Fundamentals and Applications of Dielectric Ceramics
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Module No # 08
Lecture No # 38
Phase Diagram and Measurements of Ferroelectric Materials

So welcome to the new lecture again of a course fundamentals and applications of dielectric ceramics. So let us just briefly recap the last lecture.

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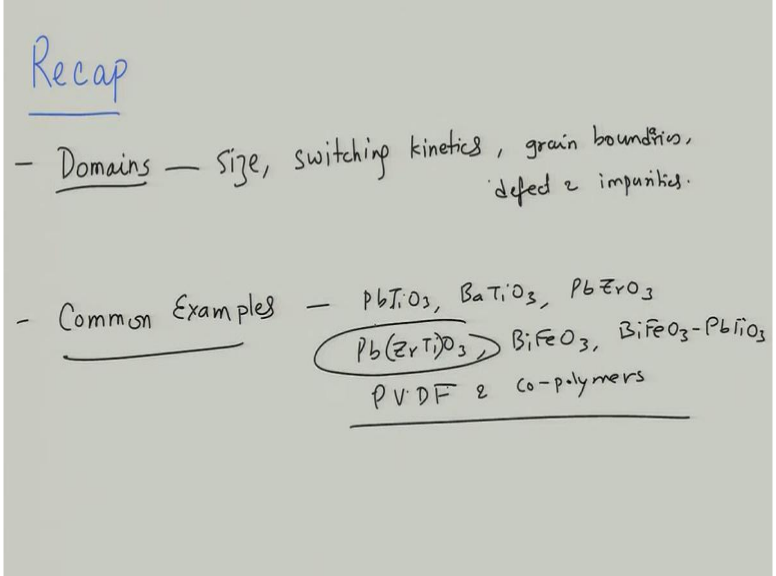

Recap

- Domains — Size, switching kinetics, grain boundries, defect & impurities.
- Common Examples — $PbTiO_3$, $BaTiO_3$, $PbZrO_3$, $Pb(ZrTi)O_3$, $BiFeO_3$, $BiFeO_3-PbTiO_3$, PVDF & co-polymers

So in the last lecture we completed our discussion on a domains in ferroelectric materials and we saw how the domains evolved during ferroelectric switching going from zero polarization to very high saturation polarization. Then reverting the switch field back to zero brings us back to the state of Remanent polarization where there is unequal the unequal volume fraction of those up domain with respective down domain so vice versa depending upon $-P_r$ or $+P_r$ and then how you have to again apply a electric field extra electric field to force the assistant back to zero polarization state which is the coercive field.

So domains are very important and there size is very importance of factor which play important role are domain size, switching, kinetics etc., which are out of preview of this course. But these are very important factors and domains are affected by for example things like grain boundaries how domain switch is a function of grain sizes the system it is also a function of defects in the system defects and impurities and so on and so forth.

So basically this is the topic which frequently face by researchers working in the area which whose aim into synthesize good ferroelectric materials and then we looked at some common examples. And common examples as we should saw our things like lead titanate, barium titanate you can have $PbZrO_3$ solid solution of PbZr and Ti which is the most common ferroelectric $PbTiO_3$.

Then we have $BiFeO_3$ we have solid solution of $BiFeO_3$ and $PbTiO_3$ and so on and so forth and of course we have polymeric material which is PVDF and it is co polymers. So there are quite a few examples of ferroelectric material of course PZT is the benchmark material because of its high piezoelectric coefficient but other materials are also equally interesting as well as useful.

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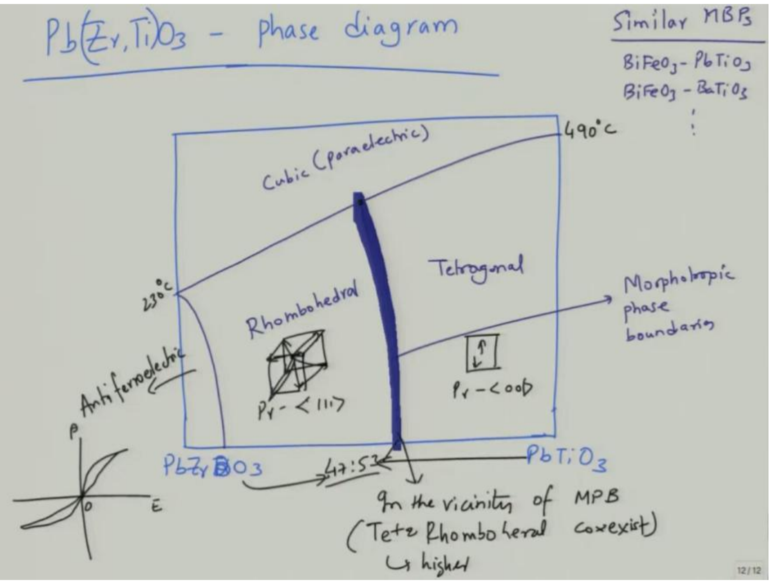

So let us just look at the phase diagram of $PbZrTiO_3$. So let us say you start from $PbZrTiO_3$ on this ZrO_3 on this side and then we go to $PbTiO_3$ on this side. So obviously that T_c is high on this side T_c is lower on this side so if you plot line between the T_c it goes something like this. So this sort of a phase boundary at lower values it is sort of have a phase boundaries again. So these are various region which go in this material.

Now as it turns out at higher temperature the materials in cubic that is in paraelectric form. At lower temperatures $PbTiO_3$ rich composition have tetragonal structure and this boundary which is here is called as Morphotropic phase boundary at which is a basically a sharp boundary between tetragonal region and the adjoining region which is rhombohedral hederal region. This boundary separates the two and basically this is a region in which these phases sort of we can say co-exist.

So within you can say the vicinity of this boundary MPB both tetragonal and rhombohedral phases co-exist. And this co-existent of two phases basically increases the number of polarization vectors as you can have material because in poly tetragonal you can have this vector or this vector. Whereas in rhombohedral you can have vectors along <111> direction.

So in this case you will have <111> P_r vectors and in this case you will have <001> as P_r vector. So when both of these co-exist number of polarization vectors are larger as a result it leads to easier switching and higher d33. So this give rise to higher d33. And this is at a composition of 47-53% nearly 47% $PbZrTiO_3$ and 53% $PbTiO_3$. So $PbZrO_3$ of 57%, 47% and 53% of PbTi.

Somewhere at the corner at low $PbTiO_3$ concentrations the material is antiferroelectric. So pure $PbZrTiO_3$ is anti-ferroelectric so antiferroelectric material we have not discussed but basically it shows loop like this something like this. So it has some sort of hysteresis. So in the first and third quadrant it shows some sort of a hysteresis but at zero electric field it has zero polarization just like a antiferromagnet. So at zero magnetic field antiferromagnet has zero magnetization.

Here also at zero electric field you have zero polarization. But when you mixed with $PbTiO_3$ gives you achieve some interesting qualities. So this is 490^0C, this is 230^0C or so. So this would be approximately the mathematical sum of two approximately speaking. So as a fairly straight line it all it little bit nonlinear but approximately just goes by the rule of mixtures. So on the left you have antiferroelectric region which is generally not very useful for most applications. But the useful application useful composition are these rhombohedral and tetragonal.

And the most useful of them is this MPB composition of nearly 50-50 or you can say 47-53. So in the vicinity of MPB people make piezoelectric which have d33 values exceeding thousand or in fact even the very high values of been reported. So this is one material that is there as a ferroelectric which is very useful. And similar MPB's are shown in you can say similar MPB effects are seen in systems like $BiFeO_3$, $PbTiO_3$, $BiFeO_3$, $BaTiO_3$ and so on and so forth.

Quite a few systems shows this MPB and this MPB is quite exploited phenomena for exaggeration of the property is in the vicinity of MPB. So these are so this is sort of an example of good ferroelectric material. Now let us see for example what happens in case of barium titanate.

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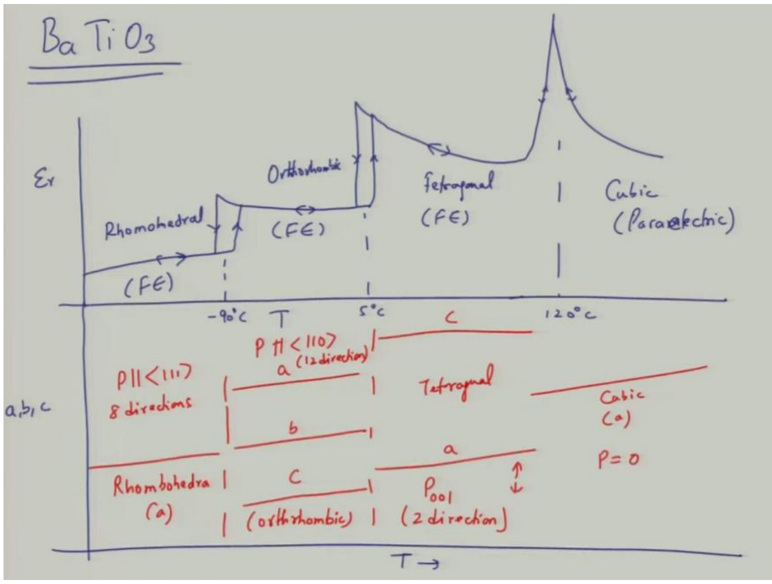

So barium titanate when it is when you measure its electric constant that electric constant of barium titanate as a function of temperature. So you start measure the electric constant it goes something like that then it goes boom up then again in sort of show of behavior like this then again and then again in shows and these the three temperatures are and this there is hysteresis as well so when you take it back in the opposite direction. So this is in the forward direction this is in the reverse direction again this is in the forward direction this is in the reverse direction.

So how you measure the make the measurements?. So there is a hysteresis in T_c but this happen at about the -90^0C and this happens at about 5^0C and this happens at about 120^0C. And the crystal of structure goes from rhombohedral to orthorhombic to tetragonal to cubic. So the cubic is the paraelectric state.

This is the high temperature paraelectric state at above 120^0C but below 120^0C it has two more transition and they are from one ferroelectric state to another. So this is also ferroelectric and this is also ferroelectric. It is just that dielectric constant changes than the tetragonal state we achieved high as a dielectric constant whereas in orthorhombic and rhombohedral region we observe lower dielectric constant of course the temperature is also lower.

So polarization of that of electrics is also lower. And as you can also plot dielectric constant when you plot the dielectric constant similarly you can also plot the lattice parameter. So in this case you will observe two lattice parameters in the orthorhombic case you will observe a three lattice parameters a, b and c whereas in case of rhombohedral you will observe only one lattice parameter.

So you can also plot across these temperatures if you plot lattice parameters a, b and c as a functions of temperatures you will see this kind of changes. So rhombohedral will show something like this and then depending upon whether you heat or cool. So you will have basically three lattice parameters here so a, b, c and then this region you will have a and c and then again you will have cubic somewhere here.

So this is the T_c region you will have so here you will have rhombohedral you will have only one lattice parameter here you will have three of them orthorhombic. So you will have let say a, b and c and then here you will have c and a so this is tetragonal and then we have cubic only a. So one can also measure lattice constants are the functions of the temperature using technics like a excess diffraction and one can see this variation in reality in these materials.

And the polarization vectors are also different in cubic you have no polarization here you have polarization long <001>. In the other case you will have polarization parallel to <110> axis in the orthorhombic case. So when you say P 001 you will have two directions you can have <001> or <00$\bar{1}$>. In the <110> case you can have twelve directions, in case of P parallel to <111> you can have 8 directions. So this is how the polar vectors will also change as you change the material.

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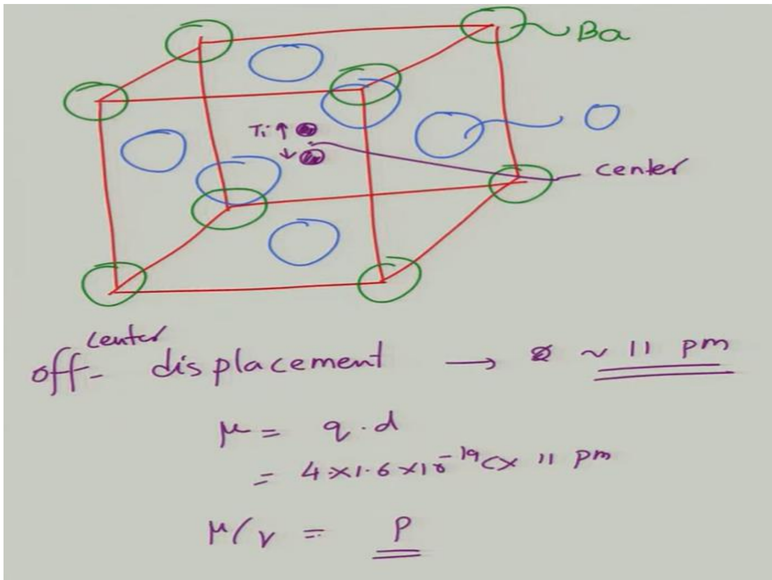

And generally, in the tetragonal form the way it happens is that in tetragonal form when you convert this to tetragonal phase from cubic phase so you will see the structure will show some sort of distortion. So these are all oxygen atoms sitting at the center of phases. This is barium atom so this is barium this is oxygen in between we will have a tiny, so this is the center of the lattice.

So titanium atom will either be here or it will be here. So this is let us say center of the unit shell the titanium will be shifted up or down and the magnitude of displacement is about if you draw the cross section that displacement is of the order of about you can say few picometers. So the displacement off center displacement is of the order of let me see the number is about 11 pm.

So you can calculate the dipole moment. So dipole moment will be:

$$\mu = q.d$$

So you can calculate the dipole moment accordingly you can calculate the dipole moment per unit volume which will give you the polarization. So sort of you can get an estimate of polarization by just measuring the dipole moment in this fashion.

So this is about $PbTiO_3$ and some examples of ferroelectric materials remember all these ferroelectric materials are also piezoelectric and pyroelectric in nature. So you will see that many piezoelectric and pyroelectric which are used in the practice they are actually ferroelectrics. So just because the materials like $PbTiO_3$ and solid solution of $PbTiO_3$ with $PbZrO_3$ they have high d33 values in the vicinity of MPB that is why they are used as piezoelectric material as well as pyroelectric materials.

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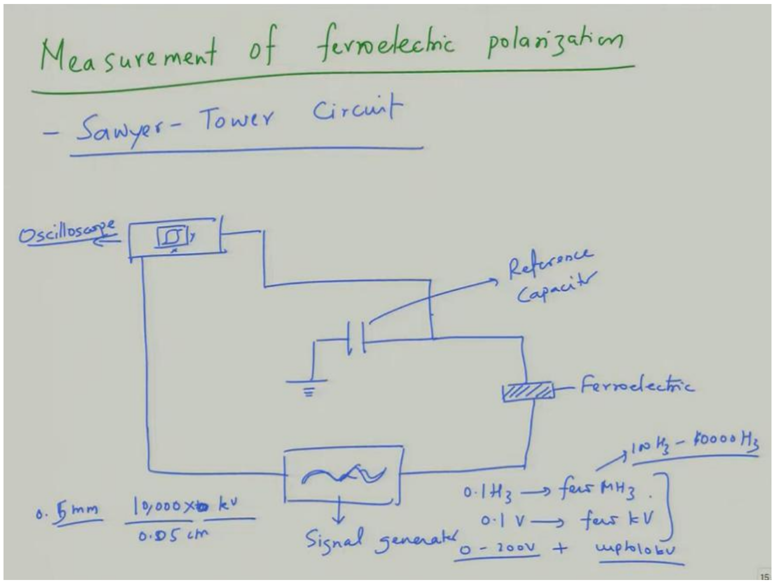

Measurement of ferroelectric polarization

- Sawyer- Tower Circuit

So now let us look at some of the applications. So we first see how do you measure the ferroelectric polarization? Ferroelectric polarization is generally measured using a circuit called as Sawyer-Tower circuit. So what you have in this circuit is basically is very simple circuit not a very difficult circuit so you have a circuit like shown.

So what you have is you have a oscilloscope on which you read the polarization. So you can have x and y so this is basically you can say as a you need oscilloscope. Nowadays you can get rid of oscilloscope you have electronic circuits and computers. So you do not need that you can just connect to computers. You need a signal generator so that you can provide a AC field so this is signal generator.

So which means you must have range of voltages and range of frequencies. Generally the frequencies that we measure use for ferroelectric are somewhere between you know 0.1 Hz to you can go up to few MHz. And the voltages will depend upon the thickness of the sample. But voltages may also vary from you know 0.1 volt to few kilo volts. They may not be available on single units so you may have a unit up to 200 V.

So 0 to 200 V you can have something which is up to 10 kV. So if you have a sample of let say thickness 1 mm or let say 0.5 mm so 10 kV will give you a field so 10 kV divided by 0.05 cm. So this is in kV/cm so this is will give you a very large field. So you can see you can do the calculation yourself and we will have fields in the order of MV/cm.

So which is large enough field so switch any ferroelectric. So if you have a 10 kV power supply with frequencies varying from 0.1 to few MHz and generally we make the measurements are about 100 Hz to 10000 Hz. This is a general range for making measurements, but it depends up on the materials and its application. So one should be able to measure most ferroelectrics if you have this system.

Now what happens in this circuit is basically you apply this signal to a ferroelectric. So this is a ferroelectric under test this ferroelectric is connected in series to a in parallel to a your reference capacity you must always have a reference. Because you are measuring the charge or polarization as a result you have to have a reference otherwise you need something to calibrate the system.

So basically, you can see the circuit is very simple you have a reference capacitor and you have a ferroelectric which you measure in comparison to this reference. You have a signal generator which is to generate the kind of voltages that you would like to apply on the sample then you have a oscilloscope. Oscilloscope is nowadays replaced by computer and software's, so it is much more easier to make the measurements.

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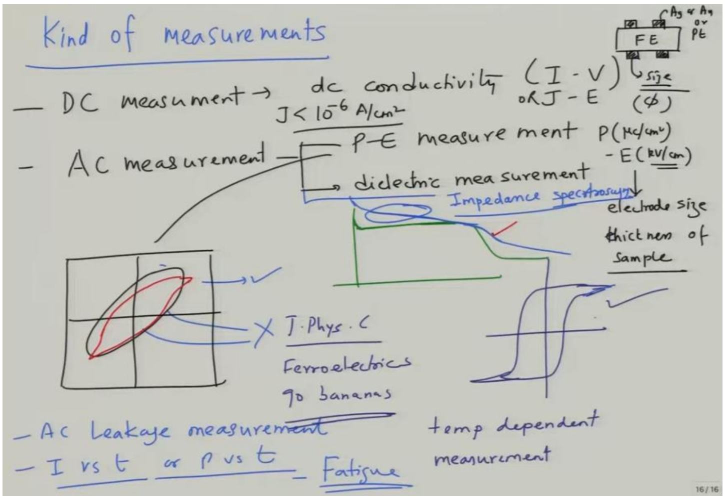

Kind of measurements

- DC measument → dc conductivity (I - V) or J - E
  J < 10^{-6} A/cm²
- AC measurement
  - P-E measurement P(μC/cm²) - E(kV/cm)
  - dielectric measurement
    Impedance spectroscopy

- AC Leakage measurement
- I vs t or P vs t - Fatigue

temp dependent measurement

Kind of measurements you make on ferro electrics are kind of measurements we make or you can make DC measurements. So DC measurements is just for measuring the dc conductivity just the ohmic and loss. But most of the measurements that you make are AC measurements that is time dependent measurement. So time dependent measurement could be your polarization hysteresis loop measurement.

You can make dielectric measurements so this is dc conductivity is basically you can say it is a I-V measurement. So you can measure ampere so you can measure either I or J. J is the current density as a function of electric field. So current versus voltage or current density versus electric field make sure that you know whether it is current to current density. If you want to have current density, then you need to have the measurement of electrode area accurately.

So generally, how you make this measurement is you have this capacitor sample on that we make these electrodes. Electrodes are typically metallic electrodes made of silver or gold or platinum you have to choose the metal which does not inject charges. You have to have a non-injecting and you should have a ohmic contact. You should have a you should not have a short key contact.

So generally, the choice of metal is silver or gold or platinum. You must try and make a electrode which makes a good contact. If you do not have a good contact, you are going to have a defect at the interface and this is going to lead to a very poor measurement. So generally we preferred the contact which are evaporated contacts and after evaporation or printing you will have to annealing them to make a better contact.

Annealing can be done in a little lower temperature but thermal treatment may often been necessary. So you have a ferroelectric which is sandwich between these two electrodes. In order to calculate the current density or the charge density you must know the size of this electrode. Size of this electrode is especially basically the diameter of the electrode is very important for the calculation of any quantity in terms of per unit area.

So polarization will be $\mu C/cm^2$ you need to know the electrode and electric field which is kV/cm and this require you to know the thickness of the sample very carefully. So what you require is electro side and thickness of sample. So dc conductivity measurement will tell you whether your sample is conducting or not. If it is conducting it is probably not worth making any of the measurement.

You just have to make a better sample because ferroelectric are supposed to be insulating. So general guideline is if your current density is less then $J < 10^{-6}$ A/cm^2 sorry then it is a good material. But if it is more than 10^{-6} A/cm^2 then it is a very bad material it is a leaky material as we say it. So this is sort of a general value which mean it varies from material to material but sort of range.

You make a ferroelectric hysteresis look ferroelectric hysteresis loop in the literature you will see people report hysteresis loops of various kinds. You will see people measuring this kind of hysteresis loop, people measuring hysteresis loop of this kind. This is a reasonably good hysteresis loop you must have saturation on nonlinear region. These ferroelectrics are bad hysteresis loops and most likely these materials are not ferroelectric.

They are leaky dielectric basically they have lot of electrical leakage in them. There is a nice paper by professor Jim scott on Journal of physics C which says that ferroelectric goes banana go bananas. You can search it this paper it shows that even if you make a measurement on a banana you will get a loop. So it is important to differentiate between a good loop, proper ferroelectric and a non-ferroelectric loop.

So any measurement which shows rounding of hysteresis loop tip where ever you have lot of rounding at the tip or a very bloated kind of electric loop that are probably not a ferroelectric. It is may be ferroelectric at a lower temperature but certainly there are there is lot of leakage in the material which does not give you the intrinsic ferroelectric character. The intrinsic ferroelectric character must always result in this kind of loop.

You must of a saturation, and this is what we are striving for this what we want. We do not want the red ones and these black ones these are not good loops. And so as a result there is a need to make if you get this kind of loops there is a necessity of making temperature dependent measurement. Because at lower temperature the ohmic contribution will become lower as a result it might get saturation at lower temperature.

So temperature dependent measurements are the key. Then also dielectric constants for a good ferroelectric the dielectric constant you should measure should show a behavior like this. Low frequency will have some interfacial polarization but in the middle frequency range you should have a pretty flat region. A lot so this is the good dielectric measurements where you do not have where between the relaxation regions dielectric constant is frequency sort of independent or sort of a poor quality of material would be like this something like this.

So your dielectric constant varies as a function of frequency. Now this poses lots of challenges in terms of measuring that two dielectric constant which means because your dielectric constant is vary other function of frequency which means the other factors which are contributing to dielectric constant and those are the factors could be defects. Generally, defects are identified from grain boundaries or oxidant vacancies or point defects.

They contribute to dielectric constant themselves polarization as a result you have frequency dependent and that is where you need to do what we call as you need to do impedance analysis impedance spectroscopy to ensure the distinction between resistive and capacitive components. Now ohmic components non ohmic components and you need to model the ferroelectric on the basis dielectric and ferroelectrics appropriately so that you can get the real capacitance and from that you can estimate what is the real dielectric constant.

You cannot calculate the dielectric constant from this measurement. You have to do the impedance spectroscopy to separate out the resistive and capacitive contribution to calculate the real dielectric constant. If anybody does that in the literature it is purely wrong measurement it is not a right way to report the data and then you can also do AC leakage measurements.

So frequency dependent I-V measurement so JE measurements and there also people do I versus T measurements or P versus T measurement that is time difference stability of polarization and current. These are all also very important measurements for various applications where for a ferroelectric you should not see a decay in the polarization and the function of time. If you have a memory for example the memory should not lose it charge as a function of time.

So that is where we make these time dependent measurements and finally if you are making memory then we what we call as what we make as a fatigue measurement where you switch the ferroelectric for more than. So if you apply pulse at ones at one cycle if you do it for million and billion of cycle it becomes fatigue measurements. And that is what you should do for ferroelectric which piezoelectric or ferroelectric which are going to be used for multiple times in various applications.

They are just few measurements the basic measurements you need to ensure that your electrode is of correct type generally a material with high volt function silver, gold or platinum. Better if you evaporated but even if you put in terms of liquid you must dry it quickly make sure that it does not percolate through the sample and make sure that you measure at its dimension correctly.

And that is why use of masks is very important and make sure sample thickness is uniform otherwise electric fields are not going to be uniform. As well as your sample dimensions are noted correctly. You can make DC measurements of leakage, you can make AC measurement of leakage, you can make ferroelectric measurement, dielectric measurements as well as impedance measurements time as well as temperature dependent and make sure when your ferroelectric when you are doing a ferroelectric work your hysteresis loop should be like this not like the one which are shown in sorry not like the ones which are shown in black and red.

They are not good ferroelectric. So we will stop here today and in the next class we will look at the application of ferroelectric, piezoelectric and pyroelectric before we finish this course.