Advanced Ceramics for Strategic Applications

Prof. H. S. Maiti
Department of Mechanical Engineering
Indian Institute of Technology, Kharagpur

Lecture - 19
Topic - Ferroelectric
Piezoelectric and Pyroelectric Ceramics

To continue our discussion on the Electrical phenomena in insulating materials. We will introduce a new variety of characteristics, new classes of dielectric material called Ferroelectric, Piezoelectric, and Pyroelectric ceramics. Well they are also dielectric materials they have the dielectric polarization, the primary difference is they do get polarize even in the absence of electric field. So, they have a spontaneous polarization, which does not need any electrical field external electrical field to get them polarized. Of course and in normal conditions you do not find polarization as such that all the atomistic level. So, on a larger volume on the bulk material and there is as such no polarization until unless we do some special treatment to them.

The groups are called Ferroelectric, Piezoelectric, and Pyroelectric ceramics; they have certain common features. So, we will be discussing them together, but to start with we will have a discussion about ferroelectric and then go to the piezoelectric as well as pyroelectric ceramics.

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Ferroelectric Ceramics

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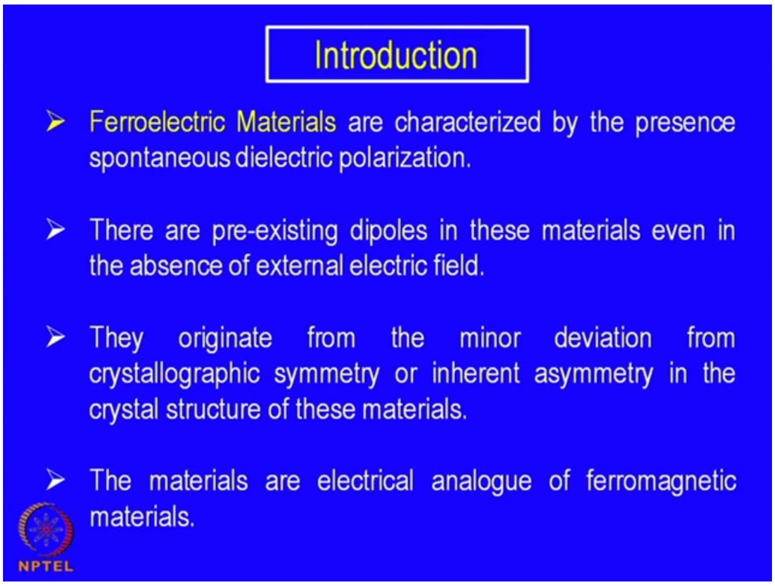

Introduction

- Ferroelectric Materials are characterized by the presence spontaneous dielectric polarization.
- There are pre-existing dipoles in these materials even in the absence of external electric field.
- They originate from the minor deviation from crystallographic symmetry or inherent asymmetry in the crystal structure of these materials.
- The materials are electrical analogue of ferromagnetic materials.

So, our discussion first starts with the Ferroelectric ceramics. While you talk about ceramics they are primarily pair of set kind of compounds, however beside ceramics there are many other Ferroelectric ceramics which are known. In fact Ferroelectric materials in general are characterized by the presence of spontaneous dielectric polarization as I have just mentioned. So, even without the electric field they have their own polarization. These polarization do are existing, because of the dipoles they have a pre-existing dipoles in this material is even in the absence of external electric field; that is the basic meaning.

They originate from the minor deviation from crystallographic symmetry. So, basically it is a crystallography which is basic which is known to be origin of this kind of behavior; of course that leads to many other thermodynamic as well as different kinds of phonons & phonon modes and so on will not be discussing all those here at primarily considering the crystallographic origin of this property.

Either they are deviations in the crystallographic symmetry or there is some inherent asymmetry in the crystal structure itself. So, both of them can lead to spontaneous polarization or dipole movement generated. The materials are electrical analogue of ferromagnetic materials as the name suggests ferroelectric materials their impact develops much later than the so called ferromagnetic materials. And, because of their similarity and many ways and they have been named as ferroelectric rather than ferromagnetic materials.

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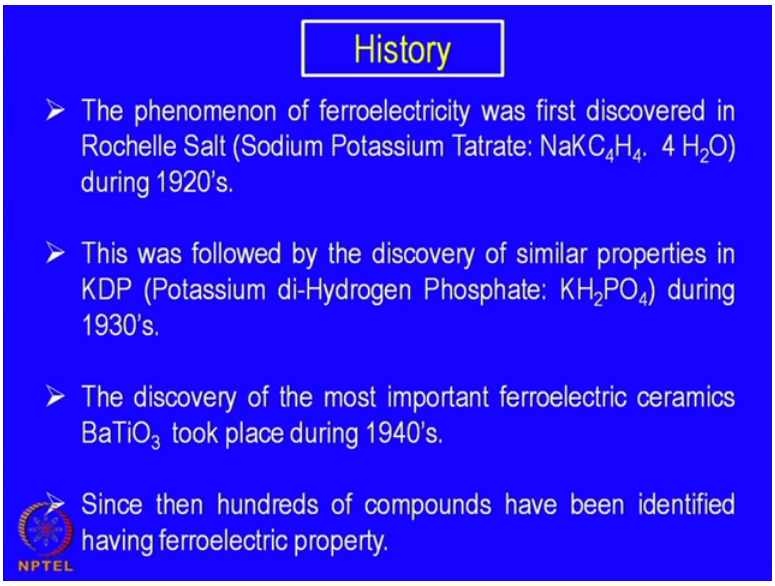

History

- The phenomenon of ferroelectricity was first discovered in Rochelle Salt (Sodium Potassium Tatrate: $NaKC_4H_4$. $4\,H_2O$) during 1920's.
- This was followed by the discovery of similar properties in KDP (Potassium di-Hydrogen Phosphate: KH_2PO_4) during 1930's.
- The discovery of the most important ferroelectric ceramics $BaTiO_3$ took place during 1940's.
- Since then hundreds of compounds have been identified having ferroelectric property.

If you go to the history of this; it was not on the Ferro oxide family or compounds which were discovered first but it was discovered in around in 1920s a in a Soluble salt called Rochelle salt which is nothing, but Sodium potassium Tatrate formula is also, given there. Later on about a decade; later a one more compound also discovered having the similar properties that is sortly in salt name is KDP; the potassium di-Hydrogen Phosphate is also a soluble salt. Those days; these are the materials of which single crystals could be grown little easily. So, because that is the reason they have been studied in the single crystal form; and the properties are basically discovered when the single crystal property will investigated.

In those days it was very difficult to grow single ceramic materials because of their high melting point. And, therefore, these are the materials which were used are could be produced in a single crystal form; and their properties which discovered in those materials. Later in 1940s the Ferroelectric ceramics was first discovered in Barium titanate. Barium titanate is a Ferro oxide family of compound we have discussed its property structure earlier. So, it is basically a mixed oxide or Barium oxide and Titanium dioxide and its melting point is much about 1000 degree centigrade.

So, it was difficult to make a single crystal of those, but it could be developed around 1940s. And, that was the beginning of a whole group of Ferroelectric ceramics which is been discovered later on. Since, then 100s of compounds have been identified having the Ferroelectric property. Not all of them are ceramics as you can see from this display, but many of them are ceramics and barium titanate is one the most important materials; which has been used for practical applications or industrial applications.

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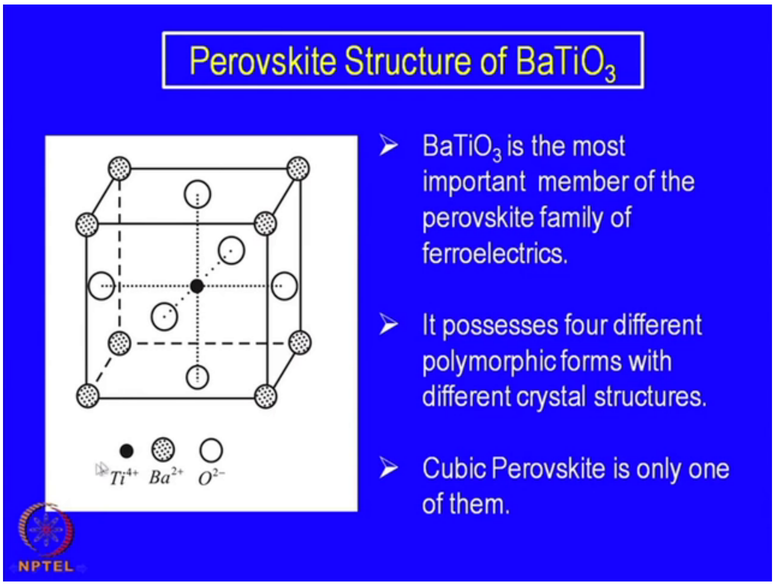

Perovskite Structure of $BaTiO_3$

- $BaTiO_3$ is the most important member of the perovskite family of ferroelectrics.
- It possesses four different polymorphic forms with different crystal structures.
- Cubic Perovskite is only one of them.

What is the structural barium titanate? As mentioned it is basically Perovskite structure and Perovskite as we discussed earlier. It is a family of compounds and although the particular name relates to calcium Titanate terminal mineral calcium titanate. But the structure it is structure type and a large number of compounds do crystallized in this particular form. And, that is all all of them are called Perovskite compounds.

So, Barium Titanate is an important member of this group. And, as per the description this is very simple description of Barium Titanate structure, there are Titanium with (( )) oxygen. So, the open circles are actually oxygen sitting in a cube cube phases. So, all the 6 phases centre of the cube phases are occupied by Oxygen; Titanium is a centre of the cube and corners are occupied by Barium. So, Barium and Oxygen together form a closed part cubic structure and Titanium occupies only a part of Tetrahedron sides.

So, that is the basic description of Barium Titanate Peroxides structures. If you look at some the characteristics of Barium Titanate structure; as it been mentioned Barium titanate is most important member of the Perovskite family of the Ferroelectrics. So, whenever you talk about ferroelectric ceramics will do talk about Barium titanate. And, that becomes a representative compound to discuss all the different properties of ferroelectric ceramics. It is possesses 4 different polymorphic forms with different crystal structures. Although whenever, talk with Barium titanate we do talk about Perovskite structure.

And, anybody asking what is the structure of barium titanate? The answer is Perovskite, but it is really it is really not true this is only one of the polymorphic forms; which has perovskite structure others do not have Perovskite structure. It have they have a different structure, different symmetric and in that we will discuss them later on in this class. Cubic perovskite is mentioned is only one of them. So, it is only one out of 4 structures where barium titanate possesses.

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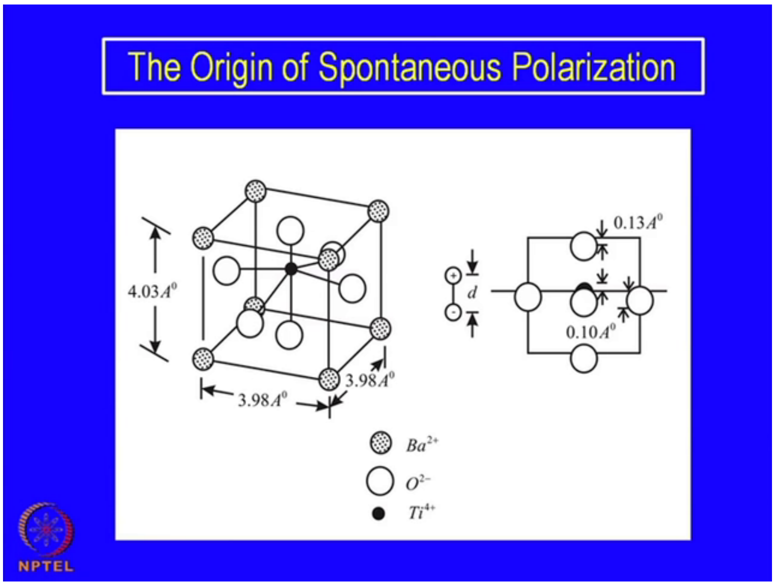

The Origin of Spontaneous Polarization

The origin of Spontaneous Polarization as mentioned. Spontaneous Polarization are even in the 0 field arises basically from the distortion of the crystallographic structure or the crystallographic lattice or the atomic positions in the crystal structure. This is what kind of distortion? Although we describe it as a cubic symmetry, but it really does not have a cubic symmetry. That is little bit of distortion in the c-direction, and there is a displacement of the positive charges, centre of the positive charge and the centre of the negative charge, even without the application of electric field. So, even in the absence of electric field the structure has the same amount of distortion. If you take the cross-section of this cube these are the these are the oxygen ions these are the oxygen ions. These are the 2 sides of surfaces, this is on the top surface, this is on the bottom surface; and this on the front surface.

So, there are 5 oxygen ions we can see here from the cross-section. And, all these oxygen ions are displaced little bit downwards and the distance which is supposed to be on the centre of this phase. It is not exactly on the centre of this phase it is about the distance is about 0.13 angstroms below. So, all of them are actually have displaced from their symmetric position. They are supposed to be on this line, but there are displaced by about 0.1angstroms. So, there is some amount of displacement distortion from the symmetric structure and because of that; that black one is Titanium, the positive will be charged and also, the barium ions in the positive hands and which are at the centre. So, with respect to the centre so with respect to the centre of deposit of all the positive charges the oxygen ions are displaced downwards. And, that is how we create a dipole? Where the positive charges are upwards and the negative charges are placed little bit downwards. So, the centre of the positive charge and the centre of the negative charges is displaced not in the exact frequents with each other.

So, there is a distance of separation of d and therefore, you have a dipole movement. So, dipole moment is generated just like that because of the distortion. So, these are the lattice parameter as you can also see here a and b, these are a and b parameters. So, a parameter as well as b parameter is exactly same 3.98 whereas c parameter the vertical axis is slightly more the vertical dimension units cell is slightly more 4.03. So, that is the origin of the Spontaneous Polarization. And, although we talk about perovskite structure, but in fact that Perovskite Structure do not have the dielectric polarization or the Spontaneous polarization.

It is the distorted form of the Perovskite or having Tetragonal Symmetry because, a b, a and b are equal and c is different. So, it is a tetragonal symmetry which gives rise to the Spontaneous Polarization. So, one has to carefully remember that Perovskite Structure really does not have the Spontaneous Polarization. In fact, that is not Ferroelectric phase actually if the distorted Ferro oxide or the some kind of Tetragonal distortion that actually gives or produces the Spontaneous Polarization.

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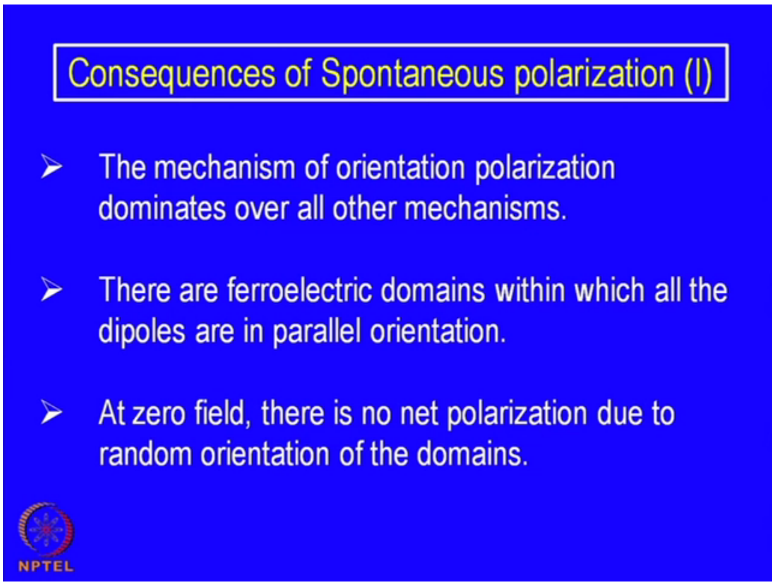

Consequences of Spontaneous polarization (I)

- The mechanism of orientation polarization dominates over all other mechanisms.
- There are ferroelectric domains within which all the dipoles are in parallel orientation.
- At zero field, there is no net polarization due to random orientation of the domains.

So, as a result of the Spontaneous Polarization, what are the things one can expect? Since, we have a Spontaneous Polarization a permanent dipole movement is already there because of the lattice distortion. Out of the four different mechanism of polarization it is the Orientation Polarization dominates here. So, that was mentioned in an earlier class that Ferroelectric ceramics are dominated by this kind of Orientation Polarization mechanism. Which is the basic mechanisms giving to the dielectric polarization.

So, that is one consequence of this Spontaneous Polarization. There are Ferroelectric domains within which all the dipoles are in parallel orientation. So, since there are permanent dipole moments dipole are dipoles are already there. So, this dipoles in fact not individually they are oriented (( )), but individually they are not oriented there are some clusters. So, in those clusters they have a parallel orientation. So, individual may be unit cells or the individual dipoles they are not completely random, but they have certain amount of auditing within certain area and these are called domains.

So, within the domains the dipoles are parallely oriented and therefore, they have a net polarization. However, there are some such large domains adjoining each other just like crystals structure as such like grain boundaries or grains in a poly crystal material. So, you have also a domains large number of domains forms the whole volume on the crystal or the material. So, these domains do have a net polarization or net dipole movement, but they are randomly oriented. So, individual dipoles are not randomly oriented always they have a groups. As a group they form a parallel orientation, but between the groups they have random orientation.

So, we will always have in any Ferroelectric material will have a domains structure just like in a magnetic ferromagnetic domains in a ferromagnetic materials. So, we have domains and we will schematically show what exactly the domain look like. At 0 field, there is no net polarization because a just indicated is this domains are oriented randomly not the individual dipole movements or dipoles, but as a group they are oriented randomly with each other. So, because of that there is no net polarization at 0 field.

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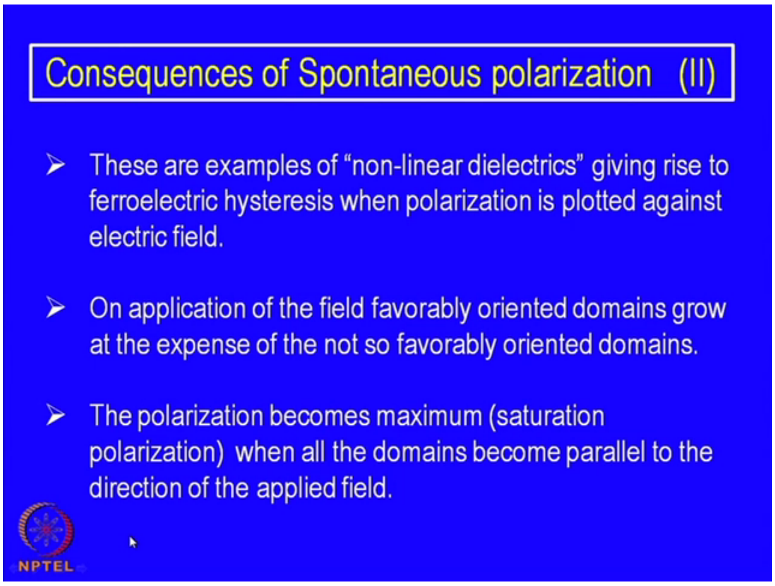

Consequences of Spontaneous polarization (II)

- These are examples of “non-linear dielectrics” giving rise to ferroelectric hysteresis when polarization is plotted against electric field.
- On application of the field favorably oriented domains grow at the expense of the not so favorably oriented domains.
- The polarization becomes maximum (saturation polarization) when all the domains become parallel to the direction of the applied field.

This we have already discussed about the linear dielectrics; were polarization is proportional or directly proportional to the Electric field. But in this material the Ferroelectric material are the examples of non-linear dielectrics giving rise to Ferroelectric Hysteresis; when polarization is plotted against electric field. So, they are a non-linear curve that produces non-linear curve and polarization is plotted against electric field. Unlike the linear dielectrics which are non dielectrics; all dielectrics are not suddenly ferroelectrics, but ferroelectrics forms a but specific group of dielectrics. On application of the field favorably oriented domains grows at the expense the not so favorably oriented domains.

When you apply an electric field dielectric change there is a change of orientation. And, all the dipoles tend to orient themselves along the along the direction of the field. However, all of them do not do it in a random manner there is a process by which this orientation changes from a complete complete random orientation to a pray for orientation. And, this is the change of domain pattern or the domain size.

So, to start with there will be some domains will be favorably oriented with the application of the with the direction of the electric field. Whereas others will be completely misalign. So, when we apply the electric field favorably oriented domains try to grow size of them try to grow and they and unfavorably oriented wants to sink. So, that is how ultimately at the end of the process. All of all the domains will have a parallel orientation aligned with the aligned with direction of the electric field. So, at the end all of them will align parallely and we have a maximum polarization possible at that stage. So, that is what we called saturation and polarization. So, beyond that it cannot change.

We will see how it develops? the polarization becomes maximum that is what we just mentioned the saturation that is called saturation polarization; when all the domains becomes parallel to the direction of the applied field. So, this is also another consequence of having Spontaneous Polarization and a domain structure.

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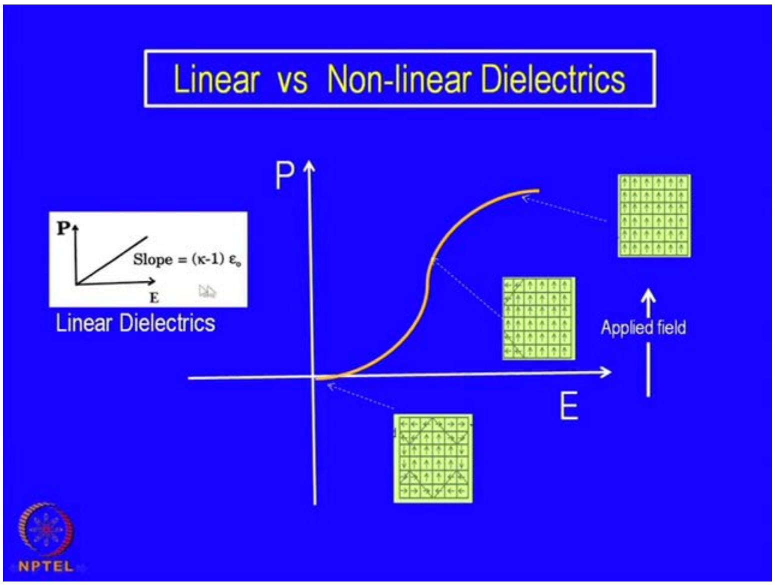

Linear vs Non-linear Dielectrics

Well, this is what we mean by a linear dielectrics and non-linear dielectrics. On the left we have a linear dielectrics that the relationship is shown in one of the earlier classes and the slope is proportional to the dielectric constant. And, here is on the right we have the non-linear dielectrics which are rises or which we see in case of Ferroelectric materials. So, when you apply electric field at 0 field of course polarization is 0. Although there is spontaneous polarization, but the overall polarization is 0. And, as we increase the electric field the polarization increases, but not in a linear fashion it follows a curve curvature here a kind of concave curvature and then becomes a convex.

So, ultimately it becomes a saturated at this some level. Now, here at the domain structures at the domain structures it is been shown here. This is a domain structure these are the individual dipoles; the arrows indicate here is a individual dipoles. Whereas the you can see the some kind of a line here these are the what we call domain (( )).

So, this is one domain one can see all the dipoles are oriented in a particular direction upwards in these case. Whereas in the next domain they are oriented downwards. On the other side this is also another domain; where the dipoles are oriented horizontally towards left, this is towards the right, and this is again towards down, and then left, and right. So, these are about different about 4, 5, 6 different domains available. And, in all the domains of course they have a parallel orientation where as with the every domains they have anti parallel or a 90 degree orientation or a 180 degree orientation. So, accordingly in fact just like in magnetic materials we have a 90 degree domain or domain boundary or a 180 degree domain and so on.

So, at 0 field of course the orientation is such the net dipole movement is 0 and you do not have a polarization. So, polarization is 0 whereas we apply electric field slowly the domains try to grow; this is the reaction of the electric field here upwards. So, which ever domain has upward orientation like this is middle domain will try to grow. And, that is what has happened here? You can see the middle domain has grown and the side domains have disappeared. So, there are of course still some side domains left here not all of them has been disappearing, but slowly it is getting disappearing as the electric field is increased. So, somewhere around this this is the situation where most of them are oriented upwards, but still 2 domains will be be left to be converted. And, when you come to this level you can see this all the domains, all the dipoles are oriented in particular direction and that is along the direction of the applied field.

So, this is where no change can take place and their basically a one can say a single domain system. So, all the domains either single or multiple domain may also be there; but they are domain they are orientation of the polarization will be all in the along the applied field direction. So, this is where we get a complete transformation from a random test to complete order tests. So, random orientation is where completely order tests. And, even after the application of further field there will be no further change in polarization; it will almost saturate here and that is the value of what do you call saturation polarizations. So, this is the relationship of non-linear dielectrics or ferroelectrics dielectrics compared to linear dielectrics which is non ferroelectric dielectric; that is the basic difference.

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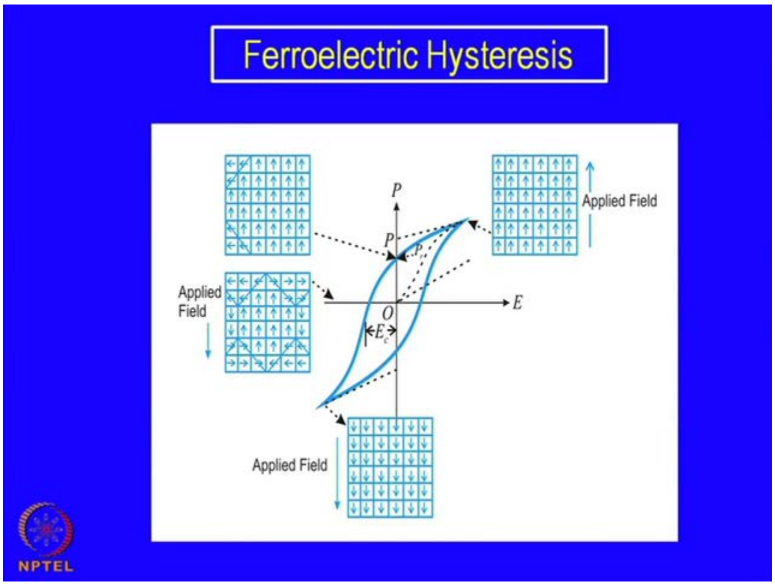

Ferroelectric Hysteresis

So, that give rise or that leads us to the discussion. What happens when we actually cycle, cycle the electric field? That means, we increase the electric field in this direction and then comes back in the negative comes to 0 and then goes to the negative direction. So, what happens to that, what happens to the domain structure? And, this is what exactly happens when if you cycle the electric field? And, this we have discussed this is your saturation polarization. We have all the domains oriented in a particular direction again in the application of electric field the action of the electric field. However, after this saturation if you try to lower down the applied applied voltage then it does not follow then it does not follow this particular path is not a reversible in that manner.

It does not exactly follow the same curve which it has been plotted. In fact it starts from 0 here, it goes to follows this dotted line comes to this. And, then will reduce the electric field it follow a separate different curve and it comes to this. Even at 0 field there is polarization a positive polarization remains there even at the 0 field. Although we have started with a 0 polarization, but ended up the positive polarization even at 0 field. So, this is what we called the remnant polarization Er, remnant polarization because this the reason is it is the way we save the electric field and the time it takes change the orientation. Because it is basically orientation Polarization so the atoms have to move atoms have to move from one place to the other. So, it is a sluggish process it is suddenly a very sluggish process. And, therefore, even if you reduce the electric field the atom has not come back to its original position.

So, as a result of that there is a phase lag. There is a phase lag between the applied electric field and the movement of the domains or the change of orientation of the domains. So, we have a remnant polarization and if you want to make it 0. That means, polarization to bring it 0, you have to apply a negative bias or negative field. So, that negative field is e is called the cohesive field. So, there is the negative bias. So, the negative fields were to needed to bring back the polarization to 0 is called the cohesive field. And, then of course if you want to go to the negative direction further then it will saturate once again in the negative direction. So, you can see here this is one kind of a situation saturation all the domains are parallel and in the direction of the applied field. But on this side here it is reversed because the applied field had changed direction of the applied field has changed; so also the direction of the individual dipoles.

So, in between of course you have a scaled domain structure like this; this is structure which is very similar which was there at this point; this also a 0 polarization, this is also a 0 polarization. So, they have more or less the same common structure which you have seen earlier at this point. So, this very similar but here it is more or less what you saw what we can saw here. So, this is how the domains actually change? And, as a result of the domain who meant who get a hysteresis; what do we call hysterias curve by increasing the applied field it follows 1 particular polarization, 1 particular curve where as by decreasing it follows another.

So, it goes on, it goes on cycle it follows like that. So, initially it started with this and once it is reaches saturation it continues in this pattern. So, this is what we call the hysteresis loop; sometimes call is this is loop is hysteresis diagram. So, all ferroelectric materials this one of the characterizes and that that is because it has a domain structure. And, the domain structure or the movement of the domains on the orientation of the domains takes larger time than the application of the electric field. So, this is our ferroelectric hysteresis.

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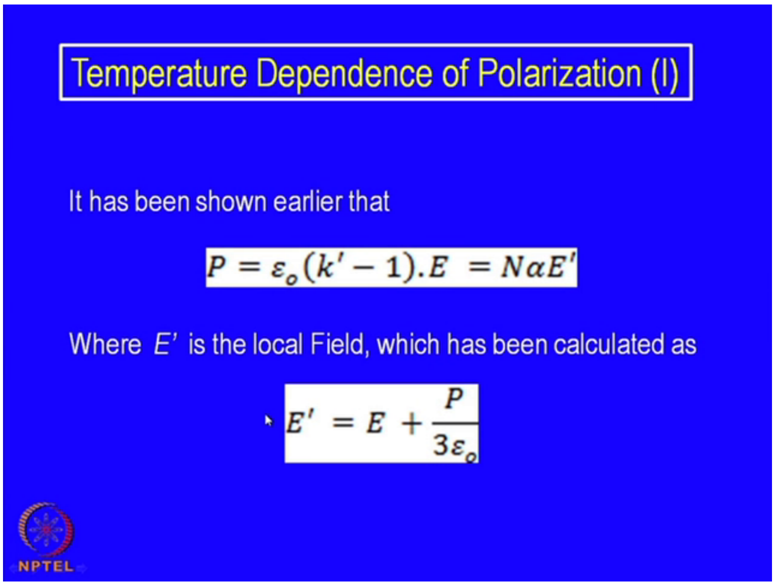

Temperature Dependence of Polarization (I)

It has been shown earlier that

$$P = \varepsilon_o (k' - 1).E \ = N\alpha E'$$

Where E' is the local Field, which has been calculated as

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

Then, we come to another characteristic of all Ferroelectric materials; there is a temperature dependence of the polarization. Temperature dependence of polarization of course is basically the mechanism is orientation polarization. So, it has that particular characteristic. We have seen this equation earlier the polarization is equal to epsilon naught k prime minus 1 E; E is a Electric field. And, that is also equal to in terms of polarizability; in terms alpha is a polarizability number of dipole movements per unit volume.

The polarizability, the polarization of each of one them and multiplied by E prime, E prime as we introduce it is a local field not the external field, but the local field experienced by the individual dipoles within the solid. So, because there are other dipole movements or the other dipoles which have also certain influence on its neighboring dipoles as there is the effective electric field is different. Then, what we have applied from outside? And, one can calculate one can calculate that this there is a relationship between the applied electric field from outside and also the polarization of that particular polymer material.

So, E prime can be related by this equation which has not been derived here, but one can accept that E prime equal to E; sorry E prime equal to E plus P by 3 epsilon naught. So, this is the expression of E prime.

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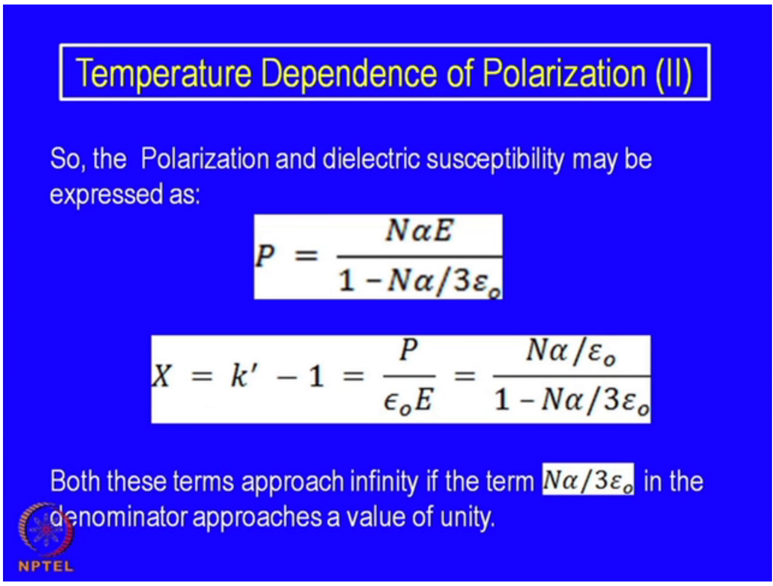

Temperature Dependence of Polarization (II)

So, the Polarization and dielectric susceptibility may be expressed as:

$$P = \frac{N\alpha E}{1 - N\alpha/3\varepsilon_o}$$

$$X = k' - 1 = \frac{P}{\epsilon_o E} = \frac{N\alpha/\varepsilon_o}{1 - N\alpha/3\varepsilon_o}$$

Both these terms approach infinity if the term $N\alpha/3\varepsilon_o$ in the denominator approaches a value of unity.

If you continue so, the polarization and the dielectric acceptability also express these are as per definition from the earlier relationship polarization. Then, in terms of their applied field in N alpha E by 1 minus N alpha by 3 epsilon naught. This is the expression of Polarization. And, this is the expression of Susceptibility dielectric, dielectric susceptibility which is again k prime minus 1; this is all been introduced and then this also in terms of because this is P. So, just place P here you will find that. Both these terms approach infinity; now both these terms have this value or this term N alpha over 3 epsilon naught; if somehow this becomes 1. This becomes 1; this becomes infinity; Polarization becomes infinity and susceptibility also becomes infinity provided this term becomes 1. Now, on the certain situation this comes really becomes 1, and that is what we will see under what conditions this term can be 1.

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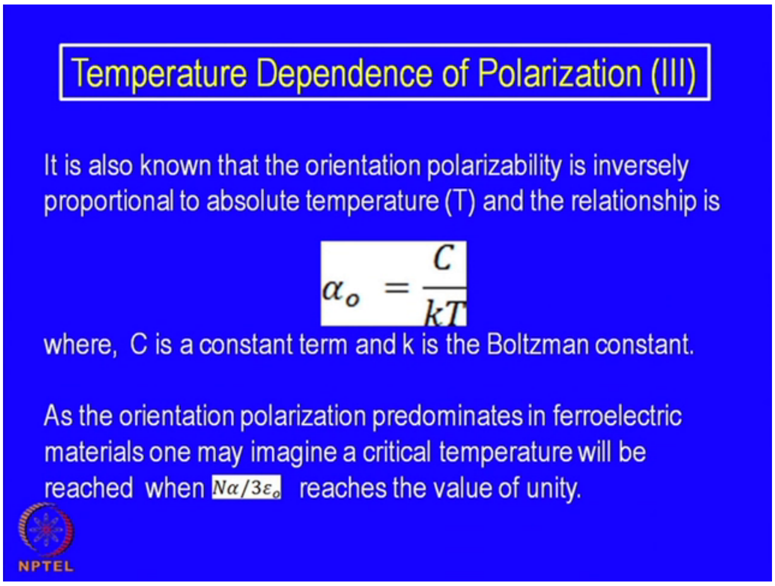

Temperature Dependence of Polarization (III)

It is also known that the orientation polarizability is inversely proportional to absolute temperature (T) and the relationship is

$$\alpha_o = \frac{C}{kT}$$

where, C is a constant term and k is the Boltzman constant.

As the orientation polarization predominates in ferroelectric materials one may imagine a critical temperature will be reached when $N\alpha/3\varepsilon_o$ reaches the value of unity.

It is also known that the orientation polarizability alpha; is inversely propositional to the absolute temperature. So, this is the actually temperature dependence of the overall polarization comes from this particular equation, that is the relationship alpha o it is not alpha0; it is alpha o; the orientation polarization. It is actually inversely proportional to the absolute temperature through this relationship C is a constant, some kind of a constant; constant terms and k is a Boltzmann constant. So, it is actually inversely proportional to temperature. So, this is one relationship of the polarizability orientation polarizability.

As the orientation polarization predominates in ferroelectric material one may imagine a critical temperature will be reached; when N alpha by 3 epsilon reaches the value of infinity. This if this alpha in fact this alpha is basically alpha 0. So, once reaches unity then at a particular temperature so that temperature becomes quite and important parameter for us thus at T equal to Tc.

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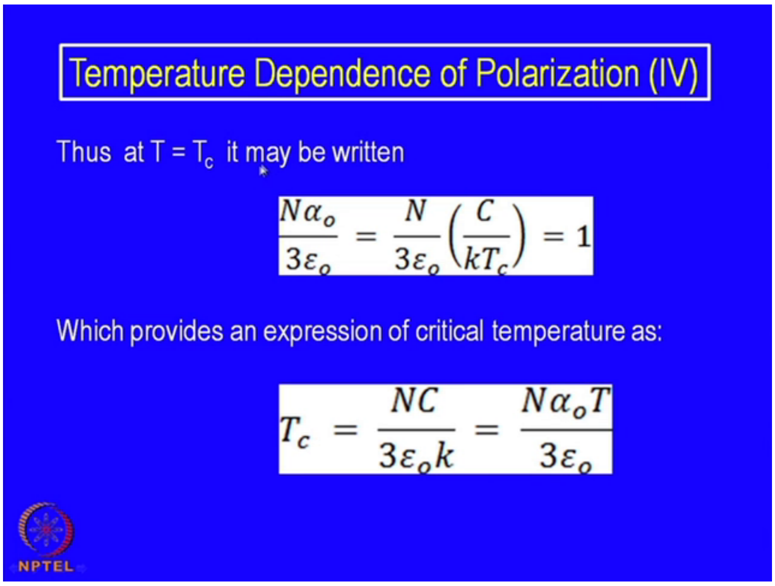

Temperature Dependence of Polarization (IV)

Thus at T = T_c it may be written

$$\frac{N\alpha_o}{3\varepsilon_o} = \frac{N}{3\varepsilon_o}\left(\frac{C}{kT_c}\right) = 1$$

Which provides an expression of critical temperature as:

$$T_c = \frac{NC}{3\varepsilon_o k} = \frac{N\alpha_o T}{3\varepsilon_o}$$

It may be written this if this satisfies. Then, so T becomes Tc when this N alpha by 3; is N alpha naught; actually naught an alpha o; and 3 epsilon naught becomes 1. So, this is situation where the temperature we consider as a critical temperature. So, it provides an expression of critical temperature as Tc equal to this value. So, N alpha just like transposing it one can find out this is the expression for Tc.

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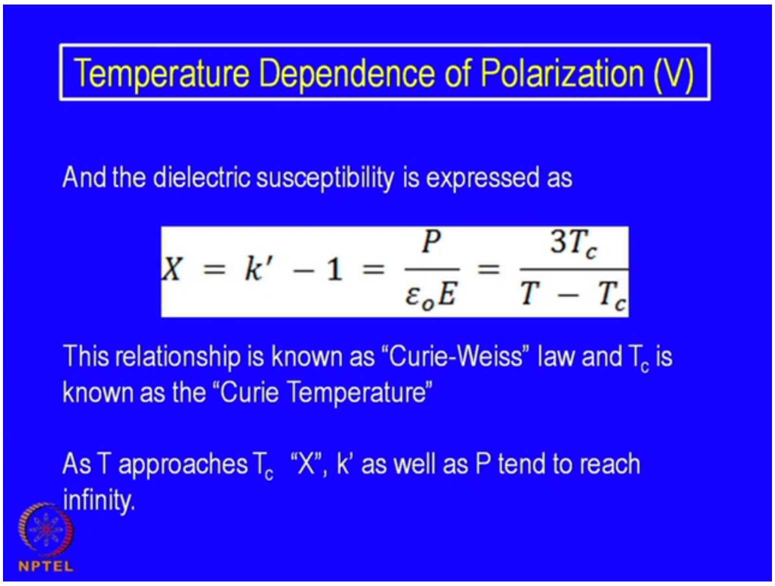

Temperature Dependence of Polarization (V)

And the dielectric susceptibility is expressed as

$$X = k' - 1 = \frac{P}{\varepsilon_o E} = \frac{3T_c}{T - T_c}$$

This relationship is known as "Curie-Weiss" law and T_c is known as the "Curie Temperature"

As T approaches T_c "X", k' as well as P tend to reach infinity.

And, therefore one can write the khai 'X' susceptibility dielectric constant and the polarization. These are related to each other then also related to this 3 Tc by T minus Tc;

this is a critical temperature and T is a actually real temperature at any variable temperature. And, Tc is the particular characteristics temperature on the Ferroelectric material. This relationship is known “Curie-Weiss” law and Tc is known as the “Curie Temperature”.

So, this is one of the very important characteristic of Ferroelectric material. All Ferroelectric material has a follows Curie-Weiss law; and also has a critical temperature known as temperature as the Curie temperature. As T approaches Tc; actually it is not T, it is not T0, it is not from Tc; ‘X’, k prime the dielectric constant as well as polarization to increase infinity. So, this a very important characteristics which arises from the Curie weirs Curie-Weiss law, and all ferroelectric material follow this particular law.

So, consequently all Ferroelectric material actually goes through the dielectric constant dielectric constsnt or the khai ‘X’ or the polarization goes through a very high peak at a particular temperature called Tc.

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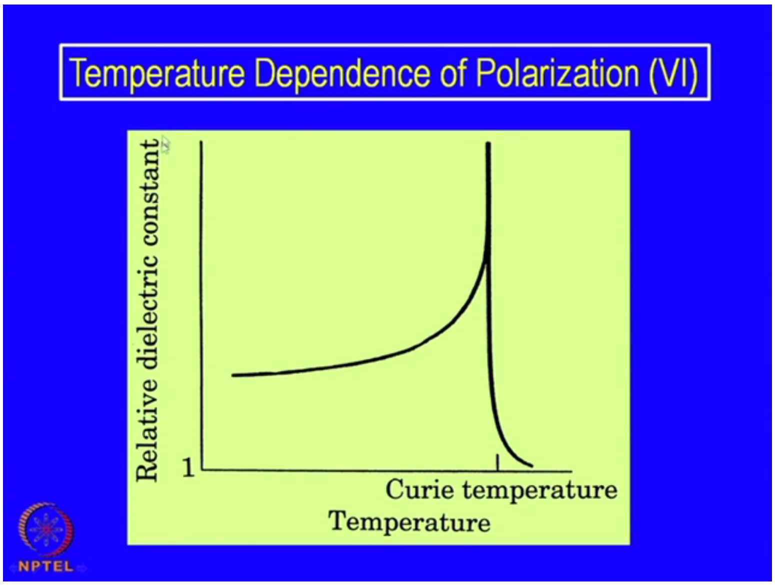

Temperature Dependence of Polarization (VI)

And, this is the characteristics. So, we have a Relative dielectric constant here on this side and Temperature on this side. So, at the particular temperature which is known as the Curie temperature? The dielectric constant goes through a very high peak characterized as mentioned it goes through a ideally it should be infinity but actually in practice it goes through very steep very steep or very sharp peak. So, this is the characteristics of the Ferroelectric behavior as a constant temperature.

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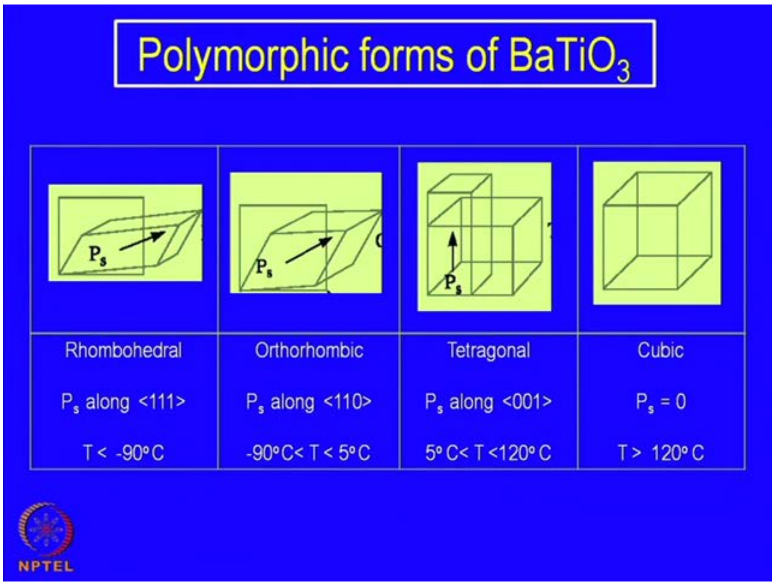

Polymorphic forms of $BaTiO_3$

Rhombohedral	Orthorhombic	Tetragonal	Cubic
P_s along <111>	P_s along <110>	P_s along <001>	$P_s = 0$
T < -90°C	-90°C< T < 5°C	5°C< T <120°C	T > 120°C

With this we come to the different polymorphic forms of Barium titanate as we mentioned earlier, Perovskite or Cubic Perovskite is only one particular structure of Barium Titanate. It has 3 different other structures at different temperature ranges. These are like this sorry these are four different polymorphic forms. Here, is cubic in fact the cubic is the highest temperature polymer and it is stable above 120 degree centigrade. Above 120 centigrade these is cubic Perovskite and is a stable polymorphic and because of symmetry because of it is absolute symmetric structure the Spontaneous Polarization is 0.

So, there is no Spontaneous Polarization or dipole movement is 0 because, it does not have a dipole because of this symmetry. Whereas, the kind of the deformation, the kind of deviation from symmetry we have discussed earlier which give rise to spontaneous polarization actually occurred in tetragonal form. So, instead of cubic, cubic has shown everywhere all these pictures that is the basic cubic structure and which has been either pulled along the phase diagonal or that has been pulled along the body diagonal. Here, it has been pulled along the c-axis. So, this is the direction of the polarization that we have seen earlier the dipole movement is along the vertical direction of the unit cell.

So, there is tetragonal distortion here. And, Ps is along the 001 one axis, this is the 001 direction points, here are the crystallography one can define this c-axis is actually the direction of 001 axis, 001 direction. And, this tetragonal polymorphic is stable within this temperature ends between 5 degree centigrade to 120 degree centigrade. So, it is pretty close to 0. So, almost slightly below room temperature to slightly above room temperature that is the range where tetragonal symmetry is stable. And, you have a Spontaneous polarization here.

If you go still lot temperatures then it has different distortion this was pulled along the c-axis, this has been pulled along 110 axes that is the phase diagonal. If you pull along the phase diagonal this result. So, you have an orthorhombic structure and the polarization direction, crystallographic direction for the polarization permanent Spontaneous Polarization is actually 110. And, this is stable between minus 90 to plus 5 degree centigrade. So, this is what happens in a lower temperature. It will go still lower temperature below minus 90 then there is another form which is more stable and that is the symmetry becomes Rhombohedral.

So, from cubic to tetragonal to orthorhombic and rhombohedral as you go down the temperature edge. And, in this case it has been pulled along 111, which is basically the body diagonal, 1 is the phase diagonal 110 is along the phase diagonal here has been pulled along the phase diagonal. And, that is how the distortion comes here. And, if you pull along the body diagonal then Rhombohedral structure comes. So, the spontaneous polarization is along 111 direction and this is stable below 90 degree centigrade minus 90 degree centigrade. So, this 4 different polymorphs and all these are Ferroelectric. All these 3 structures are Ferroelectric structures whereas this is not a non ferroelectric.

In fact this is a simple what do you call Para electric. As in case of magnetic materials you have ferromagnetic above the key temperature transforms to a paramagnetic material; here also the same thing happens and it is and it is termed as paraelectric material. So, it is actually this perovskite structure is actually a linear dielectrics. So, while these two structures are non-linear dielectrics, this structure actually linear dielectrics.

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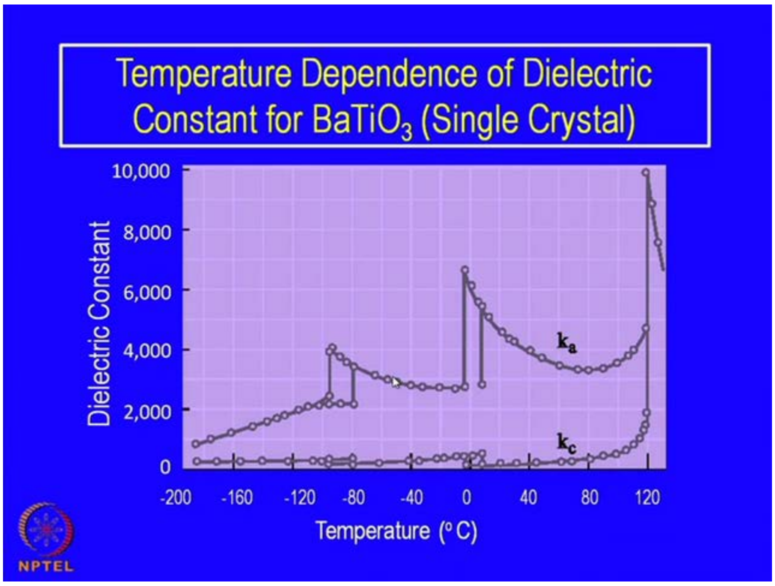

Temperature Dependence of Dielectric Constant for BaTiO$_3$ (Single Crystal)

Since, there are different forms of polymorphs and some of them are paraelectrics and some of them are Ferroelectric; and one of them is paraelectrics. If you try to plot the dielectric constant as a function of temperature over a wide range from minus 200 to 120 degress, 120 degrees instantly is a curie temperature of barium titanate. So, above that there is a or at that temperature there is a peak and then it drops; and it follows then so called linear dielectrics behavior. In below 120, they are all Ferroelectric forms and each phase transformations wherever, there is a phase transformation, this is from tetragonal to orthorhombic; and then orthorhombic to rhombohedral.

So, at each temperature there is a at each of these phase transformation. Although they are not curie temperature. But because of there is ferroelectric sorry dielectric constant also goes through a peak here where that is associated with crystallographic change not the curie temperature. These are this is the curie temperature this is the only curie temperature, but otherwise wherever there is a crystallographic change you also get a some discontinuity in dielectric parameter and dielectric constant.

So, this one phase transformation, this is another phase transformation, and then 3 phase transformations and 4 polymorphs. And, we will also notice there are other characteristics this has been taken from single crystal not a poly crystal material. Poly crystal material do not get such sharp peaks they are little blunt peaks. And, you will also see there are 2 other characteristics; one is there is a tremendous amount of an isotropic there is tremendous. So, that the properties constant along the crystallographic direction. This along the a-axis and this is along the b-axis, this is along the c-axis and this is actually along the a and b axis. So, a and b axis are same where as c-axis is different. So, the dielectric constant along the c axis is much smaller compared a along the a and b axis. So, this another more important observation.

Other one is there is also some kinds of hysterias here. So, during heating and cooling it follows slightly different path. So, this is your heating and then cooling it comes follow a slightly lower temperature. So, this is also another characteristic of this phase transformation; this is also called a some kinds of hysteresis. So, for as the phase transformation is concerned it is not a dielectric hysterias, but a different kind of hysterias there is a lag between the heating and cooling directions. So, this is the variation of the dielectric constant as a function of temperature and that is associated with polymorphic transformations at the different values of temperature. So, this for the single crystals and shows half here.

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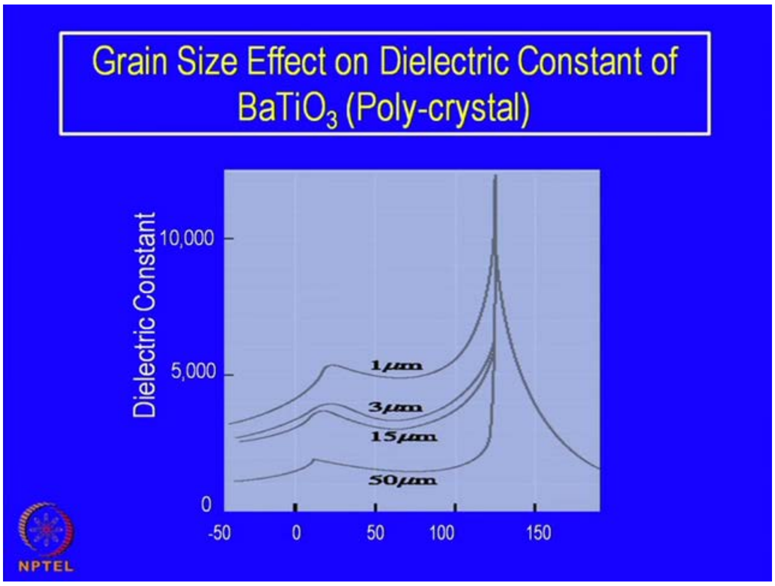

Grain Size Effect on Dielectric Constant of BaTiO$_3$ (Poly-crystal)

Whereas, if you go to a polycrystalline material which is the most common material used in the industry this are not so sharp peaks they are little blunt peaks. And, you can see peak is also little blunt and compared to the single crystal form the variation is little not so sharp. There is more another very important aspect also that is there is a fair amount of dependence on the grain boundary at the grain size; grain size particularly in a polycrystalline material. In a polycrystalline material you have different kind of grains, different sizes of grains. And, the these are actually single crystal put together; show this grain boundary is a some kind of the defect and that changes the characteristics to some extent.

So, if you have a 50 micron larger size of the grain then it causes low whereas higher characteristic are obtained sorry high values of dielectrics constant obtained when grain size is small, And, that is primarily related to the domain all movement. So, domain all there is some kind of relationship within the domain size of the domain, not size of the domains and crystals. So, that domain all movement is the restricted domain all in movement is restricted when the grain size is very small. And, therefore there is a variation of dielectric constant as a function grain size and one can see 1 micron grain size provides you very high dielectric constants. So, same materials, same composition, but just by changing the grain size one can modulate the dielectric constant. And, therefore one can design different kinds of capacitors based on these dielectrics.

You can see here the dielectric constant varies up to 5000 here and whereas this peak is more than 10,000. Now, one of the problems barium titanate is of course used as a dielectrics in many capacitors various different kind of capacitor. And, however one of the major problems of this ferroelectric ceramics being used in a capacitor in its temperature dependence. Our room temperature is somewhere here around 25 degrees, it may high up to 40 degrees. So, the capacitors are normally used in this temperature range. And, you can see from both sides from this peak as well as from this peak this tail is coming tail is coming to the temperature range.

So, because of that the temperature stability of this dielectric material is not so good. And, dielectric constant changes with temperature. And, that is one of the major problem because there is a instability for the dielectric the capacitor value is concerned because of the change in the dielectric constant function of temperature. So, there is always a attempt to make the dielectric constant as stable as possible in by changing by changing the composition as well as the grain, grain structure. And, one can see here there is a less stay price or less steep change here in the larger grains size compared to this grain size this tail; tail of this peak comes very close to the dielectric sorry room temperature.

So, one can module one can play with both the composition as well as the grain structure and grain size of the material. So, that better and better stable dielectrics can be repair. Most of the time in fact in the industry there are various grades of dielectrics based all based on barium titanate ceramics by many different dopends, many different other dopends are used which is goes in the solid solution, sometimes forms a grain boundary phase a sink is not always a single phased material. But sometimes they are multi phased materials or dual phased materials. And, that actually the impedes the motion of the domain all movement. And, therefore modulates are modifies the dielectric property as a function particularly temperature dependence at dielectric property.

So, many different compositions are available in the industry with different kind of standards. And, they are used for different purposes the capacitors some of them required very high dielectric constant. So, that the miniaturizing possible, but whenever you have high dielectric constant the temperature dependences is also high temperature varies in the also high. So, there not that stable however if you want a very stable dielectric material or stable capacitor value in the dependence of temperature then you normally dielectric constant goes down.

So, there are many different standards available in the industry and one has to play with their composition as well as the grain size of the material. So, has to generate either a very high dielectric constant material with the less of temperature stability whereas, one can also get a better temperature stability with relatively low dielectric constant. So, these are some of the you known industry needs for so for dielectric constants is concerned. However, barium titanate is a one of the major components of always been a major components of always been a major component of ceramic dielectrics primarily because of it is very high relatively high dielectric constant.

Normal linear dielectrics (( )) level of the order of 10 maximum 100 whereas here with Barium titanate one can get as high dielectric constant as several 1000 up to 20,000 to 30,000. So, that is one of the great advantages of the Barium titanate ferroelectrics of course it does not agree use the Ferroelectric property for this particular purpose except a very high dielectric constant. So, with this we discussed we come to a close of this part of the discussion. We have some more discussion still as to continue on Ferroelectric particularly in the different other. We have discussed primarily with barium titanate, but there are many other ferroelectric ceramics which we have similar properties in some applications also with that we will be continued in the next class.

Thank you. Thank you for your attention.