Fundamentals and Applications of Dielectric Ceramics
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Module No # 08
Lecture No # 37
Domain Structure and Properties of Ferroelectric Materials

Welcome again to the new lecture of this course fundamental and applications of dielectric ceramics.

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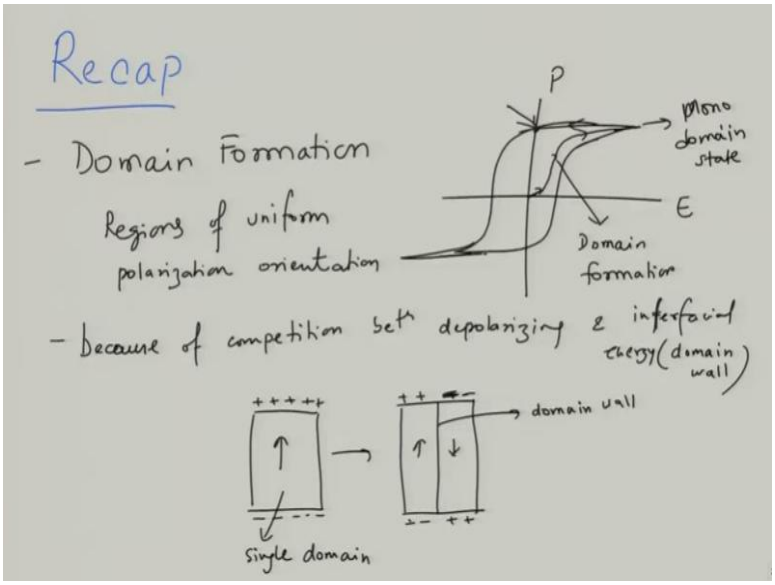

We just briefly let us just recap the last lecture so in the last lecture we were talking about the domain formation and we said that you know the ferroelectric switching that occurs in the ferroelectrics and the ferroelectric hysteresis loop is because of domain formation and domain switching. So initially when you switch a version ferroelectric it switches linearly then suddenly nonlinear region takes over and then again you go into the linear before you reach saturation.

And this is basically in this region you have massive domain formation and then somewhere here at the end of it you have mono domain state. And when you come to this point after releasing so you start in this fashion and then when you come to this point all the domains do not revert back so you have state in which so we will come back to that little later on so domains are nothing but regions of uniform polarization orientation.

And they form because of competition between depolarizing energy which wants to depolarize the material to reduce the surface charge density and interfacial energy which is nothing but domain wall energy . So as we say suppose you have a material as a dielectric if it is mono domains state then you have dipoles aligned in one direction.

So you have huge surface density suppose you create a domain which is 180^0 domain, so reduce a surface charge density and charge is modify each other but at the same time you create a domain wall and this is single domain. So this competition between the two energies leads to formation of domains and do not confuse domains with grains, grains are different domains are different there is possibility you can have multiple domains in one grain there is also scenario then multiple grains can be in single domain when you reach mono domain state.

So as a result you form a domain wall and this domain wall could be of the order of an unit cell or thick or so.

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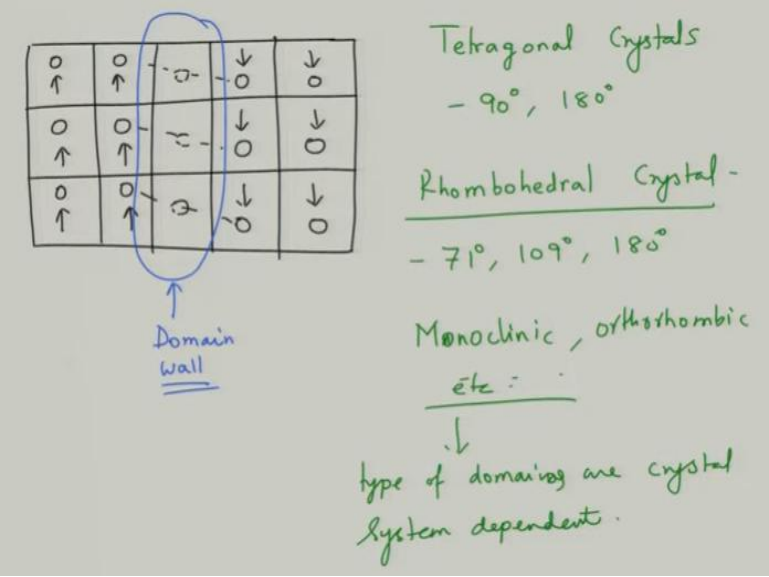

Because what happens in domain wall formation is suppose you have this as a crystal. So in this region your atoms are shifted up from the unit cell so this is basically you can say polarization up and this part of the crystal that we just shifted down as a result in this part of the crystal you have polarizing vector shifting down and somewhere in between you will have a transition you can see that you will have the transition going from one region to next.

So this is where you will find atoms sitting somewhere in the middle and this region would be the domain walls so depending upon the angle of mis-orientation of domains you can have various kinds of domains in tetragonal crystals generally we have 90^0 domains and 180^0 domains which means across the walls the polarization changes by 90^0 or 180^0.

Whereas in for example if you look at Rhombohedral crystal you may have 71^0 domains there is all, also 109^0 domains. So we have 180^0 domains, 71^0 domains and 109^0 domains. And similarly if you look for mono clinic crystal or you may have orthorhonobic crystal or whatever else so it cannot obviously cubic material will not have domains because cubic is centro-symmetric.

So as a result cubic will not show ferro-electricity so only crystals which are non-centro symmetric which show ferro electricity will have domain walls, so these are all basically types of domain walls are crystal system independent. So this is what basically would be now how the domains form in these crystals we looked at that what happens in the ferro electric materials is.

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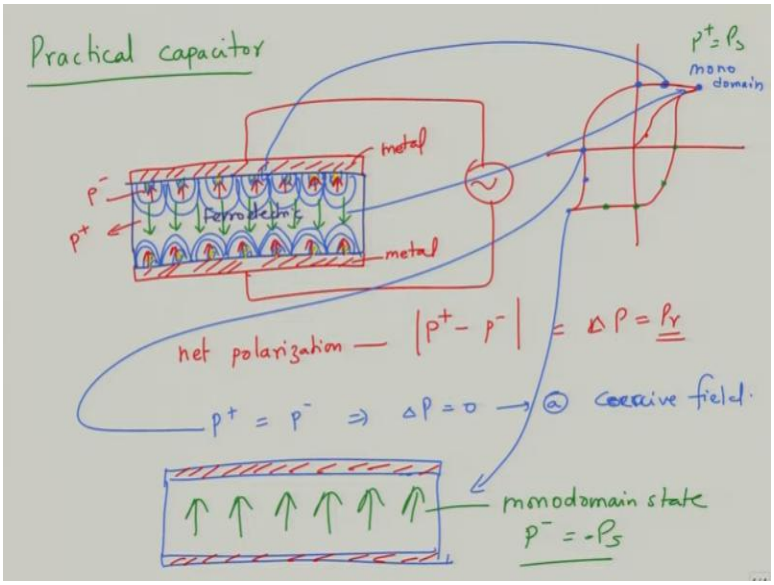

In a ferro electric material generally what happens is that in case of practical capacitor what will happen is that you will have a metal or you will have a ceramic so this is let us say your dielectric ceramic which is ferro electric in nature so this is let us say ferro electric and generally on the two sides of it you will put a electrodes so these are electrodes these are metal electrodes and when you apply electric field then what happens is that as a function of electric fields slowly we saw that the hysteresis curve is something like this.

So domains start nucleating right somewhere in early phase so what happens is that the way domains start forming is domain start nucleating here at the interface between the electrode and the sample and in between you may have domains of multiple orientation but these domains grow so what might happen to begin with is let us say in the beginning you have a scenario in which all the domains are oriented in this direction.

So this is let us say a mono domain state, once you have a mono domain state and you apply the electric field in other direction or let us say you go back to zero electric field what happens is that the reverse orientation domains they nucleate at certain locations so let us say they locate they form here these are nothing but domains of opposite orientation so you can call them as you reduce the field so this is a scenario the first scenario was this you will have mono domain state.

And then when you reduce the electric field let us say you come here somewhere here you have reduce the electric field then what might happens is that you will have domains of opposite orientation nucleating so what will happens is that you will have domains of this orientation these are oppositely oriented domains. And as you keep reducing the field strength until you come at this point when you come to this point then what will happen these domains would have grown a little longer or bigger of course they will not be of same size because the nucleation in growth phenomena.

So there will be some randomness associated with it but they will be of some certain size and a polarization in all of them will be in this direction so you can see that you will have no longer a mono domain state but you have a net polarization which is P^+ and P^- which is difference between P+ and P^- so you will have delta P:

$$\left|P^+ + P^-\right| = \Delta P = P_r$$

this is nothing but your P_r this is what is the remnant polarization this is because the not there is a unevenness in the volume of domains of each orientation. So the volume of domains of earlier orientation is still larger as compared to volume of new newly formed oriented domains as a result you form what we call as you have a P_r.

And when you reduce the electric field further what will happen is that these domains will grow further until you reach this point where this point $P^+ = P^-$ as a result $\Delta P = 0$. So this is where you will achieve at coercive field and then of course when you go to this place back again and this place back again so this in case what will happens is that you will have a situation like this so you will reach a mono-domain state but in the opposite fashion.

So this is the electrode and a polarization vector will now be all along this, so this will be again a mono-domain where $P^- = -P_S$. And at this place you had $P^+ = P_S$ and whole cycle goes on when you reduce to come here you come there and this cycle repeats itself the mechanism of domains growth and formation. So these domains are these domains can also be observed easily.

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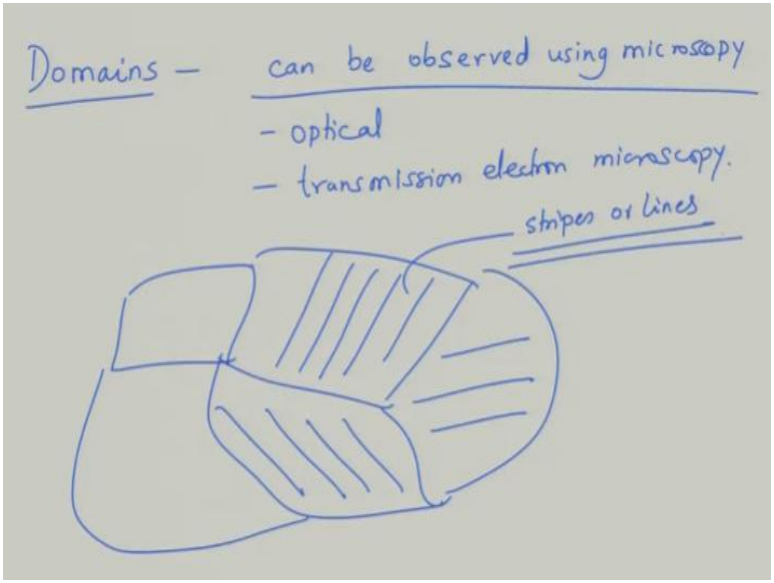

So domains can be observed can be observed using microscopy for example one can do optical microscopy one can do so if domains are big enough you can see them in optical microscopy if they are small then you can see them in transmission electron microscopy and they will when you look at the domains so let us say if this is crystal you will see them as sort of lines or stripes and crystals so these are the regions which can show domains. So you can form so these stripes or you can say lines which can be sort of imagined as domains so we will show you one micrograph.

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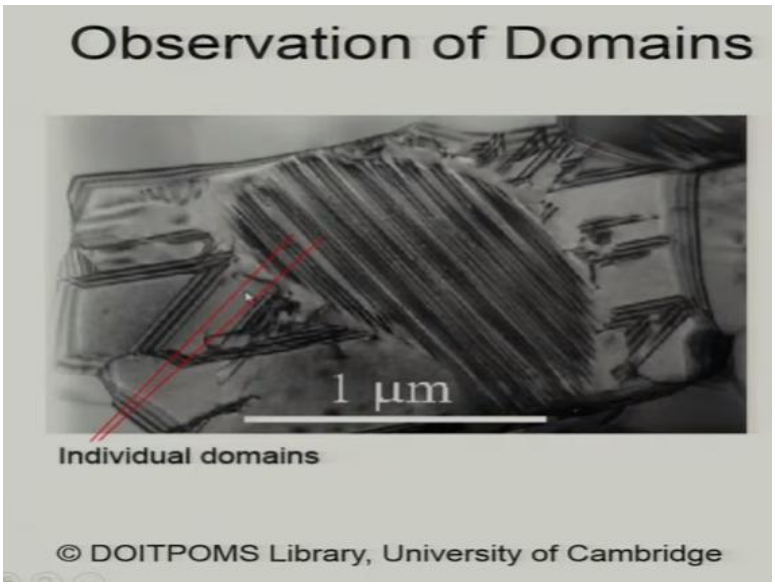

So this is the sort of picture of that domains which have been observed in microscope so you can see that these are sort of the regions in which you can see some stripes and there are regions in between the stripes which are sort of the domains so this is the microscopy image which has been taken from *doitpoms.ac.uk* so they have a library in which there are some images which domains if you go online if you look at this doitpoms library at the university of Cambridge website you will see that there are some pictures which show how the domains can be observed.

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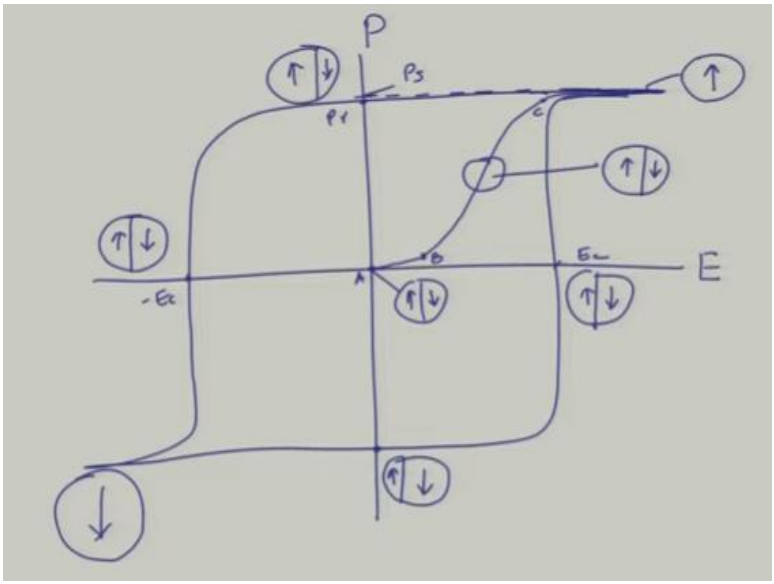

So this is about the formation of the domains and these materials now basically now it must be clear to you that let us say revisit the series of loop now. So this is a polarization versus electric

field hysteresis loop so if you start from a ferro electric which is never been poled before and then you come to this point so you start formation of domains and then you go to a linear region then again you so this is initially in a linear region then you reach the end of so you start at non-linear region at B then you finish at non-linearity at C then you again going to linear region until you saturate.

And then depending upon the type of material you can have very large difference between P_S and P_R and small difference between P_S and P_R that entirely depends upon the system where it is a poly crystalline material whether single crystal material whether thin film thick film and so on and so forth. So in thin film there is a clamping effect as well as a result clamping leads to different effects in thin films as compared to bulk.

So at this point you have mono domain state somewhere in between you will have let us say you do not have mono domain state maybe domains of one type of more than domains of another type at this point you have a situation like this where some domains come back but not all the domain come back so there is an unequal distribution at this point again the proportion of domains as such that so that the net polarization is zero.

Then again at this point you reach the mono domain state again at this point you reach regions where you have opposite polarization larger as compared to the up polarization and then again you reach at this point where up and down are equal to each other. So this is how domains switching is observed in ferro electric materials and domains we reiterate again they form as the result of competition between the de-polarization field or de-polarization field driven energy which wants to de-pole the material and the surface energy which is nothing but the domain wall energy. So one is positive one is negative as a result you have a stable domain size for a given material,

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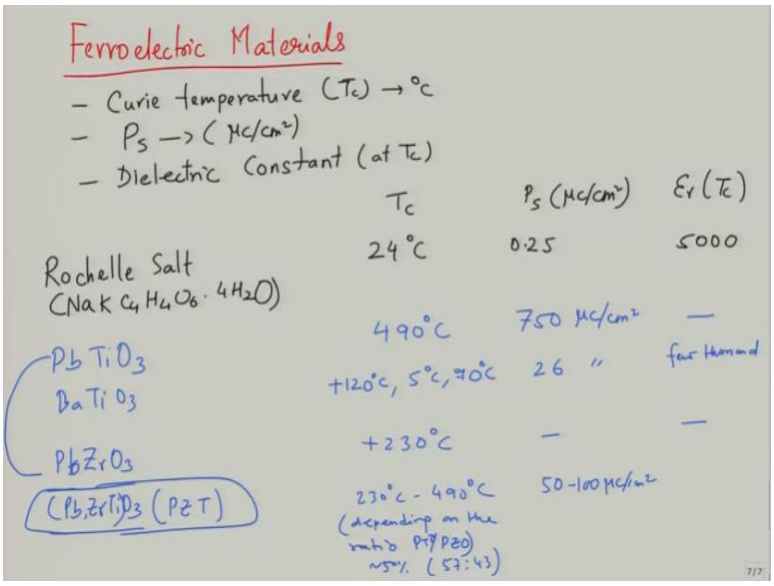

Now let us look at the comparison of the various ferro electric materials in terms of their properties so the most important properties so what we have seen ferro electric materials have characteristic such as one as curie temperature which is called as transition temperature T_c then another characteristic of them is saturation polarization P_s which is typically measured in $\mu C/cm^2$ and T_c is in ^0C or K and then you have dielectric constant.

And when you compare various materials for example something like Rochelle salt which is $NaKC_4H_4O_6.4H_2O$ which has a curie temperature of 24^0C. So it has a spontaneous polarization of about 0.25 $\mu C/cm^2$ and it has a dielectric constant at T_c of the order of 5000. So at T_c we have anomaly in that electric constant it increases all of the sudden.

So if you look at something like so this is of course Rochelle salt which has a complex crystal structure if you look at peroxide structured materials for example let us say lead titanate. Lead titante as a T_c of 490^0C very high T_c so it remains ferro electric up to very high temperature it has a polarization as high as 750 $\mu C/cm^2$ it can have very large polarization although in poly-crystals you do not see this kind of polarization but never the less and the di-electric constant is way too high it is sort of immeasurable.

And then if you look at something like barium titante has three transitions the first transition has you cool down the material occurs at 120^0C it has three ferro electric transition it is ferro electric

in three different regions but different crystal structures. So 120^0C, 5^0C and -90^0C and it has a polarization of nearly 26 and dielectric constant again reaches to few thousand and then we have something like lead zirconate titanate.

So lead zirconate titanate is solid solution of lead zirconate followed by solid solution of $PbZrTiO_3$ now lead zirconate has a T_c of 230^0C and it has a it is the anti-ferro electric in nature so it just like anti-ferro magnet is at anti ferro electric it also has a anti-ferro electric. So PbZrO3 is made by mixing $PbZrTiO_3$ which is commonly called as PZT one of the best well known ferro electric it is mixed by putting these two together $PbTiO_3$ and $PbZrTiO_3$.

So obviously it is Tc depends upon the composition and it is Tc between 230^0C to 490^0C depending upon the ratio of PTO to PZO and generally it is the composition of nearly 50-50% or to be precise it is 57 - 43% position which is the most well-known composition and this can have very large polarization the thin films of this material show polarization of the order of you know 50 to 100 $\mu C/cm^2$ this is also a fantastic piezoelectric depending upon how it is processed and how it is made it can show piezoelectric constants upto you know 1000 in fact even higher pC/N.

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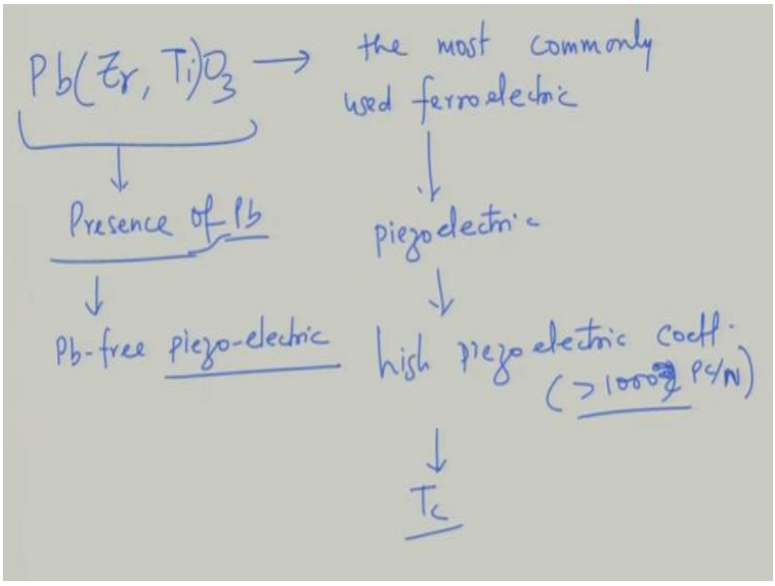

And this is a bench mark material as we say in terms of performance $PbZrTO_3$ so Pb is $ZrTiO_3$ is you can say the most commonly used ferro electric actually it is piezoelectric properties which are more exploited then it is ferro electric properties. So it has very high piezoelectric coefficient

and maybe more than 1000 pC/N or you can say you can calculate the direct piezoelectric coefficient depending upon so indirect piezoelectric coefficient etc.

So it has very high piezoelectric coefficient and reasonably high T_c is much of room temperature of course PT has 490^0C but it has reasonably high T_c depending upon the composition so this is one of the most used ferroelectric but the problem with PZT is that presence of lead and current environmental restrictions on the use of the lead are making people to look for other alternatives.

So other alternatives are you know lead free piezoelectric as we call them so sodium based ferro electric potassium based ferro electric barium based ferroelectrics. So these are all replacement for PZT to reduce the amount of to eliminate lead or to reduce the amount of lead in them.

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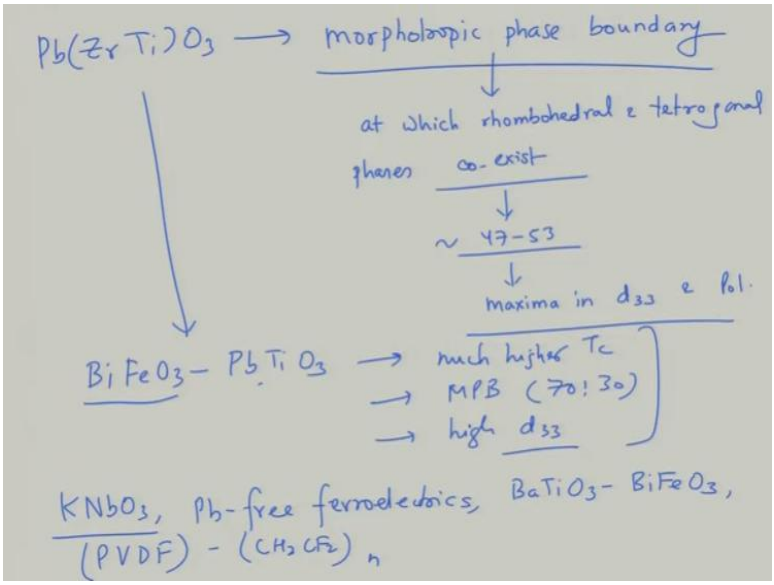

Interestingly piezoelectric PZT system shows it has a very interesting phase diagram and this phase diagram consist of what we call as a morphotropic phase boundary and this morphotropic phase boundary exist at about let me see if we have the phase diagram with me so the morphotropic phase boundary is the boundary at which Rhombohedral and tetragonal phases coexist and this is at the NPV composition which is nearly 47-53% composition so at this phase boundary you have a maxima in d33 as well as polarization.

And this is the most used compound this is the most used you can say composition for piezoelectric. There are other electric as well because it is transition temperature is little lower so

things like $BiFeO_3$ which is like also a ferro electric and solution with $PbTiO_2$ gives too much higher T_c and this also show a MPB and this MPB is at 70-30% composition 70% BFO and 30% lead titanate and this can also give rise to high d33 maybe not as high as PZT but significantly high but much higher T_c because higher this much ferrite has a T_c which is very high it is not 450^0C it is something like 870^0C.

Whereas PT has a T_c of 490^0C so if you mix them you have T_c which is higher than 500^0C so it has much higher T_c but d33 values are lower than PZT but still comparable. So there are lot of other choices you have potassium niobate as a ferroelectric also you have as we said you have lead free piezoelectric lead free ferro electrics you can say you have solid solution of $BaTiO_3$ with $BiFeO_3$ which is again lead free ferro electric which again show a MPB or morphotropic phase boundary we will show the phase diagram in the next class but we do not have time to go through phase diagram in this class.

So and then you have other polymeric options such as PVDF which is nothing but CH_2-CF_2 so PVDF again is a polymeric ferro electric which has it does not have very high piezoelectric coefficient of polarization but still useful material because it is a polymeric you can make lot of flexible devices out of it so we will stop here we will come back to some more aspects of these ferro electric, piezoelectric and pyro electric material before we look into their applications.