Advanced Ceramics for Strategic Applications
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Lecture - 23
Relaxor Ferroelectrics

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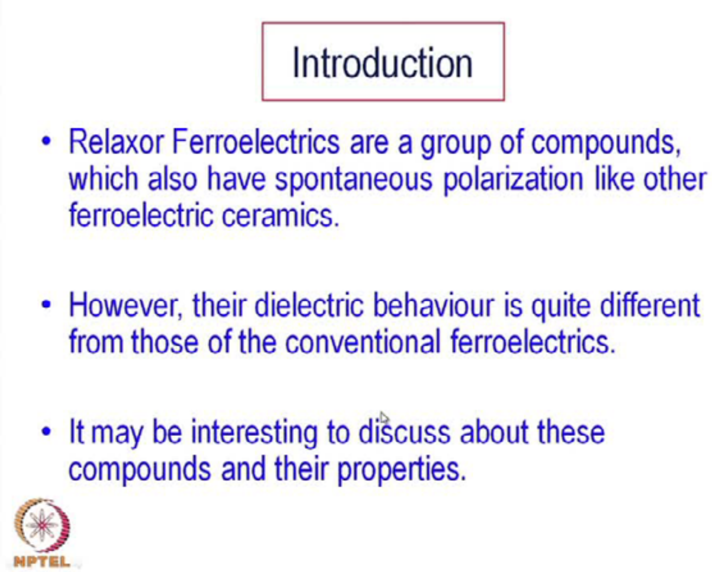

Introduction

- Relaxor Ferroelectrics are a group of compounds, which also have spontaneous polarization like other ferroelectric ceramics.
- However, their dielectric behaviour is quite different from those of the conventional ferroelectrics.
- It may be interesting to discuss about these compounds and their properties.

Welcome. Today our topic is relaxor ferroelectrics. Earlier, we have discussed in quiet a great details about the normal ferroelectric material based on Perovskite's, particularly barium titanate and so on. So, they have their known normal ferroelectric materials. There are another group of ferroelectrics having many similar properties that of normal ferroelectrics, but there named as relaxor ferroelectrics. We like to look at it. What is there characteristics, what are the compounds and why they behave slightly differently than the normal ferroelectrics materials?

To introduce this group of materials, relaxor ferroelectrics are a group of compounds which also have spontaneous polarization like other ferroelectric’s ceramics. One of the basic characteristics of the ferroelectric ceramics or ferroelectric material is their spontaneous polarization, or even in the absence of electric field. So, these relaxor’s, these ferroelectrics called the relaxor ferroelectrics also do have the same property. However, there dielectric behavior is quite different from those of the conventional ferroelectrics. We will look in to that how the dielectric property changes as a function of different parameters with this. The behavior is slightly different than that of normal ferroelectrics. It may be interesting to discuss about these compounds and their properties. So, we will devote this particular lecture on this discussion.

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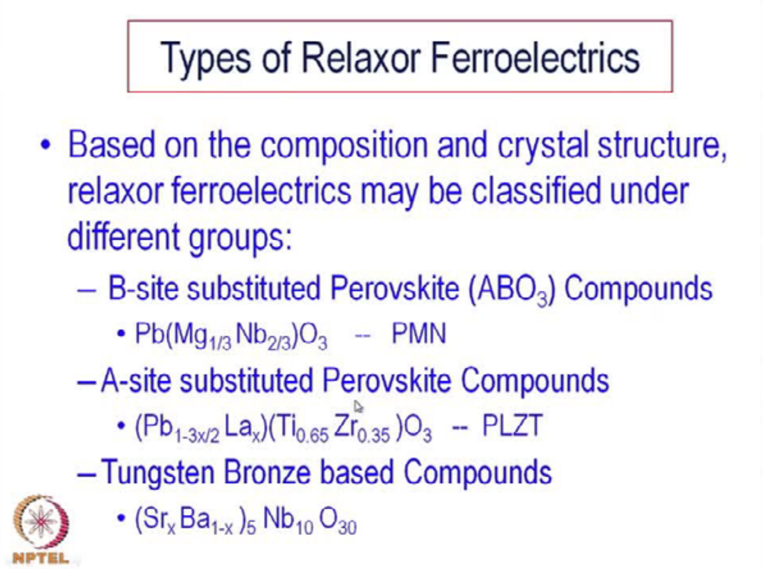

Types of Relaxor Ferroelectrics

- Based on the composition and crystal structure, relaxor ferroelectrics may be classified under different groups:
  - B-site substituted Perovskite (ABO_3) Compounds
    - $Pb(Mg_{1/3}Nb_{2/3})O_3$ -- PMN
  - A-site substituted Perovskite Compounds
    - $(Pb_{1-3x/2}La_x)(Ti_{0.65}Zr_{0.35})O_3$ -- PLZT
  - Tungsten Bronze based Compounds
    - $(Sr_xBa_{1-x})_5Nb_{10}O_{30}$

To start with the types of relaxor ferroelectric, there are groups of relaxor ferroelectrics. They can be classified under different groups based on the composition and crystal structure, relaxor ferroelectrics may be classified under different groups. Primarily three different groups. One is called the B-site substituted Perovskite. As we remember that Perovskite's have the general formula ABO 3. So, this is what will call the B side substitution. That means, P atom MN here can be substituted by some other ions as for example, one of the very important material or most common material to have relaxor ferroelectrics behavior is called PMN led magnesium, where a site is occupied by b led and B-site. You have two different ions. One, magnesium one-third and niobium two-third. So, B-site is occupied by two different cations. One is the magnesium ion and another is niobium ion in a particular ratio.

In addition to that, you have another kind of relaxor ferroelectrics called A-site substituted Perovskite compound, not only B-site which has been quite common and PMN is one of the measure and the most important member of this group are the site substitute. Perovskite compound is PLZT, where it is again solid solution. We will have discussed this particular compound in greater details as piezoelectric material, very important piezoelectric material PZT, but here it is not PO PZTA. Lanthanum has been used as a dopant. So, led part of the led has been substituted by lanthanum. So, the formula follows led 1 minus 3 x by 2 lax and then, T i 0.65, Z r 0.35 O3. So, it is about that is not in the morphotropic phase boundary, but it is away from it and it is 65 mole percent of led titanate and 35 mole percent of zirconium titanate, sorry Led zarconate. I am sorry, 65 mole percent of led titanate and 35 mole percent of led zarconate. These two forms a solid solution in which a part of led is substituted by lanthanum. So, that forms PLZT. We will discuss these things, the properties and how they are prepared greatest within a few minutes.

The third group comes not exactly on Perovskite's, but a derivative of Perovskite structure which is a tungsten bronze structure and that tungsten bronze compound is basically niobium based tungsten bench, that is N b 10 O 30 and added to that, we have strontium and barium in some proportion. So, strontium has been substituted for barium in certain fraction and then, the total compound, the total formula becomes strontium, x barium 1 minus X 5 N b 10 O 30. So, these are the three main groups of compounds. There are large numbers of compounds available. In these, one of these three categories and all of them has so-called relaxor ferroelectric behavior.

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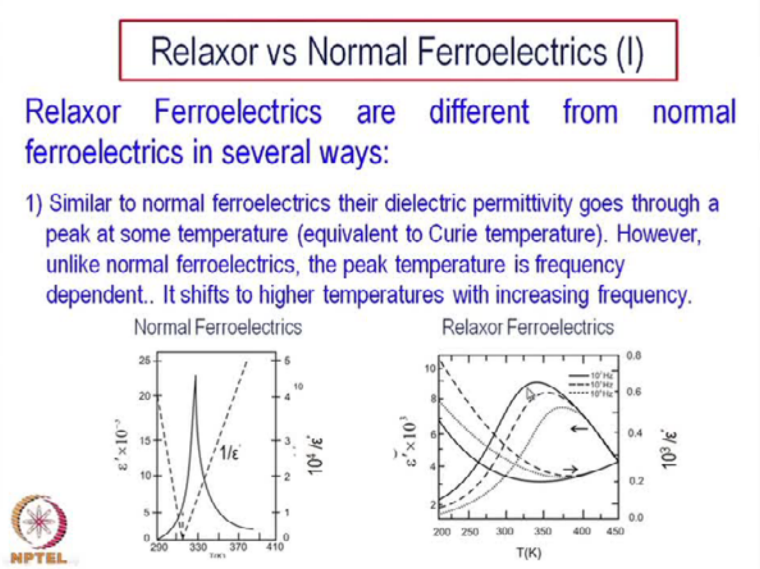

Relaxor vs Normal Ferroelectrics (I)

Relaxor Ferroelectrics are different from normal ferroelectrics in several ways:

1) Similar to normal ferroelectrics their dielectric permittivity goes through a peak at some temperature (equivalent to Curie temperature). However, unlike normal ferroelectrics, the peak temperature is frequency dependent.. It shifts to higher temperatures with increasing frequency.

Now, what are the basic differences between normal ferroelectric material and relaxor ferroelectrics? There are three or four main points or more points of difference. Let me look at it. Relaxor ferroelectrics are different from normal ferroelectrics in several ways.

First one is similar to normal ferroelectrics. There dielectric permittivity goes through a peak at some temperature equivalent to Curie temperature. So, if we remember the dialectic behavior of barium titanate which is in representative of a normal ferroelectrics goes through a peak at the ferroelectric paralelectric transition, that is it curie point, the temperature around 120 degree centigrade. Their dielectric permittivity of dielectric constant goes to peak and it becomes infinity following to so-called Curie voice law. Similar thing happens here also at certain temperature. Also, dielectric peak does not go through a peak. A final no is a function of temperature, but unlike normal ferroelectrics, the peak temperature is frequency dependent. This was not the case of barium titanate.

The frequency is an independent frequency of the Curie temperature or the peak temperature is independent of the frequency, but here only major difference from that group of ferroelectrics to this relaxor ferroelectrics. It is dependent on frequency. The peak temperature shifts to high. Temperature is within increasing frequency. So as frequency increases, the peak temperature also increases. This is unlike normal ferroelectric or really does not follow so-called universal handler. These are the two pictures, are the two diagrams showing this difference. This is normal ferroelectrics wire. It goes through a peak, a very strong peak; very sharp peak around 330 degree 30 Kelvin. It is of course owned by Uppsala in prime straight-line whereas, here these also goes through peak, but one can see the distinction between this peak and this peak. This peak is a sharp peak and this peak is a very broad peak and not only that, three different frequencies, this is 100 hertz, 1 kHz and 10 kHz. So, the peak temperature shifts, shift from this is nearly about 332, around 360. So, there is a shift in this peak temperature.

The same is of course reflected in the external double prime. So, this is Uppsala double prime and Uppsala prime. So, there is a broad peak and that peak also shifts with frequency. These are two very important differences from the norm ferroelectrics which is very sharp peak and it is in different of the frequency of the measure.

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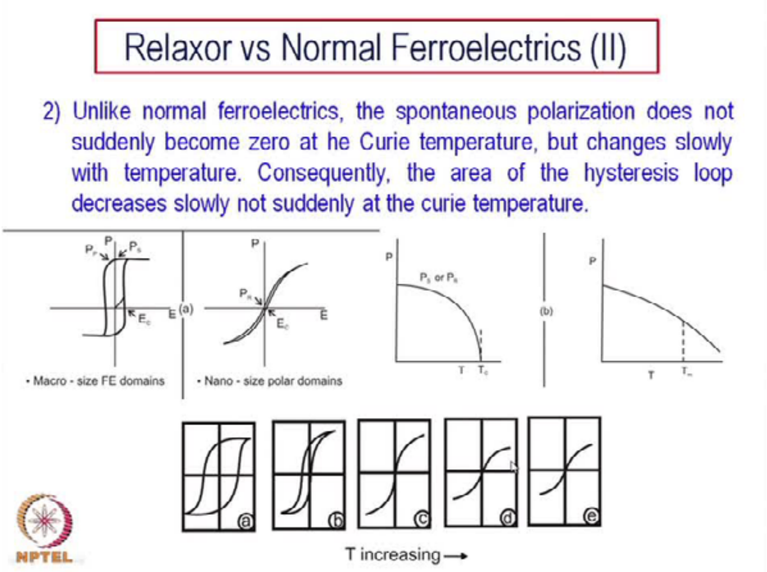

Relaxor vs Normal Ferroelectrics (II)

2) Unlike normal ferroelectrics, the spontaneous polarization does not suddenly become zero at he Curie temperature, but changes slowly with temperature. Consequently, the area of the hysteresis loop decreases slowly not suddenly at the curie temperature.

The second point of difference is, unlike normal ferroelectrics, the spontaneous polarization does not suddenly become zero at the Curie temperature, but changes slowly with temperature. Consequently, the area of hysteresis loop decreases also very gradually, slowly, not suddenly at the Curie temperature. Once again, these are the comparison hysteresis loop. Public changes as a function of temperature. So, this is before the change of the function of temperature how the hysteresis loop at all looks like. They are much broader hysteresis peak for the normal ferroelectric like this. Of course, this looks like a Square hysteresis, square loop hysteresis. Not necessarily it will be square hysteresis, but the coercive freed is large and there is a pre distant raiment polarization compared to that relaxor ferroelectric. There is also a hysteresis loop, but it looks like quiet different. This is not only the width, hysteresis loop is much smaller. So, the coercive field is much smaller as well as the raiment polarization is also a very small. So, it looks more or less like linear dielectrics. Although, that is a small hysteresis loop.

So, because of this spontaneous polarization, there is a spontaneous polarization, but that does not give very broad hysteresis. Not only that, this spontaneous polarization in case of a normal fellow ferroelectric, actually till very close to the very Curie temperature, the normal ferroelectric constant, spontaneous polarization more unless constant and then, suddenly drops and the Curie temperature. So, this is the Curie temperature varied suddenly drops whereas, look at the variation of this spontaneous polarization as the function of temperature in relaxor ferroelectrics. It is actually much over change gradual, much gradual change and not only that, it remains beyond Curie point. It is just the income to this is the so-called Curie point. In fact, it does not follow exact Curie wise law. So, this temperature is not always called the Curie point, although there is a peak, minute peak of a direct constant at this permission, but normally, it is referred to as Tm. It is something like a glass transition temperature kind of situation, where you have the spontaneous polarization beyond that also, although it goes through dialectic peak, but it is not the end of the ferroelectric behavior.

The ferroelectric behavior continues beyond the temperature and this much more gradual change for a particular value of spontaneous polarization. It will go very gradually to 0. Not a sudden change in polarization at the Curie point. Consequently, you have a slow change in the hysteresis loop as such of course is much more magnified view of this situation. So, from the Curie temperature or the transition temperature here, we have a much broader peak and slowly, it changes to almost a line like behavior, non-linear behavior. This is much more slow change compared to the normal ferroelectric. So, this is second characteristics.

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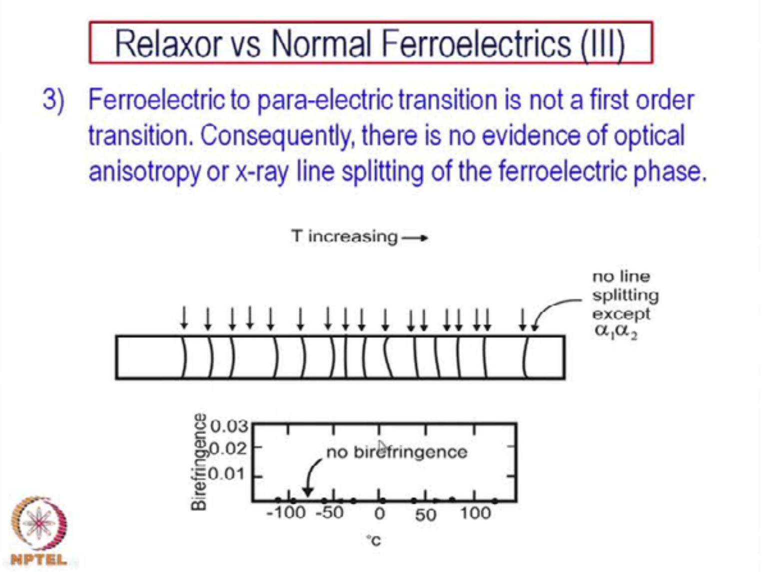

Relaxor vs Normal Ferroelectrics (III)

3) Ferroelectric to para-electric transition is not a first order transition. Consequently, there is no evidence of optical anisotropy or x-ray line splitting of the ferroelectric phase.

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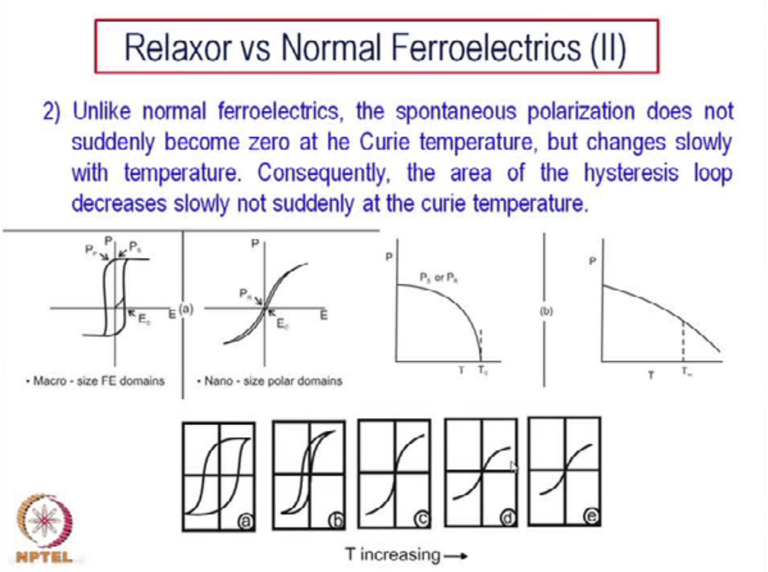

Relaxor vs Normal Ferroelectrics (II)

2) Unlike normal ferroelectrics, the spontaneous polarization does not suddenly become zero at he Curie temperature, but changes slowly with temperature. Consequently, the area of the hysteresis loop decreases slowly not suddenly at the curie temperature.

Then, we have a third variation. The point of variation deviation is the ferroelectric. Paralelectric transition is not a faster transition impact. First order transition and foster transition will be associated with change like this, discontinuity like this, but since it is not a first order transition, it follows more gradual change. So, ferroelectric to para electric transition is not a first order transition. Consequently, there is no evidence of optical anisotropy or x-ray line splitting of the ferroelectric phase. These are the two very important consequences of the ferroelectric transition of normal ferroelectric materials. Because of the ferroelectric to para electric transition add the curie points, there is always a optical anisotropy evidence of optical and anisotropy from one still structure it to another and also is associated with a what you call the x-ray line splitting of the ferroelectric phase.

Now, however this kind of evidence is not there in relaxor ferroelectrics. It does not have the splitting behavior x-ray line splitting. These are all single lines. There is no double line or splitting lines except of course alpha 1, alpha 2. Splitting is there, but also there is another change or another deviation in the optical properties. There is a lot of (()) because there is a t increasing crystallographic change. So, the (()) or the normal dielectrics were here. There is no birefringence. So, the optical refractive index is not dependent on the particular crystallographic direction. So, these are another third point of difference between the normal ferroelectrics on the relaxor ferroelectrics.

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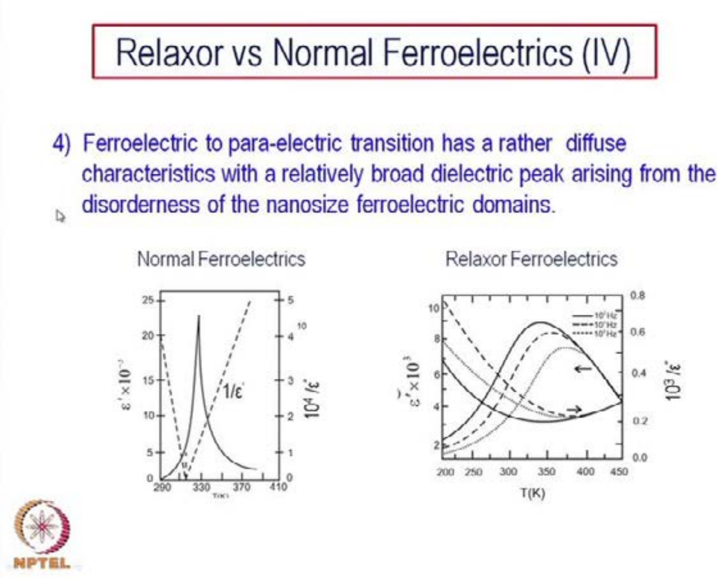

Relaxor vs Normal Ferroelectrics (IV)

4) Ferroelectric to para-electric transition has a rather diffuse characteristics with a relatively broad dielectric peak arising from the disorderness of the nanosize ferroelectric domains.

Also, there is a fourth which has been mentioned earlier when we were discussing the same diagrams. The ferroelectric to para-electric transition has a rather diffuse characteristic with a relatively broad dielectric peak arising from the disorderness of the nanosize ferroelectric domains, while the one of the reason, a simplified way to look at it why this kind of broad peak appears is there is a nano sized domains. The size of the domains is much smaller compared to the normal ferroelectrics and these are some kind of disorder structure. So, domains do not follow a very nice pattern, nice crystallographic orientation, but it is a disorder. It is more random in nature, even when it is ferroelectric, ok.

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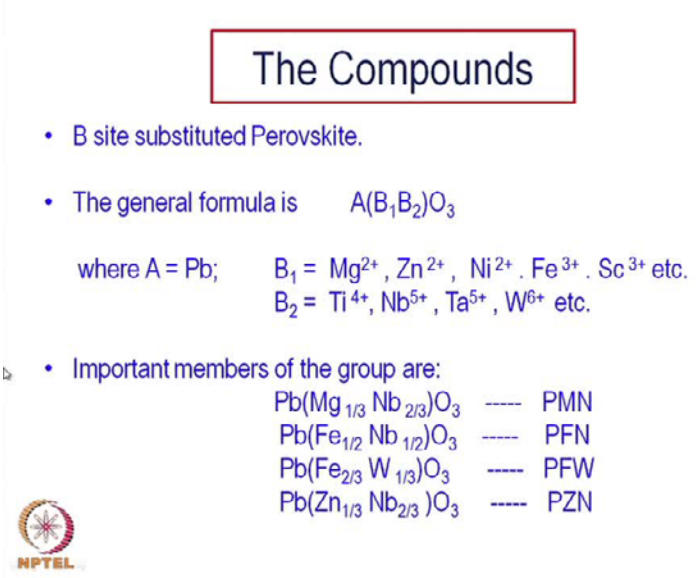

The Compounds

- B site substituted Perovskite.
- The general formula is $A(B_1B_2)O_3$

where A = Pb; $B_1 = Mg^{2+}, Zn^{2+}, Ni^{2+}. Fe^{3+}. Sc^{3+}$ etc.
$B_2 = Ti^{4+}, Nb^{5+}, Ta^{5+}, W^{6+}$ etc.

- Important members of the group are:

$Pb(Mg_{1/3}Nb_{2/3})O_3$ ----- PMN
$Pb(Fe_{1/2}Nb_{1/2})O_3$ ----- PFN
$Pb(Fe_{2/3}W_{1/3})O_3$ ----- PFW
$Pb(Zn_{1/3}Nb_{2/3})O_3$ ----- PZN

So, these are the four different points between the normal ferroelectric and a relaxor ferroelectric. Now, what are the different compounds? We have already seen that there are three groups under which all these compounds can be classified, grouped depending on that particular stock structure, crystal structure. Here are latest look at sound, the specific compounds. The first group is the so-called B-side substituted Perovskite's. So, a, b, c three structure you have A, B 1 and B 2 instead of b. We have two different compounds to different atoms and two different irons B 1 and B 2. So, these a A is normally late as the only possibility as far is the A-site is concerned, but in B-side different combinations are possible.

One can be magnesium zinc, mostly a divalent or trivalent oxides trivalent elements like magnesium, zinc, nickel 2 plus F e 3 plus scandium 3 plus extra. So, either it is 2 plus or 3 plus. Consequently, B 2 will be either 4 plus or 5 plus or it can be 6 plus 7. So, these are the atoms in the B-site. Possible atoms T i 4 plus niobium 5 plus tantalum 5 plus and tungsten 6 plus. These are the different irons which can be there in the B-site and B 1 will correspond to magnesium, zinc, nickel, iron and scandium, either that 2 plus or 3 plus. Accordingly, you have several compounds here which is been listed. This we have already discussed. The PMN will be the most important member of this group a led magnesium niobiate, then led iron niobiate. It is also there. PFN magnesium is replaced by iron here. You can have PFW. This is iron plus niobium has been replaced by tungsten. So, that is also possible. Of course, ratio will be different to satisfy the Charles neutrality and then, ledging niobiate, ledging navid is also another one member. So, all these compounds are actually relaxor ferroelectrics and have been four different characteristics which you have mentioned earlier.

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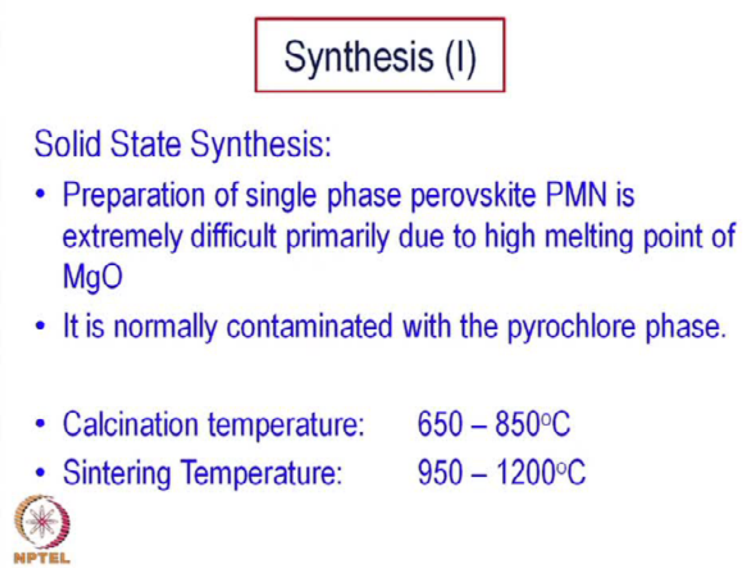

Synthesis (I)

Solid State Synthesis:

- Preparation of single phase perovskite PMN is extremely difficult primarily due to high melting point of MgO
- It is normally contaminated with the pyrochlore phase.

- Calcination temperature: 650 – 850°C
- Sintering Temperature: 950 – 1200°C

How to synthesize this compound? Particularly, the representative one is the PMN led magnesium navid. So, normally it is been prepared or it is the solid-state synthesis, but the other are liquid chemistry root or the soluble root r and there are many other techniques by which the PMN led magnesium niobiate kind of ferroelectrics can be synthesized. Preparation of single phase Perovskite PMN is extremely difficult, primarily due to high melting point of MgO. So, compared to led and niobium ibiom oxide, led oxide and magnesium oxide had much more melting point and therefore, this diffusivity is very low. Magnesium diffusivity is squirt low and therefore, we have some amount of difficulty in synthesizing this compound and it is normally contaminated with Pyrochlo refills while a derivative Perovskite’s, it is also Pyrochlo phase. It would be to 207, that kind of compound and this Pyrochlo phase are not non-ferroelectric in nature.

So, even relaxor behavior is not there and as a result, that needs to be avoided during the normal synthesis root. The calcinations temperature of this compound is nearly 650 to 800 degree centigrade by the sintering temperature around 950 to 1200 depending on the particular compound used to make this relaxor ferroelectric. This temperature as you can see is relatively low temperature compared to the barium titanate. So, the sintering as well as Carlson temperature, calcinations temperature, both are relatively low. So, there are relatively low melting compounds compared to barium titanate.

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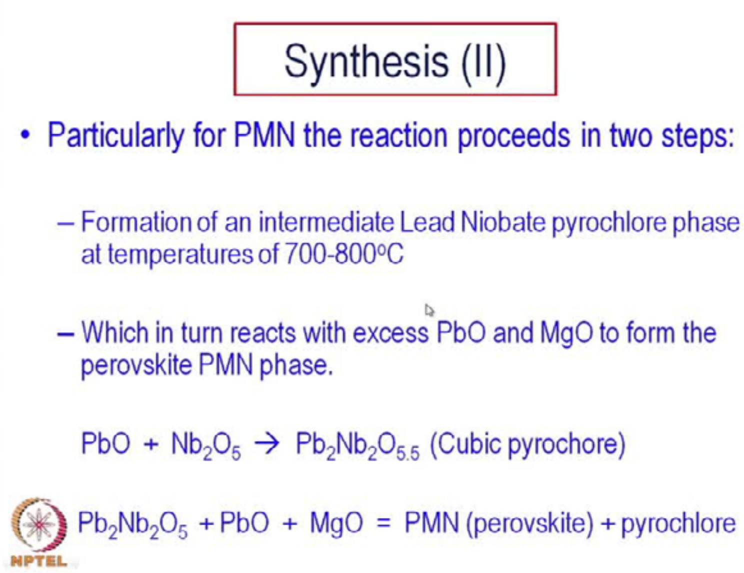

Synthesis (II)

- Particularly for PMN the reaction proceeds in two steps:
  - Formation of an intermediate Lead Niobate pyrochlore phase at temperatures of 700-800ºC
  - Which in turn reacts with excess PbO and MgO to form the perovskite PMN phase.

$PbO + Nb_2O_5 \rightarrow Pb_2Nb_2O_{5.5}$ (Cubic pyrochore)

$Pb_2Nb_2O_5 + PbO + MgO =$ PMN (perovskite) + pyrochlore

Looking at the case of PMN, as far as synthesis is concerned for PMN, the reaction proceeds into different steps. The first step is a formation of an intermediate lead niobiate pyrochlore phase. It is there 2 or 3 (()) with oxygen and there action rates are little different, diffusion rates are different. So, you are directly in during form, the led magnesium niobiate, instead the first phase which appears is lead niobiate. So, it is a binary phase, binary composition. So, it is not already own obviously. So, the formation of the intermediate lead niobate pyrochlore, it also has a pyrochlore structure and this pyrochlore structure is little bit detriment to the ferroelectric property of either the normal Perovskite's or the relaxor's ferroelectrics. Pyrochlore phase in terms reacts with the excess of PbO and MgO to form the initially lead niobate pyrochlore phase and then, that lead non-pyrochlore reaction be the excess amount of de-oxide and magnesium oxide to form the Perovskite of the PM in structure. So, these reactions has been represented like this, PbO plus Nb2 O5 go as Pb2 Nb2 O5.5 that is cubic pyrochlore structure in this Pb2 Nb2 O5.5. Sometimes, it is written as 5, some times in some cases 5.5. It is not basically, it is cubic pyrochlore phase. It reacts with excess PbO and MgO to form the PMN perovskite structure plus pyrochlore.

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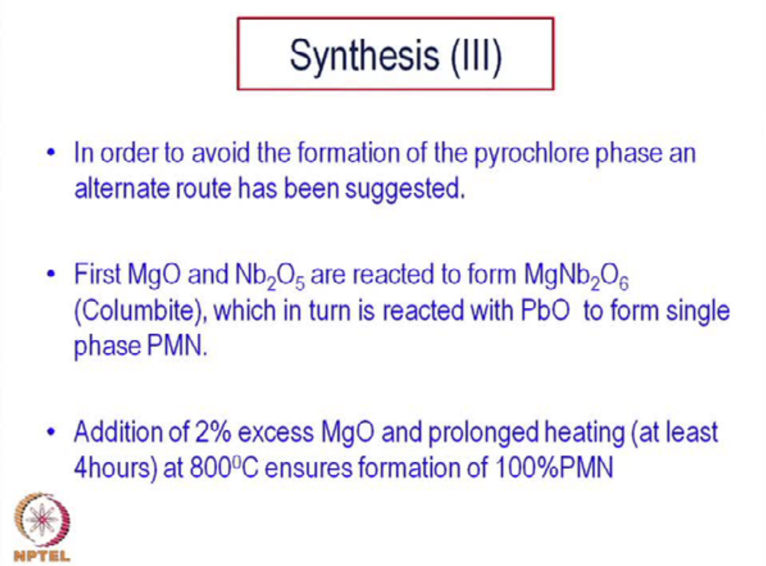

Synthesis (III)

- In order to avoid the formation of the pyrochlore phase an alternate route has been suggested.
- First MgO and Nb_2O_5 are reacted to form $MgNb_2O_6$ (Columbite), which in turn is reacted with PbO to form single phase PMN.
- Addition of 2% excess MgO and prolonged heating (at least 4hours) at 800^0C ensures formation of 100%PMN

Now, this pyrochlore phase of course is accepted second phase. So, we have to avoid the formation of the pyrochlore phase and an alternate route also has been suggested. Once again it is solution, not solution chemistry, but it is basically solid that deficient solid-state route have. First MgO and Nb2 O5 are reacted to form MgNb2O6 or sometimes, called columbite which in term is reacted with PbO to form the single phase PMN. So, the pyrochlore phase, sorry columbite phase lead magnesium niobate, not only magnesium niobate, initially it is allowed to react to the oxide and also allowed to react to PbO. It shows that it gets transformed to form single phase PMN. For completion of the reaction about 2 percent excess of MgO and a prolonged heating is necessary more than 4 hours. Sometimes, actually more is added and degree centigrade to ensure the formation of 100 percent PMN. So, its synthesis of PMN is slightly difficult before it has a tendency to form the pyrochlore phase here to avoid the formation of this pyrochlore phase sometimes.

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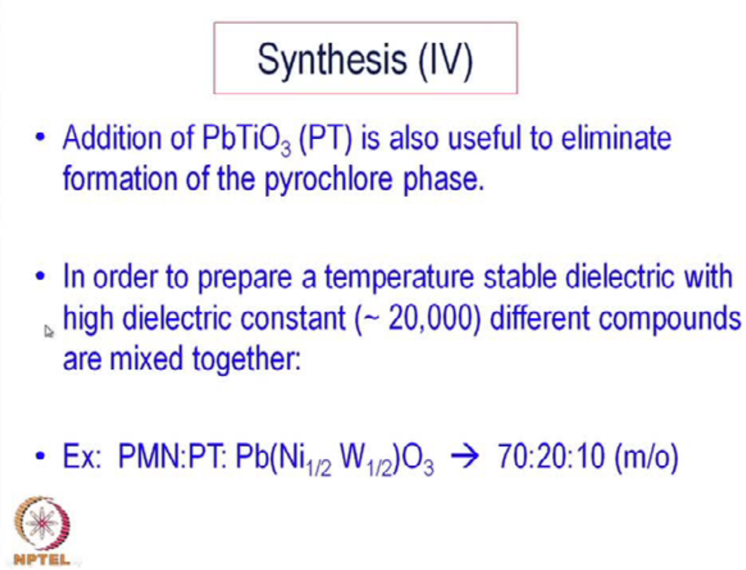

Synthesis (IV)

- Addition of $PbTiO_3$ (PT) is also useful to eliminate formation of the pyrochlore phase.
- In order to prepare a temperature stable dielectric with high dielectric constant (~ 20,000) different compounds are mixed together:
- Ex: PMN:PT: $Pb(Ni_{1/2}W_{1/2})O_3 \rightarrow$ 70:20:10 (m/o)

Addition of late titanate is also useful to eliminate the formation of the pyrochlore phase. So, by making a solid solution with another titanate, lead titanate which is a simple reason to prepare. Some amount of lead titanate is added when a solid solution forms with the lead titanate and PMN, the pilot surface formation is avoided. In order to prepare a temperature stable dielectric with high dielectric constant of about 20,000, that is a peak dielectric constant, different compounds are mixed together and primary to stimulus stabilizer in the perovskite fits. So, one example is PMN with PT. PT means lead titanate and lead nickel tongstate. Some amount of lead nickel tungsten is also added which also have a relaxor ferroelectrics structure. So, this solid solution actually is sometimes used for practical purposes.

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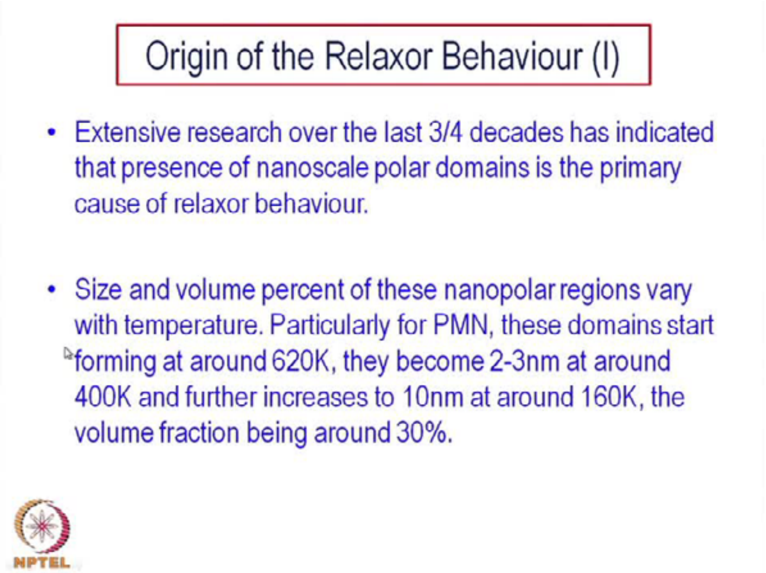

Origin of the Relaxor Behaviour (I)

- Extensive research over the last 3/4 decades has indicated that presence of nanoscale polar domains is the primary cause of relaxor behaviour.
- Size and volume percent of these nanopolar regions vary with temperature. Particularly for PMN, these domains start forming at around 620K, they become 2-3nm at around 400K and further increases to 10nm at around 160K, the volume fraction being around 30%.

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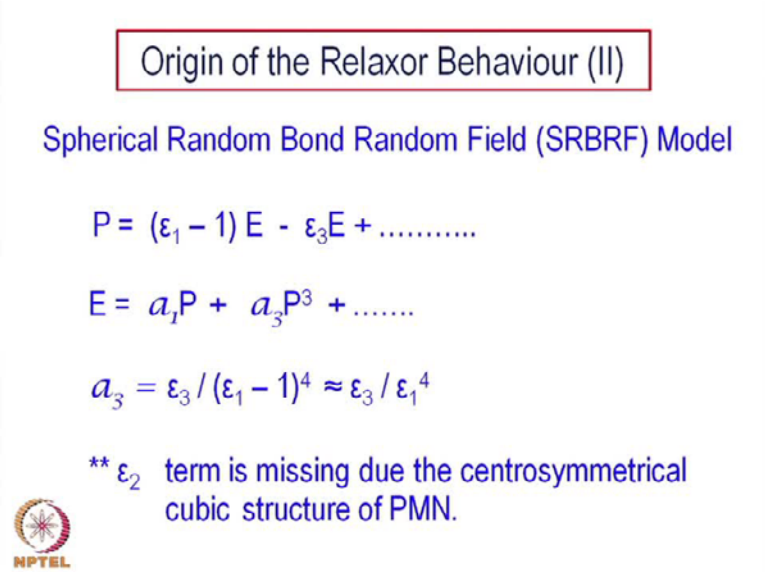

Origin of the Relaxor Behaviour (II)

Spherical Random Bond Random Field (SRBRF) Model

$$P = (\varepsilon_1 - 1) E - \varepsilon_3 E + \ldots\ldots\ldots.$$

$$E = a_1 P + a_3 P^3 + \ldots\ldots.$$

$$a_3 = \varepsilon_3 / (\varepsilon_1 - 1)^4 \approx \varepsilon_3 / \varepsilon_1^4$$

** ε_2 term is missing due the centrosymmetrical cubic structure of PMN.

The next thing is what is this origin of this particular property called? Diffuse. This transformation is called diffuses and then, you have a glass like structure so on. So, what is the basic difference? So, for the internal structure of the perovskite, normal perovskite and relaxor perovskite extensive research of the last 3-4 decades as indicated that the presence of nano scale polar domains. So, it is actually nanoscale polar domains. It means, basically the ferroelectric domain, all ferroelectrics are supposed to have domains, ferroelectric domains of certain types and certain other characters.

So, in this case also, we have domains, but basic difference is compared to the normal domain size of the order of my accounts. One, here it is nanoscale polar domains, very fine nano scale domains and they are not fully a (()) order structure or fully crystallized structure. They will crystallize, but so far as the domains are concerned, they have a disorder structure. Because of this disorderness, a staff, a single relaxation time as in case of a variant titanate, multiple are a sprayed off sometimes or distribution of relaxation times. So, each one of them relaxed are having the EEE. Each one of these domains have a different relaxation time and because of that, you have a different relaxation process is occurring, killing and their time constants are also defined. Because of the time constants are different, they respond to different frequencies. So, that is one of the reason why there is a broad peak, instructs a sharp peak in case of normal ferroelectric. In normal ferroelectric, the sharp peak arises from single relaxation time.

So, the structures in much more order and they have a larger domain. Size and volume percent of these nanopolar regions vary with temperature. Particularly for PMN, these domains start forming around fewer cooling from high-temperature and then, these domains start forming at around 620K, they become about only 2 to 3 nanometers. So, that is basically in the ferroelectric phase and venue cool down around 400K for the increase in the domain size around 9-10 nano meter size of domains formed around 160 degree k and the volume production being 30 percent. So, 30 percent of the polar domains, nano structure domain form and that is having a disorder structure distribution of relaxation time and therefore, you have broad peak while going to little more details. There is a different theory of this phase transition or para electric to ferroelectric transition and the presence of nano domains in nanopolar polarization and nano polar structure. This has been explained by a theory or model called spherical random bond or random field model. A spherical random bond, random field model which is in brief is called SRBRF. SRBRF model says that as just mentioned that we have variations in the domain structure and there characteristics of each of these domains are different. Not only their size is small, but each one of them has a different election time.

So, the polarization can be expressed as a sigma epsilon minus so on minus epsilon 3 minus. Epsilon 3 is the electric field. So, normally we write this question epsi1on minus 1 E. That is the relationship between polarization and electric field, but because of the distribution of relaxation time, we have a different parameter. A kind of polynomial is written as the relationship between polarization and electric field. So, epsilon 1 minus 1 multiplied by e minus epsilon 3 e and so on. So, this can be written in other way equal to a 1 P plus a 3 P q, where a 3 efficiently epsilon 3 by epsilon minus 1 whole to the power of 4 is equal to, approximately equal to E to the power 3 by the epsilon to the power 4 epsilon power to the power 4. In this case, epsilon 2 terms is not there because of the centre cemetery cubic Structure of PMN. So, the polarization reaction, other polarization expression for the relationship between the polarization and electric field is quite different here compared to the normal ferroelectrics.

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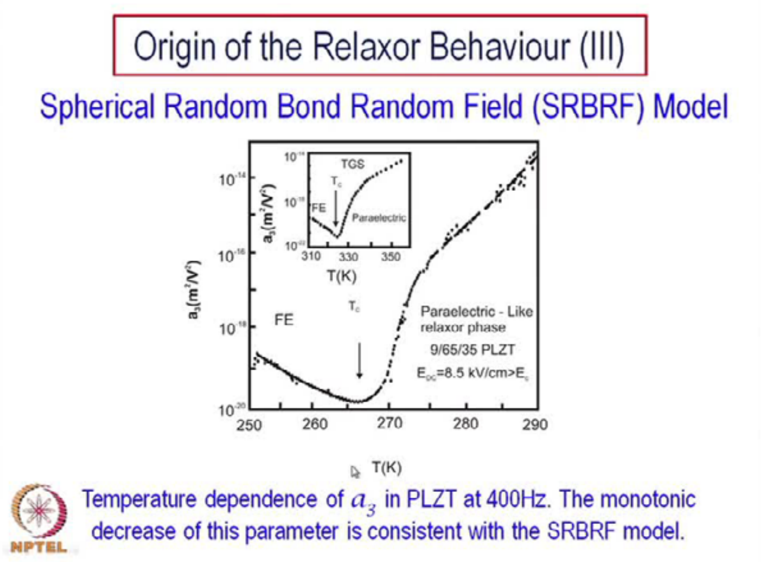

Origin of the Relaxor Behaviour (III)

Spherical Random Bond Random Field (SRBRF) Model

Temperature dependence of a_3 in PLZT at 400Hz. The monotonic decrease of this parameter is consistent with the SRBRF model.

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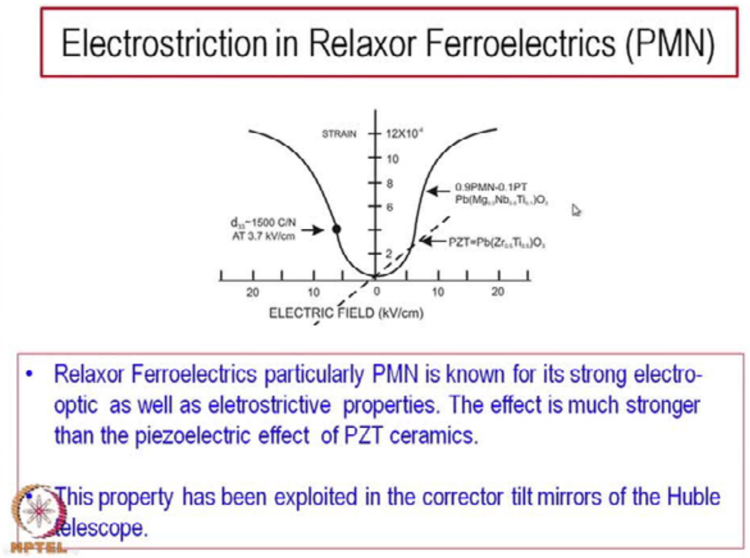

Electrostriction in Relaxor Ferroelectrics (PMN)

- Relaxor Ferroelectrics particularly PMN is known for its strong electro-optic as well as eletrostrictive properties. The effect is much stronger than the piezoelectric effect of PZT ceramics.
- This property has been exploited in the corrector tilt mirrors of the Huble telescope.

This is a three parameter and it can be written as, can be determined for different PMN style, sorry, ferroelectric relaxor, ferroelectric structure. Here are two examples. They have been determined from the optical parameters of the optical measurements refractive index measurements and one can see a three parameter changes monotonically as a function of temperature. The temperature dependence of a three in this PLZT, you can see this is one of the relaxor ferroelectrics lanthanum, though is at a voltage of 8.5 electric field of 8.5 kV percent square which is greater than 0. This is 3 years plotted here. So, this is a three parameter of PLZT of 400 hertz. The monotonic decrease of this parameter is consistent with the SRBRF model.

So, this kind of a change, monotonic change actually is an indication of the relaxor ferroelectrics and also, it provides a clue that the actual nano sized domains are present in this ferroelectrics are compounds. This is also another one are trying to this sulphide. So, this is the para electric phase, this is the transition phase. I am not going to details of this analysis accepts. So, that it is Gibson indication that the nano sized domain do exist which is different from that of the normal ferroelectrics and these nano sized domains actually do have different relaxation time and that reduce size to frequency dependency at different frequencies, a different set of domains becomes operative. That is the reason one gets a distribution of the relaxation time and you get a broad peak.

The relaxor ferroelectrics materials are also characterized by another very important parameter; another very important property that is electro strict property discussed earlier that electro strict properties have some amount of similarity with the piezoelectric properties where actually as a function of applied field, there is a strain through the dimensional changes as a function of applied field. So, it is more or less equivalent to the piezoelectric material. So, relaxor ferroelectrics, particularly PMN is known for its strong electro-optic as well as electro strictive properties. The effect is much stronger than the piezoelectric effect of PZT. So, this is another very interesting property particularly for PMN and that was the reason, this is one of the reasons why this property has been exploited in the corrector tilt mirrors of the Huble telescope. So, basically it is an actuator. One can use it as an actuator in addition to a good dielectric material. One can use it as a good transducer material and actuator. So, if you want to need a very stable actuator, then that is really possible with this kind of ferroelectric relaxor ferroelectrics.

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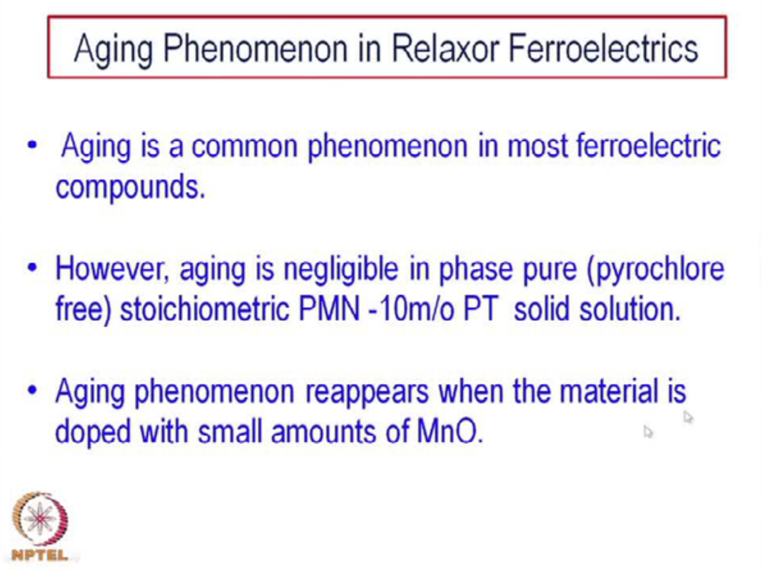

Aging Phenomenon in Relaxor Ferroelectrics

- Aging is a common phenomenon in most ferroelectric compounds.
- However, aging is negligible in phase pure (pyrochlore free) stoichiometric PMN -10m/o PT solid solution.
- Aging phenomenon reappears when the material is doped with small amounts of MnO.

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One of the reason why it is a better actuator material than PZT is its ageing characteristics. Ageing is a common phenomenon in most of the ferroelectric compound whereas, in case of ferroelectric relaxor, ferroelectric ageing is negligible in phase pure particular pyrochlore free stoichiometric PMN and it is much better when it is a matter solid solution with more percent of PT and that is a very stable material and its completely pyrochlore free, a pure material pure perovskite’s of course sizes such as perovskite’s solid solution and that ageing property is almost negligible. So, with time the property the lithium changes. However, the ageing phenomenon may once it is doped with small amount of MnO is added, it is been found that this ageing characterizes appears. So, because the ageing properties of this ferroelectric or the electro strictive properties are negligible, they can be a good actuator material.

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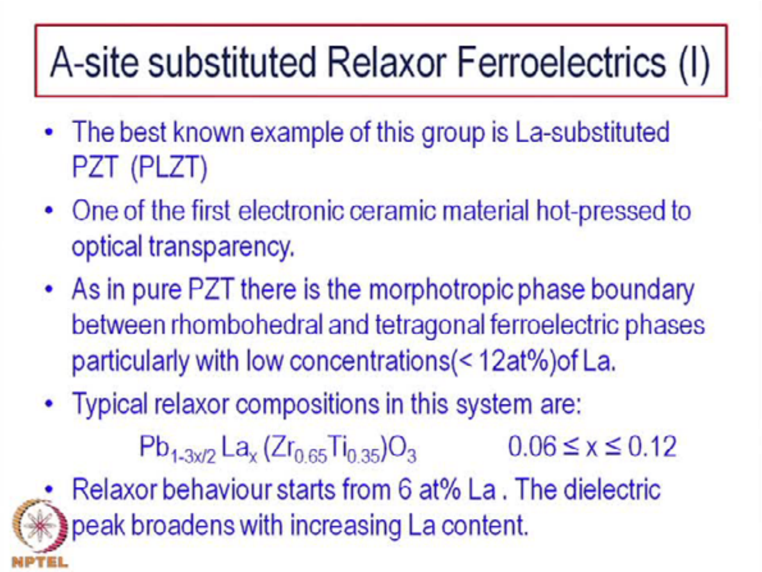

A-site substituted Relaxor Ferroelectrics (I)

- The best known example of this group is La-substituted PZT (PLZT)
- One of the first electronic ceramic material hot-pressed to optical transparency.
- As in pure PZT there is the morphotropic phase boundary between rhombohedral and tetragonal ferroelectric phases particularly with low concentrations(< 12at%)of La.
- Typical relaxor compositions in this system are:

$Pb_{1-3x/2}La_x(Zr_{0.65}Ti_{0.35})O_3 \qquad 0.06 \leq x \leq 0.12$

- Relaxor behaviour starts from 6 at% La . The dielectric peak broadens with increasing La content.

That was all about the B-site substitution. The other group as we mentioned earlier is the A-site subsidiary relaxor ferroelectrics and once again, this is based on the most popular piezoelectric material that is PZT. PZT has been substituted where some of the fraction of late has been substituted lanthanum and of course, this PLZT lanthanum substituted PZT has a very important characteristics and it is one of the first electronic ceramic materials hot pressed to optical transparency. So, a transparent piezoelectric material is actually PLZT, but PLZT is also characterized by relaxor ferroelectrics at a certain percentage of lanthanum. As in pure PZT, there is the morphotropic phase boundary between rhombohedral and tetragonal ferroelectric phases that were seen earlier PZT ceramics while we were discussing the piezoelectric properties of PZT. At the morphohedral phase boundary, you know the coupling coefficient is maximum, the energy conversion is maximum and that is the reason why we use a composition very close to the morphotropic phase boundary. Here also, you have a morphotropic phase boundary and rhombohedral and tetragonal phyroelectric phases particularly with low concentrations of lanthanum.

So, less than 12 atom percent, we have a morphotropic phase boundary that is the characteristics of the phase diagram. However, the typical relaxor composition, this system is about lead 1 minus 3 x by 2 La x Zr 0.65 Ti0.35 O3. This composition was presented earlier and the x value changes from 0.06 to 0.12, that is about 6 atoms. 6 to 12 atoms percent relaxor behavior starts from about 6 atoms percent lanthanum and the lanthanum percentage increases. The dialectic peak broadens with increasing lanthanum content and that is possibly presented in the next slide.

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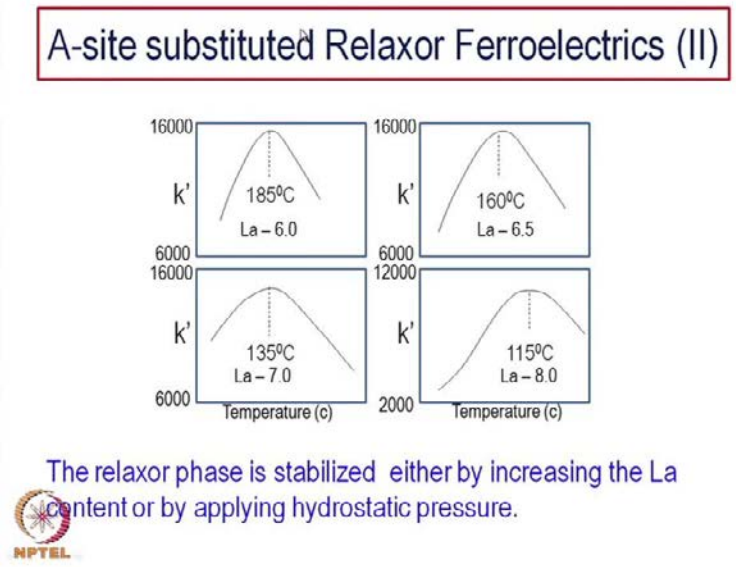

A-site substituted Relaxor Ferroelectrics (II)

The relaxor phase is stabilized either by increasing the La content or by applying hydrostatic pressure.

This is substituted relaxor ferroelectrics and as you can see, there are four different diagrams, basically schematics here. The relaxor face is stabilized either by increasing lanthanum or by applying hydrostatic pressure. That we will see in the next slide. So, here this is l a 6 atoms percent, l a, this is our 6.5 atoms percent and this is lanthanum 7n atom percent and 8 atoms percent. So, as mentioned up to x can carry between 6 and 12. Here about four compositions had been presented and you can see the typical peaks, this peak is about 185 degree centigrade and you can see a slight narrower peak whereas, the broadness of the peak increases as we increase the lanthanum content from 6 percent to about 8 percent. Not only that, the peak temperature also shifts from 185 to 160 and then, 135 and finally, with 8 atoms percent, it shifts to 115 degree centigrade. So, not only the peaks shifts, it turns. The peak also broadens quite a bit compared to this. This is a much broader peak and not only that, you also see the peak dielectric constant is also different here. The maximum here is about 16000 here in maximum 12000. So, the peak dielectric constant is k prime value is lower compared to this value. So, this is what happens. That means, as such PZT as such lead, zarconate, titanate is not a relaxor dielectrics or relaxor ferroelectrics. It is normal ferroelectrics, but as you dope lanthanum or substitute part of lead with lanthanum, it becomes a relaxor ferroelectrics.

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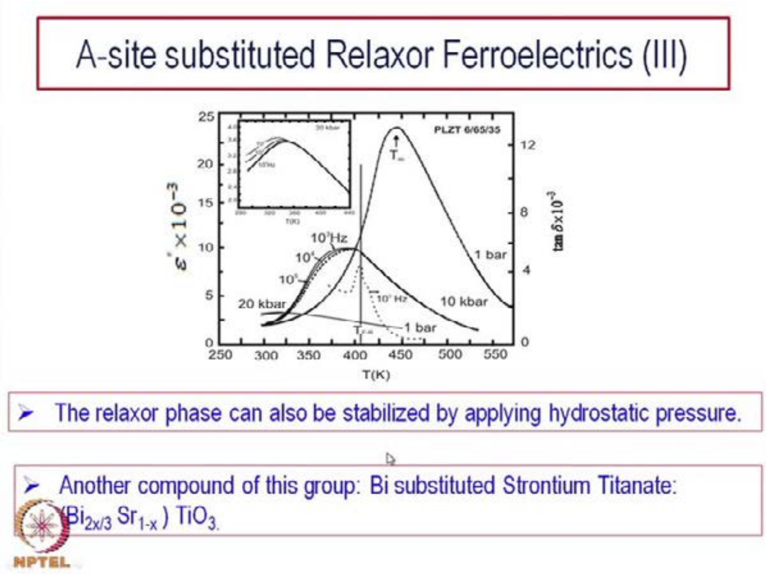

A-site substituted Relaxor Ferroelectrics (III)

- ➤ The relaxor phase can also be stabilized by applying hydrostatic pressure.
- ➤ Another compound of this group: Bi substituted Strontium Titanate: $(Bi_{2x/3}\,Sr_{1-x})\,TiO_3$.

Now, this kind of relaxor properties can also be induced or stabilized by applying hydrostatic pressure. So, not only lanthanum addition changes the normal ferroelectrics to relaxor ferroelectrics, but by applying higher pressure, the relaxor ferroelectric behavior can be brought in and that is what has been shown here. This is A 1 bar pressure and that is 10 bar pressure.

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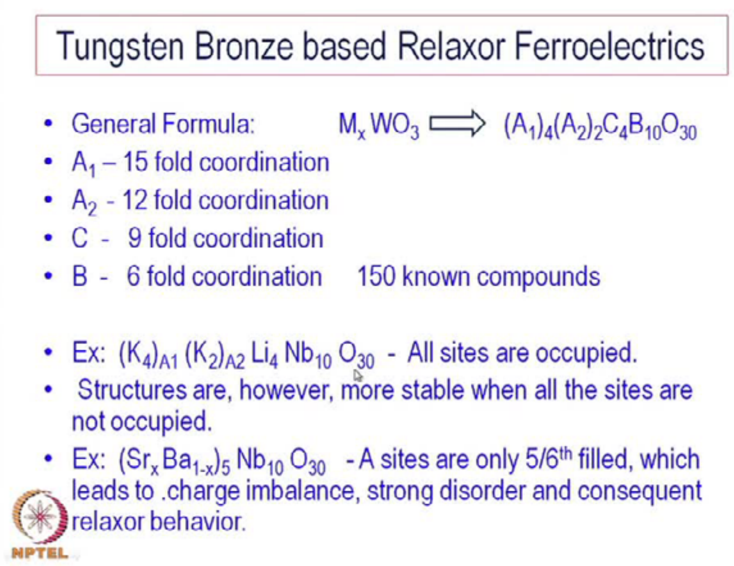

Tungsten Bronze based Relaxor Ferroelectrics

- General Formula: $M_xWO_3 \Longrightarrow (A_1)_4(A_2)_2C_4B_{10}O_{30}$
- A_1 – 15 fold coordination
- A_2 - 12 fold coordination
- C - 9 fold coordination
- B - 6 fold coordination 150 known compounds

- Ex: $(K_4)_{A1}\,(K_2)_{A2}\,Li_4\,Nb_{10}\,O_{30}$ - All sites are occupied.
- Structures are, however, more stable when all the sites are not occupied.
- Ex: $(Sr_xBa_{1-x})_5\,Nb_{10}\,O_{30}$ - A sites are only 5/6th filled, which leads to .charge imbalance, strong disorder and consequent relaxor behavior.

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One bar you can see here is over 6 atoms percent is PLZT. This is 1 bar and this is 10 bars. So, you have a much broader peak here and it decreases in the temperature range whereas, if you have 1 bar, it has much sharper peak with 6 atoms percent which is the lower limit of lanthanum, where one can expect the relaxor behavior. However, it becomes quite distinct when higher percent is used and another compound in addition to lanthanum doped is at; there is another compound which is also in the same group that is substituted relaxor ferroelectrics. This is one thing the bi substituted strontium titanate. So, the bi substituted strontium titanate were strong part. Strontium has been replaced by bismuth that also has a relaxor ferroelectric behavior, but the details of the data are not here on. The third group is this one that is the tungsten bronze based relaxor ferroelectrics.

So, the general formula here is this one is a slightly complicated, different kind of formula is A1 4 A2 2 C4 B10 and O 30. So, there are many different compounds known over 150 different compounds are known in this group in this general formula. So, there are A1 A2 C and B. These are four different cations involved and the molecular formula is also complex, but one can have a large number of compounds in this. The description of the structure is like this. You have A1 15 fold coordination, A2 is 12 fold coordination, C is 9 fold coordination and B is 6 fold coordination. So, the comp structure is quite complex in nature. One of the compounds example of this particular structure is K4 A1 K2 A2 potassium lithium niabate all sites are occupied. All A1 4, there are four sites are two sites, here are four can and so on. So, all of them are occupied compared to this particular formula and one can see all of them are occupied. There are two different types of potassium. One is the A-site, another is a two sites have different coalition numbers. Structures are however (( )) when all the sites are not occupied. So, it the sum occupancy factor is little less than the structure. It seems are more stable. So, one of those structures are strontium barium niobium oxide or niobate. A-sites are only 5/6th filled.

So, out of here is A6 including A1 and 2. There are six sites, here it is five of them are occupied and that too partly, it is strontium and partly barium. So, one-sixth is vacant here and it seems the stabilizes structure better which leads to charge imbalance strong disorder and consequent relaxor behavior is basically a relaxor ferroelectric structure is a disorder structure and you have a distribution of different sizes of nano domains. That is the origin of the relaxor behavior ferroelectrics. Although, there is a spontaneous polarization, but it is the disorderness. Disorder structure is the key for getting this or getting the relaxor behavior is here also that sort. Because of this vacancy or the unfilled sites, we have the charge imbalance and then, strong disorder and consequent relaxor ferroelectrics behavior. I think that more or less summarizes. This completes our discussion on relaxor ferroelectrics and also, the discussion on all the different groups of dialectics. Initially, we have discussed the normal dielectrics and then, non-linear dielectrics ferroelectric materials spill phyroelectric material and finally, we have discussed the so-called relaxor ferroelectrics.

So, there are different groups before I close on this particular subject. One of the applications of ferroelectric, material relaxor ferroelectrics of course is the utilization of the electrostatic property that is one can use a very stable as well as efficient actuator material for different kind of actuators. One of the examples which has been given is to correct the tilt for the Huble telescope it is being used. There is one of the good grading relaxor ferroelectrics, but other important application is in the multilayer dielectrics. As you can see the relaxor ferroelectrics, particularly PMN as a lower centre lower melting point or lower sintering temperature. It can be found at a much lower temperature relatively lower temperature than barium titanate and therefore, it can be used with the low melting are base metal electrodes.

If you are having a high melting point of 1200 to 1400 degree centigrade, then you have to use a costly and noble metal electrodes in multilayer structures of capacitors. Multilayer capacitor structure like silver palladium and so on. More amount of paladin is to be added. Paladin is very costly and therefore, they increases the cost whereas, if you have relaxor ferroelectrics like PMN which can be centered at a much lower temperature, so one can use either silver or copper base materials and not only you have relaxor ferroelectrics have a much broader temperature coefficient. Sorry, the temperature effect are broad peak of is dielectric constant. So, it is more temperature stable and therefore, one has advantage of using it as a multilayer capacitor or dielectrics for multilayer capacitors.

So, both an electro strictive material as well as a multilayer capacitor material or dielectric material, relaxor ferroelectrics contents slight advantage over the other and also, you do not have an ageing characteristics, right. So, these are some of the advantages of the relaxor ferroelectrics over normal ferroelectrics or normal dielectric material.

So, with this, we come to the end of our discussion on dielectric materials including ferroelectric, phyroelectric as well as relaxor ferroelectrics. Thank you very much for your kind attention.

Thank you.