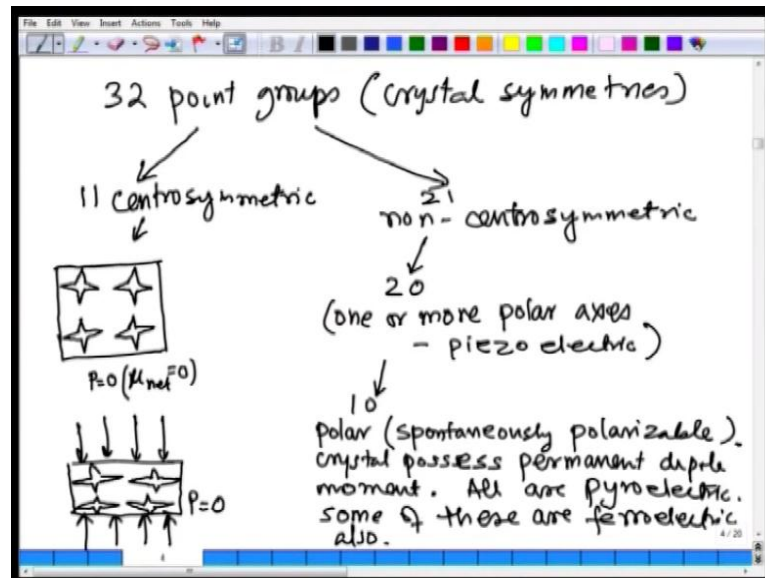
Then, you can also look at another kind of material, just one second, which is called pyroelectric material. In this case, if you apply temperature gradient, if you change the temperature, in that case you get, what is called as spontaneous polarization. What does that mean? As opposed to polarization, here you had polarization that means, you apply stress, then you will have polarization. But if you do not apply, then there will be no polarization, whereas in this pyroelectric electric material, if you apply temperature gradient, if you change temperature, then will result in a spontaneous polarization, that means, it is permanent in nature. Even when you remove ΔT some of it may, polarization may remain in the material that means, even when the temperature is taken back to its state, some polarization may remain. That means, if you were to start with something, start, which is unpolarized, apply temperature and polarization may increase, but and this, this will be spontaneous. So, this will be sort of permanent in nature and remain there.

Third material, which we will look at, is ferroelectric material and this is what barium titanate is, and this is where I was taking you through and they are all, three of them are connected. The point I am going to make eventually is, if a material is ferroelectric material, it has to be pyroelectric also and if it is pyroelectric, it has to be piezoelectric, but not conversely. That is, if it is piezoelectric, then it need not be pyroelectric and if it is pyroelectric, it need not be ferroelectric. But this way they would connect and hence, I am talking about all those three, though in principle I want to talk in this, in this lecture at, mostly we want to talk about this ferroelectricity, which is what relates to non-linear, non-linear dielectric behaviour.

And this means, in this case if you apply electric field, then it produces a spontaneous polarization. That means, a material initially may be in unpolarized state because because of, you know, many, many different gains. But if you apply electric field, these dipole moments will align and they align to produce polarization. Of course, that happens in all materials, if you apply electric field they produce polarization. But the point is, in this material they will be so polarized, that once you remove the electric field, some polarization will remain and that is what is meant by spontaneous polarization.

So, these are the three, three types of materials, how are they connected. Let us look at this one, one time, let us look at now all, and take this, what I am writing as a statement of fact because it is not part of the course here.

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We have 32 point group, point groups or crystal symmetries. Out of these, 11 are centrosymmetric; 11 of them are centrosymmetric. For example, a cubic crystal, a centrosymmetric, for, for there is a there's a centre about which there is a complete symmetry; 21 of course, then are non-centrosymmetric. Out of these, at least 20 are, 20, at least 20 have one or more polar axes, polar axes and these materials are piezoelectrics. It is the non-centrosymmetry, the point I am making is, that it is the non-centrosymmetry, which gives rise to piezoelectricity and this, as an example I am going to show you in a minute. So, this gives to piezoelectric material.

Now, if you look at this and then out of these 20 there are, there are 10, which are polar, which are polar and these are the ones we are interested in and they can be spontaneously polarized, spontaneously polarized, spontaneously polarisable. They all are crystals, possess permanent dipole moment, all are pyroelectric because they can be spontaneously polarized, hence they are all pyroelectric. Remember, you need spontaneous polarization for pyroelectric material; of course, for ferroelectric also. Some of these are ferroelectric, ferroelectric also. So, these ferroelectric are always pyroelectric and all pyroelectric are piezoelectric, because they belong to this 20, 20 of the point groups, which are non-centrosymmetric.

Now, what do I mean? I may show you, I will show you 3 through a picture and then through a schematic and that will illustrate the point little bit better and let us do that as

follows. For example, let me show you something, which is centro, first let us start with centrosymmetric, which means, I am taking this as an example, may be I do it here itself, then I do it here itself, this example I will do right here.

If you were to take a material, which look like this and which I am going to make. Since structure is centrosymmetric, so dipoles existing in it would also be centrosymmetric and hence, I am going to make it something like this, let us say. What have I drawn? I am drawing as if these are the directions of the dipole moment, this direction, this direction down, this direction on right, this direction on the left. Similarly, here for different, different locations what will happen? In this case all the dipole moments will cancel out, all the dipole moments, one on the, one going, pointing this way will cancel out, with one pointing out this way, one pointing out this way will cancel out, one pointing out this way and net polarization would be 0 because net dipole moment is 0, net dipole moment is 0. So, net polarization would be 0.

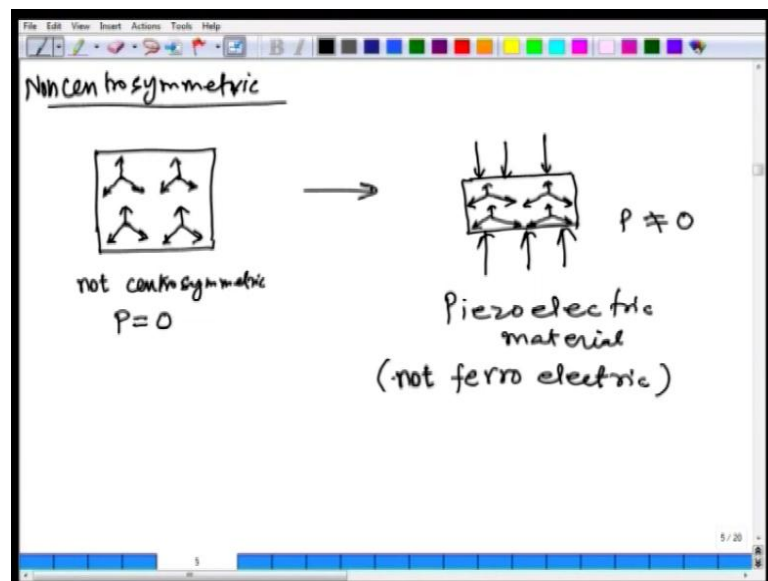
If you were to, for example, apply a stress on this material, a compressive stress, then let us say, this material got compressed in this direction because you applied compressive stress. Mechanical stress if you apply on this what is going to happen? In this case, in this case I am going to show, that this dipoles in this direction getting stretched because you applied stress and if you remember, this is only a schematic. We are showing you direction of the dipoles and and the length of this is showing you the magnitude of the dipole direction and the magnitude here, the magnitude was equal, it was being drawn in symmetric way. Hence, this case, this is long and this direction is short, shorter because when you applied this stress, sort of D has shrunk, whereas it expanded in this direction. The D has expand, the distance between the dipole the positive and negative charge centres have, has increased.

So, if that is the case, then as you apply a stress this happens. But then again this dipole moment pointing this way will cancel, the dipole moment on pointing this way, dipole moment pointing this way will cancel with the dipole moment cancelling with this way though dipoles have changed, dipole moments have changed, but net dipole, dipole moment continues to remain 0, and P is equal to 0. This is the nature of the centrosymmetric structures, that if you apply electric, if you apply a stress, if you apply a stress, there is no change in polarization. Whereas, in piezoelectric material we expected,

that when you apply a stress, then some polarization must be generated and that we will see, will come because of non-centrosymmetry and that is what.

But if it is centrosymmetric like these 11 point groups, in that case, like example, for example, cubic material in such cases, even if you apply a stress, polarization will be 0. Of course, it can still be linear dielectric, that means, if you apply electric field to this material, these dipoles, which will change, dipole moment will change and there will be a, there may be a net dipole moment, there will be some net dipole moment as a consequence. So, that would still be happen, this will have some dielectric constant, which will be a low dielectric constant, but we will see what happens if this was non-centrosymmetric and what happens as a consequence of non-centrosymmetry when spontaneous polarization becomes possible. These are the two aspects we need to look at as heading towards barium titanate. So, now, so this is a centrosymmetric.

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Now, let us look at non-centrosymmetric; now let us look at non-centrosymmetric crystal. In fact, let us add word non- here, therefore now let us look at, now one of the non-centrosymmetric. Let us take an example like this. Now, what if, if these dipoles are pointing like this? And it was nicely symmetric, but now in this form, or notice this, is not centrosymmetric. Inversion symmetry is not there; therefore, it is not, not a centrosymmetric structure.

But in this case, polarization is still 0, polarization is still 0 because these three vectors, dipole vectors, when added vectorially would produce P equal to 0. The length of these each dipole, I am showing extended means, which shows you the magnitude of dipole direction and the length shows you the magnitude of the dipole, they still are equal and hence, what will happen is net polarization would be 0.

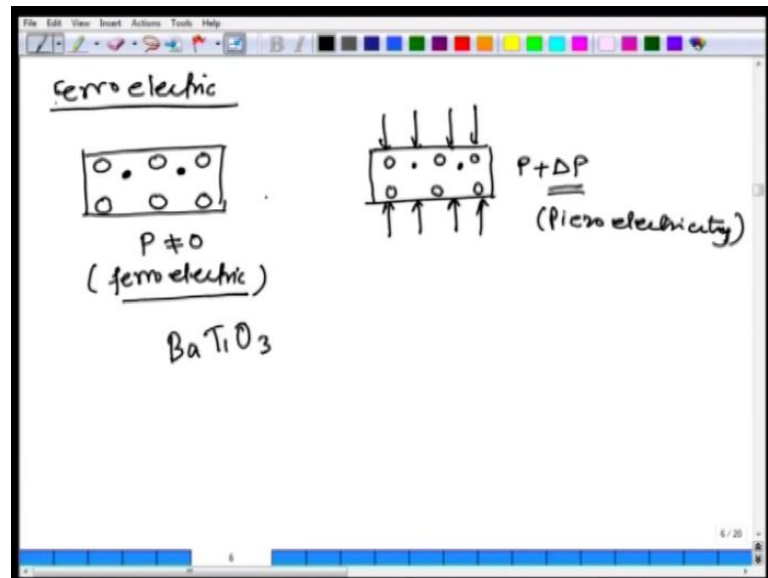
Now, in this case let us apply stress to the crystal. What happens when you apply a stress, let us say again compressive stress, something like this. You applied a compressive stress on this material, but now something will happen. As a consequence of this compressive, strength, stress, let us say, now this has become like this. These two have got elongated, these two have gotten elongated, this has become, this has shortened in comparison to here because of the stress, which is applied.

Now, what we think? Now, if this happens you will get value of P , polarization is not 0. Remember, these three vectors when added would not result in 0. Now, there will be net dipole moment in this direction, there will be a net, there will be a net dipole moment, which you are going to see as a consequence in this direction, you are going to see a net dipole moment because of you, because of you have applied a stress and these materials are piezoelectric. This is an example of piezoelectric material. Let us go back, if you remove the stress it can go back to the state and hence, this is not spontaneous. This polarization, which we get is not spontaneous, it is not permanent, it is not permanent in nature, it can, it go away. Such are piezoelectric materials, which I had pointed out.

Non-centrosymmetry leads to one or more polar axis and you have now seen the polar axis in one direction, which is this direction. Polarization can result if you apply stress in this particular schematic. So, what you get is a piezoelectric material and this piezoelectric material was defined as if you apply a stress, it produces polarization, it does not say it is spontaneous, however.

Now, if you further move forward and take another example where you will see, that we could have also, we could also have spontaneous polarization, what do I mean by that. That means, even when you not apply, if you have not applied any stress, still even if, even, even, but this is not. So, this is not ferroelectric I should write, that is all I should do because it is not spontaneous.

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Now, I am going to give you an example of ferroelectric material. Let us say, we go to third case, which is let us say ferroelectric. Of course, in this case also it will be piezoelectric, ferroelectric materials are always piezoelectric or pyroelectric for that matter, but now in this case what I am going to do is let us take a structure, which is like this. Let us say we consider ions as negative ions, let us say these are negative ions, which I am drawing, these are negative ions and hence, positive ion, let us say these are the positive ions, sorry, so these are the positive ions, what you see?

You see, the centre of charge of positive charge, centre of positive charge and centre of negative charge are not identical. So, there is some distance between some, there is some separation between centre of positive charge and negative charge. If such a situation arises, this material will have some polarization, which is not equal to 0, that means, even in its native state it has polarization. Such materials are ferroelectric.

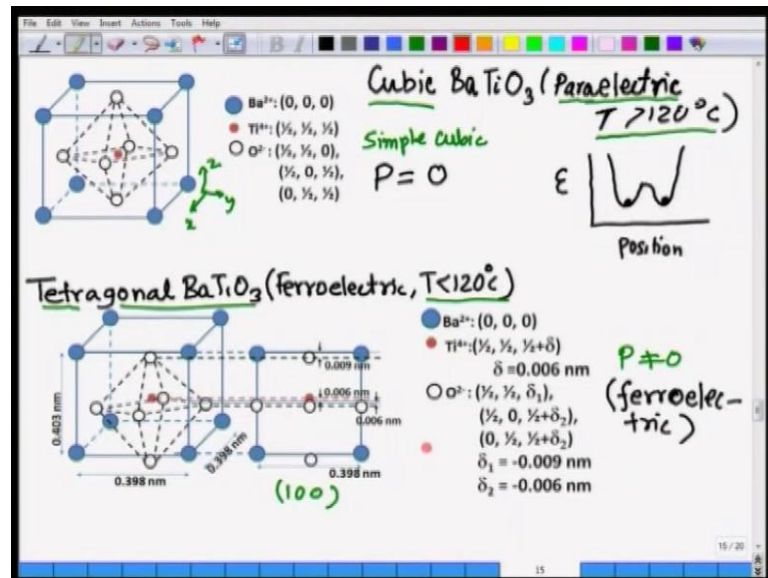
And if you apply for such, since, since it is a ferroelectric material, it can also demonstrate piezoelectricity and this we can see as follows, that if you were to apply stress in this material, the fact there is spontaneous polarization even when you have not done anything, P is not equal to 0 implies, that it is a ferroelectric material. Since ferroelectric material is also piezoelectric material, therefore let us look how that electricity plays out in a ferroelectric material.

So, you apply this stress and what happens in the consequence is that you have these centres of negative charges and this ion positions further change. As opposed to here, they have slightly moved up further with respect to these centres for negative charges and in this case, you have P plus some ΔP , some additional polarization. This is showing you a behaviour, which shows piezoelectricity. Of course, if you take away the stress, you will come back to the state where there will be again some net polarization, but of lower value, which is P , of lower value, which is P , so that polarization will continue to be there.

So, this is the nature of ferroelectric material, which is where we are heading, that the point you need to remember is, that the non-linear dielectrics, which we are about to deal with, I am going to talk about more about ferroelectric materials, these are the non-linear dielectrics. They must have, they must be non-centrosymmetric, they must be non-centrosymmetric and must have a polar, must be polar materials; these must be polar materials, so that there is a spontaneous polarization; there is a spontaneous polarization is there and and and as a consequence of which ferroelectricity will arise.

So, let us, in order to look at this material, let us look at, so now let us start with barium titanate as an example of this ferroelectric, non-linear, non-linear dielectric, non-linear dielectric ferroelectric, I am using it interchangeably, let us use barium titanate as an example of this. And see first physically, let us see how this situation, which I have shown you as schematic, how that is realised in actual crystal. Once we have seen physically as to what happens, then we will go through the mathematics of it and finish of this lecture.

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To understand ferroelectricity in barium titanate let us see it through this, this slide, this, these pictures I have put here and in order to understand ferroelectricity, let us start with this structure in barium titanate, which is not ferroelectric.

So, what we do is we start with the temperature, which is greater than 120 degrees centigrade. In this case the structure is cubic, the structure is cubic and since structure is cubic, as you know this cubic is a centrosymmetric structure, so it is not possible for this material to be ferroelectric because cubic centrosymmetric and you require non-centrosymmetry for any ferroelectricity. So, now, since this is not ferroelectric we are calling it paraelectric and we are borrowing this name in much the same way as you have ferromagnetism and para, paramagnetism, a ferro, a ferromagnetic material above some temperature called Curie temperature turns into a paramagnetic material when it loses its magnetism. So, similarly, since this material at some is going to be ferroelectric and but at T greater than 120 degree centigrade, it loses its ferroelectricity. Hence, we are calling it paraelectric in the same analogy and it has lost its, it has lost its ferroelectricity because it is cubic in, because it is cubic, alright.

So, let us try to understand this cubic structure first and then we try to go on to ferroelectric phase. So, what do we have this particular material is simple cubic simple cubic and basis set of atoms is, which is 5, 5 atom basis, that is, 1 barium atom 1 titanium atom and 3 oxygen atoms and at what location? Barium is at 0, 0, 0; that means, if I draw

a cube like this here, this cube drawn here, then at the corners we have what is called, what are 0, 0, 0 positions. So, if you wish what we can do is we can put a coordinate axis something like this, this is x, this is y and this is z. So, we can put a coordinative axis something like this and what that means, is that barium is at 0, 0 position. Then it is at this position, let us say this is, this is x-axis, this is y-axis and this is z-axis. So, this is 0, 0 position and if you displace, then by lattice parameters, which is A in this case then.

So, if you go from here to here you get equivalent atom, that is also 0, 0, 0 position. Therefore, or you move by lattice position, lattice display, lattice distance A, then again it is 0, 0, 0. So, these corners are 0, 0, 0 positions. One barium atom, these are some, blue ones are one equivalent to corner of cube means one barium atom in the centre at half, half, half, right here, half, half, half. We have a titanium atom and on the FCC, like positions, that means, on let us say, half, half, 0.

So, if this is x, this is y and this is z, then in that case, half, half, 0 is moved, half in this direction and half in this direction. So, this is half, half, 2. So, this is half, half, 0 oxygen atom and equivalent if you move a lattice parameter, you get an equivalent atom. So, therefore, this is also equivalent half, half, 0 atom. Similarly, you have got half, if you look at half, 0, half, I should erase this, so if you look at this half, 0, half, so I have moved half and then and half this way, 0, half is right here, in z you move half. So, you get this particular oxygen atom and this is an equivalent oxygen atom. Every time you move by lattice parameter, you will only get an equivalent atom.

And similarly, there is 0, half, half, that means, 0, half and half, 0, sorry, 0, half and half. So, you get this at particular atom, 0, half, half, if this particular atom and this is equivalent atom and this particular atom is on this phase, right here, this phase and this particular oxygen, equivalent oxygen atom is on this particular phase of the cube. So, this is simply a, this is a simple cubic structure, it is centrosymmetric. And therefore, as a consequence you see, where is the centre of positive charge, you see these are barium atoms, it is centre of positive charges is right in the centre and titanium, of course, is right here at the same place at half, half, half. So, centre of all the positive charges is, is at half, half, half.

Similarly, if you consider this octahedron made by this oxygen atom, centre of that is also at half, half, half. So, centre of negative charge is due to oxygen, is also at half, half,

half and therefore, the centre of positive charge and centre of negative charge are coincident on them, on each other and a consequence is, therefore what we will have is total polarization as equal to 0, because there will be no net dipole moment in a unit cell and therefore, polarization will be 0, centrosymmetric structure leads to that. So, that is a simple cubic structure.

So, now, let us look at ferroelectricity, how does ferroelectricity comes? Now, suppose you start cooling it down to, cooling it down below 120 degree centigrade. So, if you go down to at temperatures less than 120 degree centigrade, then what happens? And in fact, from 120 centigrades I write, may be from something less than, less, from temperatures anywhere from room temperature to onwards to 120 degree centigrade. In fact, from temperatures even less then room temperatures to 120 degree centigrade, the barium titanate goes into a tetragonal phase; so barium titanate goes into a tetragonal phase. So, phase transformation happens at 120 degree centigrade as you cool it down, cool this down from temperatures greater than 120 degree centigrade. And then when you cool down to less than 120 degree centigrade, at 120 degree centigrade, this particular material changes its phase and it becomes tetragonal. So, this particular tetragonal phase is ferroelectric.

And how does this ferroelectricity arise is what I want to show you. So, how does this happen, so let us look at this. So, what is happening is consider a go back here to this, this particular diagram of simple cubic. Now, imagine what you are doing is, that you are pulling this axis up, you are elongating this axis a little bit and may be squeezing this little bit. So, what you have in a tetragonal one is, that this particular dimension is 0.403 nanometers, whereas these two a and b axis are equal and they are 0.398 nanometers. Now, let us this, tetragon I have formed by placing the barium atoms. So, these barium atoms, again we are calling at 0, 0, 0. So, this is the 0, 0, 0, 8 barium atoms, which are the, which form the cage, tetragonal cage. Now, we are going to place all other atoms with respect to this particular cage.

So, if you look at, so now what I am doing is, that in order to explain to you what has happened, that imagine for this cage, this blue line, particular blue line going through is the centre line, is a centre line, is the centre line of this cage. What is this diagram? This diagram, I am showing this particular phase, this particular phase is being shown on this

diagram. In other words, I am showing you one 0, 0 projection of barium; I am showing you one 0, 0 projection of this particular barium titanate tetragonal structure.

So, ok, so if that is the case. So, if I am, I am, what I am doing is I am taking a centre line and I am drawing a blue centre line. Now, think like this, that this (()) in this look, at this simple cubic there was a, this is the octahedron formed by oxygen atom, atoms here by this 6, these 6 hexa-oxygen atoms, had formed an octahedron. Now, imagine this octahedron slightly shifts down, this, this octahedron has slightly shift down with respect to the central line. So, what I am showing you here is, now in this case this is gone here.

So, now what I am showing you here is, that with respect to those blue lines in the centre, these particular oxygen atoms have moved slightly down. What am I showing you, that this is the oxygen atom, these four oxygen atoms, so if I take one 0, 0 position, then this particular atom is shown right here, this particular atom is shown right here and these two will fall on top of each other and that is the atom, oxygen atom here and with respect to those blue line, which represented the centre of the cage, this barium cage, then this oxygen octahedron has moved down a little bit by this 0 point. So, this is, this distance is between blue line and the black line, 0.006 nanometer is, has moved down.

Not only that something more has happened in fact. This octahedral is distorted, these two oxygen atoms has not simply just displaced down, they have moved, they have been squeezed, squeezed, these two atoms have been squeezed further and then they have displaced by with respect to this top line. They have not just moved 0.006, instead they have moved 0.009. So, this octahedron has even, in fact, from the simple cubic this octahedron has distorted also. So, these two things has, have happened.

Now, if you look at the titanium, titanium atom, then this particular titanium atom, with respect to this blue centre line has slightly moved up. This is the distance, this is an arrow showing spacing between the blue line and the red line and this titanium atom has slightly moved up by amount 0.006. So, that is what has happened in this barium titanate structure and consequence of that now will be, now you can imagine, you can think like this. The centre of these barium, centre of positive charge, due to, due to these barium atoms will, of course, will be smack in the centre where the blue line is the centre of all the positive charges due to barium. And titanium charge is positive charge due to

titanium is, where it is shown, right that is where titanium atom is. So, somewhere net positive charge will be above this blue line.

Whereas, if you look at the oxygen, now oxygen cage right here, the net positive charge will be negative charge, would now be slightly blue below the blue line and therefore, now the centre of positive charge and centres of negative charge are not going to be coincident on top of each other, consequence of that is, that this particular, in this particular material P will not be equal to 0, P will not be equal to 0 and that means, will, there will be net polarization or net dipole moment in cell and in material they can be, therefore a net polarization and such a material therefore, we will say, it, so this particular material, therefore acquires ferroelectric, electricity, ferroelectric. So, this becomes a ferroelectric material.

The fact, that it has a spontaneous dipole moment. Now, now that it has a spontaneous dipole, this material in this structure, tetragonal structure, the one what I have described you here, described here, the fact that it has a net dipole moment polarization, that means, it is not 0, therefore this material can be ferroelectric. In fact, since there is a spontaneous polarization, therefore for sure, it is pyroelectric, it is pyroelectric and as you know, that some pyroelectric material can be ferroelectric, in this particular instance this is also ferroelectric, alright, and this all this is happened because the structure is not centrosymmetric. So, as long, so this is the point, which needs to be understood why because of structure electricity in barium titanate arises.

So, as a consequence what happens, before we go on to describe this particular material, let us one more time do the mathematics of it as to what happens, then what, what is going on in this material and we, we will describe this by using the same equation as here. Remember, I had shown you, that dielectric susceptibility is given by this quantity. Now, imagine, now imagine what happen, in fact, why I want to speak about one more thing in terms of why this structure has happened like this.

I want to connect to something I had discussed earlier also, you will recall, you go back a lecture and you will recall I had drawn a curve something like this. I was talking in terms of, I was talking about dipolar mechanism, for, in context of dielectric constants, I was saying, I was talking about dipolar mechanism and I had plotted energy versus position and I had position for, and in this I had shown a plot, which was something like this. And

I was saying there could be two equivalent positions, these two positions and atoms could hop, ions could hop from one to another position and from, from this position they are two, two, two positions in energy are equivalent positions, so they are equally probable, that is what we are talking about.

Now, let us connect this idea back with this ferroelectric, back with this, this ferroelectrics idea right here in this structure. And what does it mean? What is this hopping involved? I was talking about, in dipolar mechanism there is hopping involved and what is that about, now we, let us connect that and understand its dielectric property. So, now I will come back again to the simple cubic structure, which was symmetric, nice symmetric structure. Let us see how we are going to get this tetragonal structure.

What we will do is, let us do this, take these four oxygen atoms, take these four oxygen atoms in order to make tetragon. Start squeezing these four atoms slightly inside while extending these two oxygen atom, pull them up, pull this up and pull this atom down, imagine, stretch these two particular atoms further apart and as consequence, these two, four oxygen atoms pull them closer. If you do that what is going to happen? You see the titanium is nicely sitting in the centre. If you are going to squeeze this oxygen atoms in, then the only way out is, that this titanium atom should pop out of the pocket, either it can go up or it can go down.

So, now this is what you can see here, that as you convert it to a tetragonal structure, in this structure, that I have shown, that what I am showing you is, this is what has happened is this titanium atom decided to pop slightly out of plain of these four oxygen atoms and it went up a little bit and this whole cage, this whole cage, which I am showing you here, this cage are formed by oxygen atoms, has moved down a little. So, titanium moved up a little bit and oxygen atoms, cage of oxygen atom moved it, moved down a little bit and this all happened because you squeezed these four atoms in, ions in, of, and these two ions further apart, pull them apart and that led to a tetragonal structure. So, this is what has happened and hence this kind of structure forms.

But notice, that instead of titanium popping up it was equally possible, that this titanium would have popped down, it could have popped down also and in which case this oxygen cell could have moved slightly up those usually equivalent structure. One, I have shown you is, in this case titanium has popped up and oxygen moved down, but you can easily

imagine this cage moving up and this titanium moving down. So, these are two equivalent positions and now, therefore, back. So, these two equivalent positions; so these are the two equivalent positions for titanium ion.

Now, you can see, so this is, now if you apply electric field, if you apply electric field in particular direction, then one of this can become more favourable, one of these can become favourable and that nature of electric field will decide. Therefore, whether titanium would pop up or titanium will pop down depending on which of these two positions becomes more favourable and it is this mechanism, which then leads to, to, to, to dielectric constants, one of the high dielectric constants in barium titanate.

With this connection let us move on. Now, if you look at the, look at the mathematics of this, then again go back to this structure, which I was talking about. This, the dielectric constant or dielectric constant k' connected to susceptibility is given by $n^2 = \epsilon_0 \alpha / (\epsilon_0 \alpha - 1)$ and remember this α is the quantity, which is called polarizability.

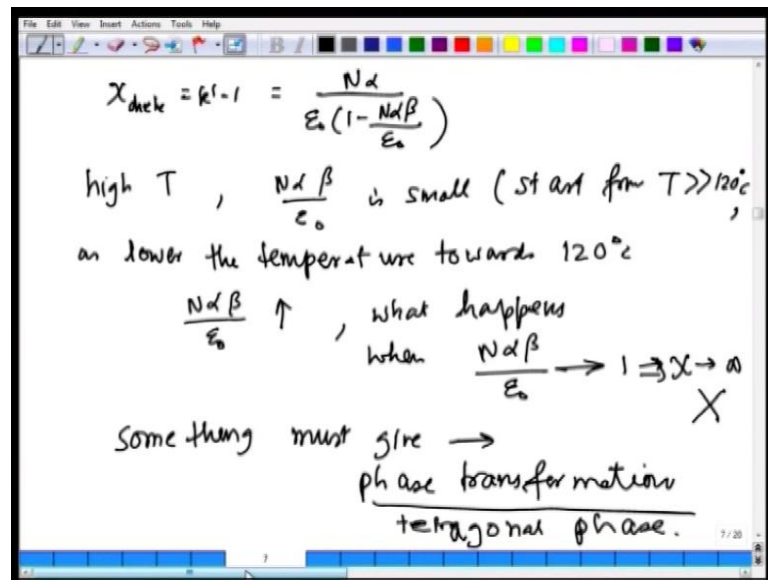
Now, suppose you are at high temperature greater than 120 degree centigrade and at that high temperature what is going to happen? You are going to have dipole moments, but the kT temperature will try to randomize these directions of these dipole moments and as a result. So, if I have a dipole pointing this way, some dipole pointing this way, some dipole pointing this way, some dipole pointing this way, in all different directions because of this barium titanate crystals, I have, I have this, this way.

I apply an electric, I apply electric field, which will, then all these dipoles will, whatever the polarization, which has been created because of electric field, sorry. So, cubic, we are talking about cubic barium titanate at temperatures greater, greater than 120 degree centigrade, there is no permanent dipole moment. When I apply electric fields, direct dipole moments are created and these dipole moments are pointing in random directions, any direction they are pointing out and this kT energy is trying to randomize them.

Now, what happens when you cool down? As you begin to cool down, your cool down, the affect of kT , that means, effect of k temperature trying to randomize the polarization direction will become, become lower and lower and hence, your dipole moment is, net dipole moment is going to increase in the direction of electric field that you are applying because polarization dipole moments will like to follow electric field. It is only the kT

energy, which is trying to disturb them from out of their position. So, as you cool down, your polarizability is going to increase, this polarizability is going to increase and high temperature, this term may be very small. In fact, let me, let me take this, write this expression one more time.

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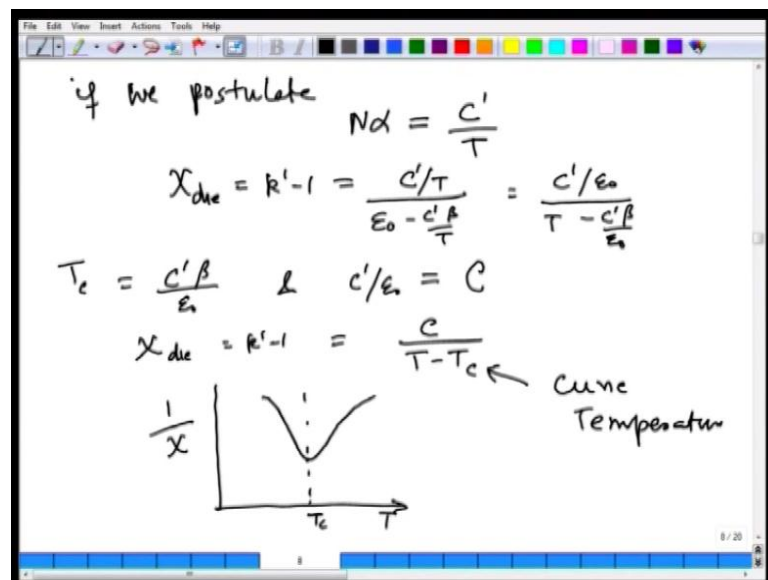
So, the expression I had written is that dielectric is equal to k prime minus 1 equal to N alpha epsilon naught 1 minus N alpha beta by epsilon naught. And high T, high temperature N alpha beta epsilon naught is small because very high temperature, this alpha is, small temperatures are trying to, temperature is trying to randomize, randomize all the dipoles. And this quantity is small, you can neglect it in comparison to 1 and you will get some small dielectric susceptibility value. But at, as you low, as you lower the temperature and I am saying, start from, start from T much greater than 120 degree centigrade and we are heading towards 120 degree centigrade. So, as you lower the temperature towards 120 degree centigrade, what happens? Your alpha is going to increase and this term is going to increase, this going to increase, N alpha beta by epsilon naught is going to increase.

What happens? When N alpha beta epsilon naught approaches 1? That is an interesting question because you can see, as it approaches 1, this term, this quantity is going to blow up, dielectric constant will blow up, it will start going towards infinity. You can see this because this will become divided by 0 and this number will blow up and dielectric

constant of material cannot be, you know, it is a polarization, it is dipole moments per unit volume, the dipoles cannot go to head towards infinity.

So, something is wrong, this cannot happen, physically not feasible. So, something must give, in fact, that means, implies, we will tend towards, move towards infinity, that cannot happen, something must give. And what happens is phase transformation and this is because of this reason at higher temperature of 120 degree centigrade when this value is tending towards 1 and crystal would fly apart if nothing happened and since crystal does exist. So, what has happened is it requires phase transformation and you get what is called as tetragonal phase, tetragonal phase, which I have shown of barium titanate. So, that is what you start getting the, the, of barium titanate tetragonal phase is what you get.

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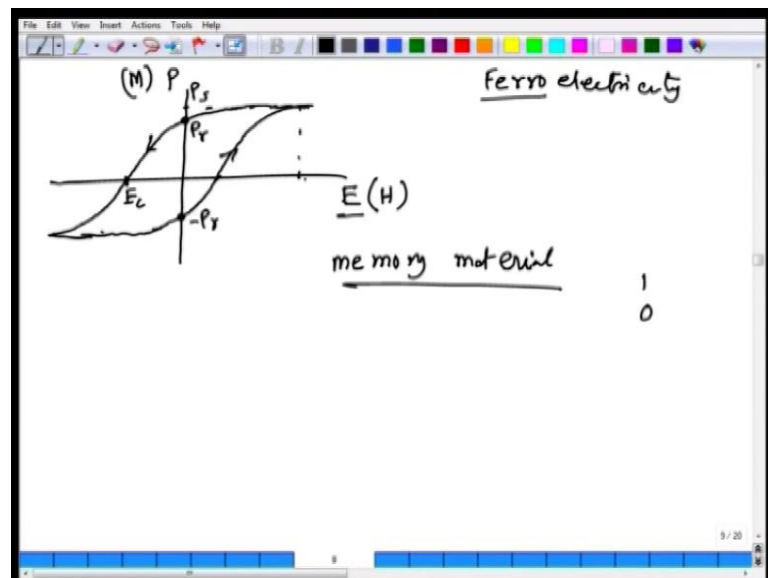


Now, if you, if you postulate, if you, if we, if we postulate, if we postulate, that this polarizability, which we are talking about is proportional to some constant divided by T, remember I said, as temperature decreases, polarizability increases. So, we postulate, that it is inversely proportional to power 1 of T, then in that case we can write dielectric susceptibility as or dielectric constant as C prime by T divided by epsilon naught. Remember, what I am doing is I am substituting in here for N alpha, I am substituting into this expression, I am substituting value of N alpha, this is what I am substituting it here.

So, if I do that this is $\epsilon' - \frac{C}{T - T_c}$, we shall be going to write as $\frac{C}{T - T_c}$. And if we define $\frac{C}{\epsilon'}$ as some temperature T_c and $\frac{C}{\epsilon'}$ as another constant C , in that case I will write dielectric susceptibility as or dielectric constant as equal to some C divided by $T - T_c$, which is well known Curie-Weiss law. So, that is a well known Curie-Weiss law.

And what is it and if I, therefore now what I can do is I can plot susceptibility versus temperature, temperature versus susceptibility and in that case, for temperatures, sorry, χ by susceptibility is what I want to plot. Remember, what happens, let us say this is T_c , so this is T_c , remember this is going to go something like this. As we lower the temperature susceptibility increases and therefore, χ by susceptibility decreases. And what happens, at this point of phase transformation occurs and if phase transformation occurs and otherwise, this would have gone down, this would have continued to go down towards a value of 0, because and that means, susceptibility gone to infinity, something like this and because of phase transformation you get a behaviour, which is something like this and starts increasing again according to this, this expression and this is what is called as Curie temperature.

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In final, in final (()), another five minutes, let me try to now show you the behaviour of this particular barium titanate material, that if you look at ferroelectric materials, they will show you much the same way as ferromagnetic materials, they will show you what is ferroelectricity then. What is ferroelectricity? What it means is, that if you have such a material, then it could, would show a behaviour, which is something like this, a hysteresis between polarization and electric field. So, if you apply electric field it produces polarization. Remember, you have applied a magnetic field, it produces magnetization and in ferromagnetic material and this is a very similar thing and that is why the name ferroelectricity have been given here because it is a curve between P and E, this hysteresis.

As you apply a field, electric field, you get what is called saturation polarization. This is the saturation polarization in this material because this titanium atom, remember, has popped out in one direction, there is, and then popped out and you get some polarization, very large polarization. And when you remove this electric field you get some remnant polarization. This is the remnant polarization and if you want to remove this remnant polarization, you have to apply a cohesive field E_c and this story repeats if you go on other direction. That means, you can apply a field and you can reverse direction of polarization and move electric field. This still is some minus P_r or plus P_r , which is this polarization, which is still available in this material and hence, this is a good memory material.

You can use electric field to apply, you can apply electric field and create polarization, remove electric field and the state remains. If you apply electric field up to here, for example, you can, and then remove electric field, you will have this P_r , electric field, call it bit 1, bit 1. And if you want to create bit 0, then what you have to do is apply electric field up to this extent, right here, and then remove their electric field. You would have written minus P_r , let us call that 0 and hence, you can write one of 0 on it and this could be a good memory material, but this is a behaviour of this material and these are ferroelectric material, very important class of materials in, in general.

Thank you.