Non - Metallic Materials

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Module - 10
Measurement of the mechanical electrical, thermal, magnetic and optical properties of non - metallic materials
Lecture - 54
Novel ferroic composites: Synthesis and measurement

Welcome to my course Non Metallic Materials and this is module number 10 measurement of mechanical electrical thermal magnetic and optical properties of non metallic materials. And this is lecture number 54 where I will be discussing a Novel ferroic composite its synthesis and measurement techniques.

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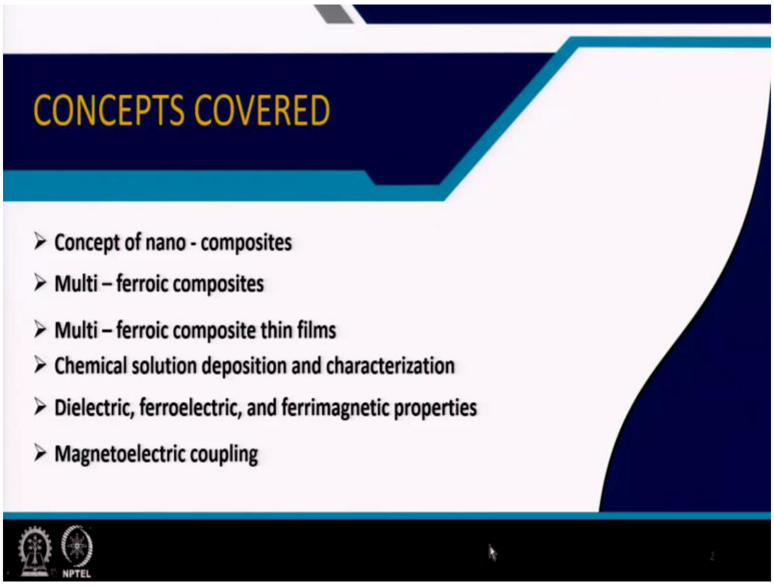

So, first we will talk about the concept of nano composites and then I will introduce multi ferroic composites which is relatively new field. Then multi ferroic composites thin film in particular we will be talking about and how to synthesize this films by chemical solution deposition and how exactly they are characterized that will be described.

And the dielectric, ferroelectric, ferrimagnetic properties of this composite films will be described. And finally how to measure the magnetoelectric coupling that will be described.

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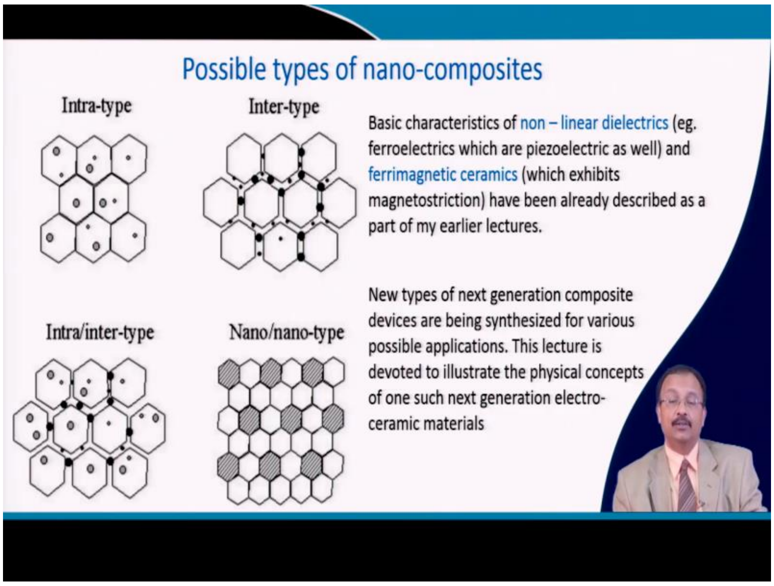

As you can understand that we will be talking about the composite material already we introduce the concept of composite the and the polymer; composite polymer ceramic ceramic ceramic composites metal ceramics composite they have introduced part of other lectures in my earlier lectures.

But these are nano composite where either the both grains of the material guest and host material they are in the form of nano crystal in size less than 100 nano meter or at least 1 of them are in this particular dimension. So, you can have four different types of nano composite the first one that is intra type where the guest nano particles are embedded in the host.

It can be intertype where this guest are deposited in the grain boundary region and both intra and inter type where as you can see there in the in the grain boundary as well as inside the grain. And then finally nano nano type, so one of the guest and host alternate or either well distribute or most of the cases there will distribute otherwise if they agglomerate they will form they will not form nano composites so they are well homogeneously distribute in the guest matrix.

So, the basic characteristics of the non-linear dielectrics that is ferroelectric that already I have talked about. So, this ferroelectric material they are piezoelectric as well and also we talked about ferro ferrimagnetic ceramics which usually exhibits a property like magnetostriction so that also I have described part of my earlier lectures. Now, it is quite relevant to make a composite of this exotic materials. So, for example, if I can make a composite of a piezoelectric material with a ferrimagnetic material whether it is possible.

If yes, if it is possible then what kind of special property we will get out of it. So, that is the part of the discussion of this particular lecture. So, it is a new generation of composite device that basically are synthesize for various possible applications. So, in this particular lecture we are devote our self we devoted to illustrate the physical concept of such electro ceramic material and where exactly they can be used.

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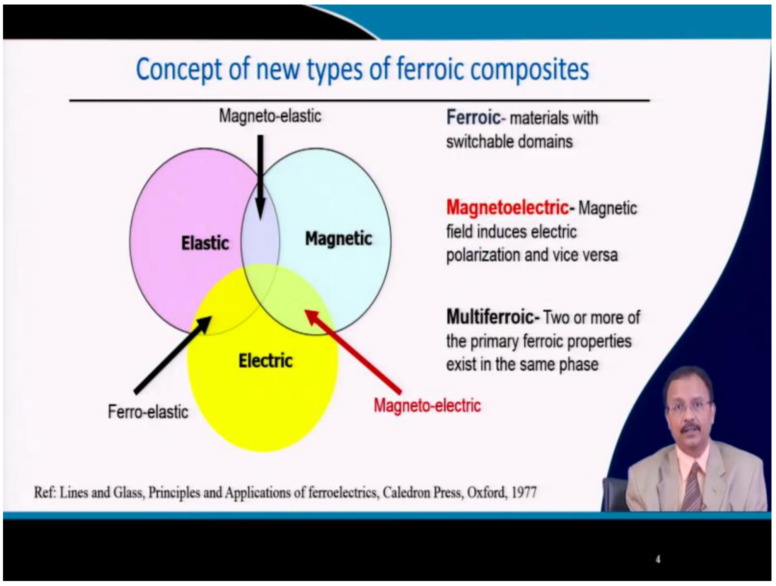

So, if you see the ferroic material which is having a domain structure. So, ferroic material they have a switchable domain structure. So, it could be ferroelastic in nature where with the application of force you can switch the polarization. And all ferroelectric material in fact they are ferroelastic also. And you have the ferrimagnetic or ferromagnetic material we are more interested in ferrimagnetic material which are ceramic type magnets.

So, and then we have a polarization switchable ferroelectric material. So, this ferroelastic material if I can make a composite of the ferrimagnetic material then they can offer the so called multiferroic properties. So, two different types of domain structure in a single material so that is why it is multiferroic in nature. So, as you can see this combination of elastic and magnetic that can generate a magneto elastic effect simply electric and elastic ferroelastic effect that is already there in a ferroelectric material.

And this polarization and magnetization this cross breed region it is called magnetoelectric coupling. So, this is important to consider in the composite form whether this multiferroic nature we can just adopt to make certain exotic devices so.

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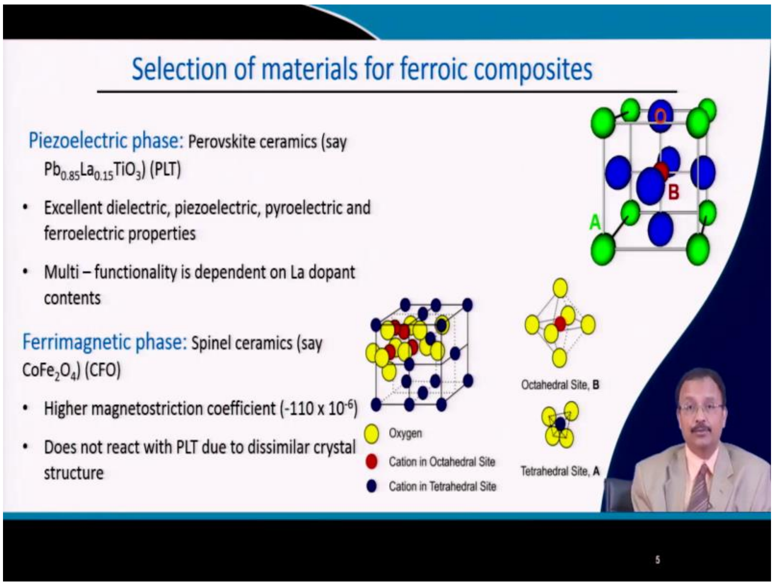

One example can be given that is ferroelectric in nature so you know that a b o three type of material particularly lead titanate is a ferroelectric is a well known ferroelectric material and it is doped with lanthanum. So, lanthanum is in plus three valence state which is replacing mostly plus two lead but it has a probability to go to titanate side also.

So, from your defect chemistry you can understand that a lanthanum can act as a donor dopant if it replaces lead and it can also act as an accepted dopant if it replaces four valent titanium. So, depending on that it can create cation vacancy it can create anion vacancy oxygen vacancy. So, this vacancy creation that actually have a major influence in controlling its ferroelectric property.

So, actually this lanthanum dope lead titanate they exhibit excellent dielectric properties you know that all ferroelectrics are dielectric it also exhibits a good piezoelectric coefficients pyroelectric coefficients and of course, they are good ferroelectric material. And also I have not talked about it, but these are good electro optic material whether where by the application of electric field you can change its refractive index it changes by (Refer Time: 08:47).

So, it is a multifunctional material by itself so it is quite interesting to make a composite of this lead lanthanum titanate with another interesting material which is a ferrimagnetic cobalt iron oxide. We also talked about this material you know that it's having a spinel structure and by this time you know what is spinel what is inverse spinel; so cobalt iron oxide is an inverse spinel structured material and it exhibits a very high magnetostriction.

You know what is magnetostriction when magnetic field is applied then the dimension of this material changes and its having a high magnetostrictive coefficient about 100 minus 100 10 to the power minus 10 to the power 6 order so it is quite large minus 100 10 into 10 to the power minus 6 is a quite large value. So, this magnetostrictive material can be chosen for this kind of composite.

So, they are two dissimilar material and as you understand that when you mix it together it can form a compound it can form a solid solution or it can form a composite. So, in this case since the crystal structures are very different one is perovskite and one is spinel then actually they do not react to form a compound. So, it remains a dissimilar kind of structure.

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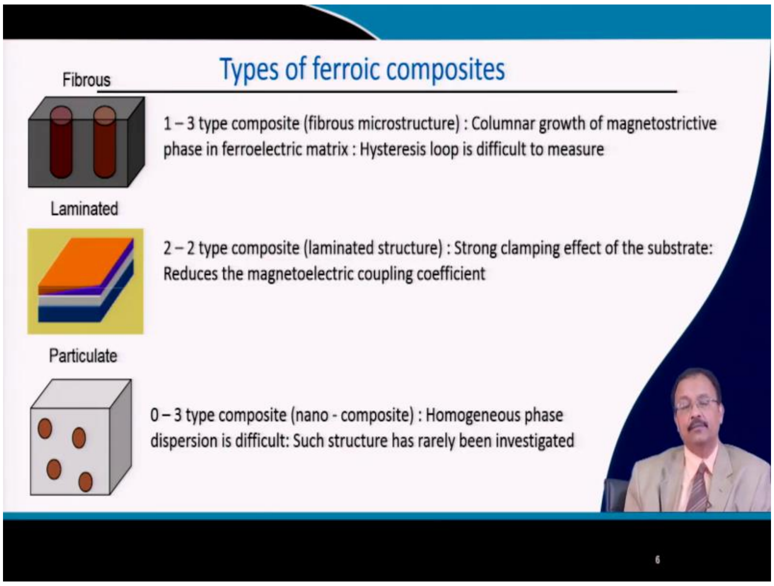

So, this distribution of one phase into the other that could be a various types and various different types of composite is possible. The three prominent examples are 1 -3 composite. So, here 1 is the dispersed phase which is in the form of a fiber as you can see and 3 is a three dimensional structure. So, that is why it is a 1 - 3 type of composite so it is having a fibrous microstructure.

So, it is possible a magnetostrictive material that can have a columnar kind of growth in a ferroelectric matrix, but you know that this phase is having relatively higher conductivity as compared to the ferroelectric material. So, if you deposit two electrode here and try to measure its hysteresis loop it is problematic because these are conducting in nature so that is not very attractive.

So, 2 - 2 composite can be done as the name suggest it is a multilayer kind of structure. So, in case of multilayer kind of structure there is a strong coupling between the substrate and the film and that will eventually reduce the magnetoelectric coupling because of the substrate constrained so that is also not a good idea to grow this kind of composite.

So, another type which is quite interesting is nanoparticle which is dispersed in a 3 dimensional matrix. So, we call this is a 0 - 3 kind of composite and here the challenge lies that to disperse homogeneously this 0 phase in a 3 dimensional lattice, but this kind of composite as per as this multiferroic composite is concerned this is relatively less studied. So, few reports you can find in the literature of this kind of composite. So, therefore, this is needed to be studied in a bit details.

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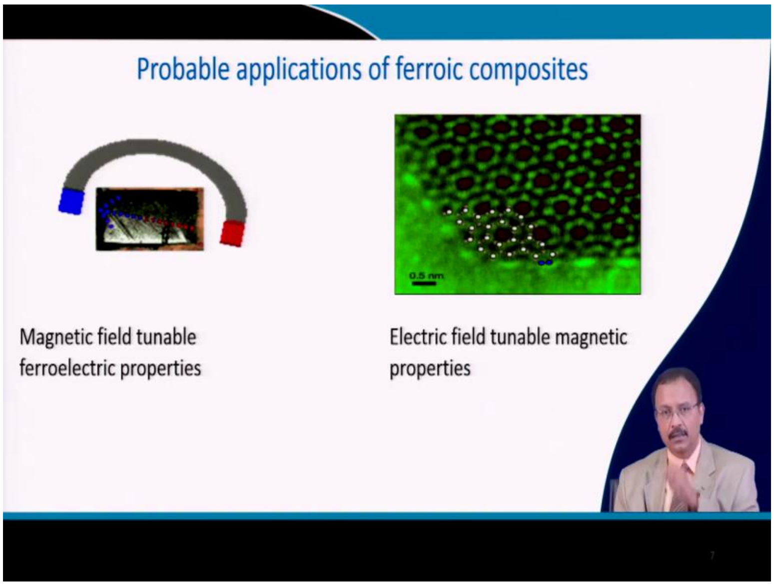

So, the probable applications this is not yet in the market, but as you can understand you can tune a ferroelectric material by the application of a magnetic field. So, magnetic field can be used to polarize the material electrically. So, those kind of device that can be generated where magnetic field can tune the ferroelectric or dielectric property of this composite or vice versa electric field also can tune the magnetic property so that is also possible.

So, this various types of sensor and actuator types of device can be made if this material can be properly synthesized and characterized accordingly. So, that is also interesting for futuristic device application for this type of composites.

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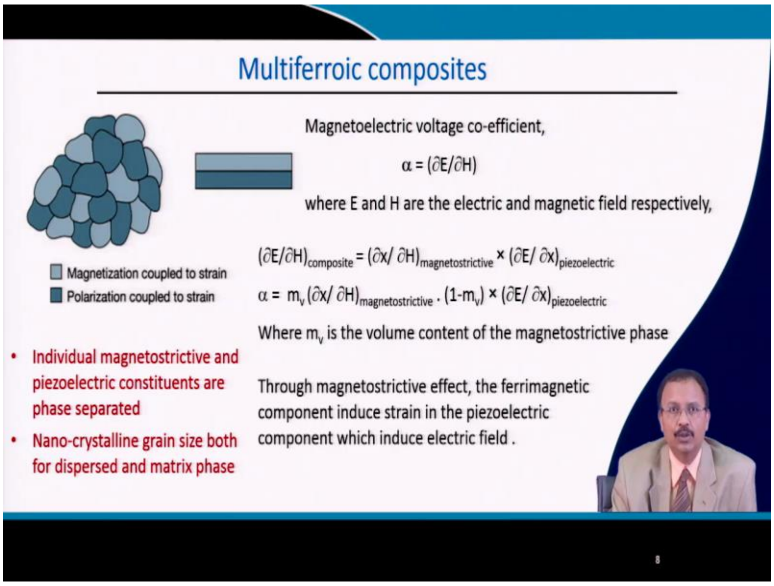

Now, if you consider this multiferroic composite either it can be a 0 - 3 composite where very homogeneously this magnetic ferrimagnetic component is dispersed in a ferroelectric media. Or it can be a multi layered film one after another you can deposit a ferroelectric film and ferrimagnetic film, but this clamping effect will be there.

So, this magnetoelectric coefficient how much interaction is there that is basically given by this relation which is denoted by alpha which is with the change in magnetic field how much voltage is generated in this material. This is quite unusual you are applying magnetic field and you are generating electric field out of this material.

So, this can be understood in a composite term that partial derivative of this electric field with respect to the magnetic field in the composite that you can write as del x by del H which is the magnetostrictive part. So, you know the magnetostrictive part you are applying the magnetic field and you are getting due to magnetostriction it is strain.

And this is the piezoelectric part this strain can induce electric field you know that when you apply a stress which is proportional to strain then eventually it generates electric field. So, this is a cross effect of this two different phase. So, this magnetoelectric voltage coefficient that is given by the fraction of the volume content of the magnetostrictive phase and remaining volume content of the piezoelectric phase and you can just measure the value of alpha.

So, what is happening here that, once you are applying a magnetic field in this composite then this ferrimagnetic material that will induced strain due to the magnetostrictive effect. Now, each of this ferrimagnetic grains are very strongly attached side by side with a piezoelectric grain.

So, this strain will induce voltage so, eventually due to this magnetoelectric coupling you are applying and magnetic field and you are getting the electric field out of this material which is quite interesting.

So, individually the magnetostrictive and piezoelectric constituents there should be phase separated right they should not have any interaction between them and there should not be a diffuseness in their boundary. So, they are sharp their boundary should be quite sharp and diffusion across the boundary phase with constituent cations or anions that will be detrimental for a strong magnetoelectric coupling.

So, what is eventually needed is a nano crystalline grain which are very individual nano crystalline reigns they are homogeneously distributed throughout the matrix. So, this is a nano nano kind of composite that is quite interesting to grow.

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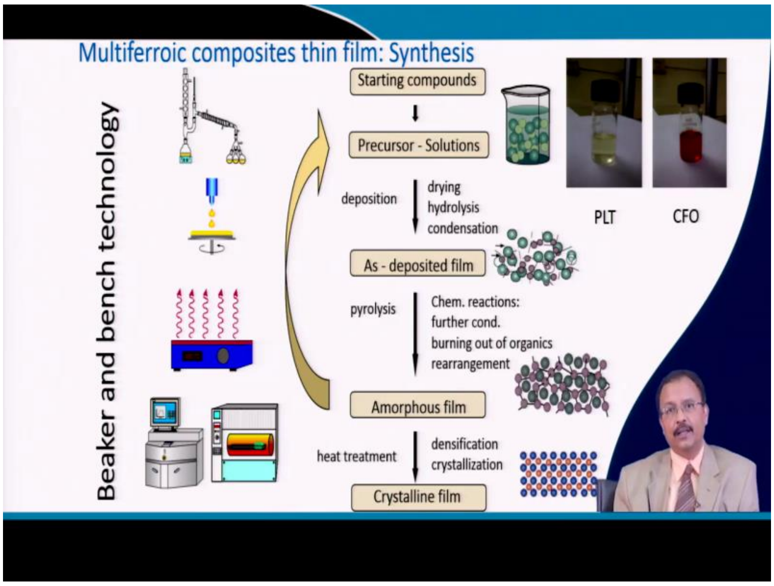

Now, for a bulk state one can make it by mixing these two things together, but it is already as I have mentioned that once you are talking about a device that you will have to make an integrated device which is integrated to silicon semiconducting silicon circuitry film. So, there it is quite important for you to grow it is in the thin film form. So, and integrate with the silicon silicon substrate underline silicon substrate.

So, thin film of this material will have to be made and the same chemical solution deposition that is usually used to make this kind of thin film where a precursor of individual lead lanthanum titanate that is one example I have cited and the ferrimagnetic cobalt iron oxide individually they are prepared by the chemistry root and then they are mixed together mixed together.

So, there is a molecular level mixing between this two precursor solved and then they are deposited by spin coating baked and then they are annealed. So, eventually they form the crystalline part. So, unlike a single component system now this ferrite and the ferroelectric part is mixed intimately together to form a nano composite.

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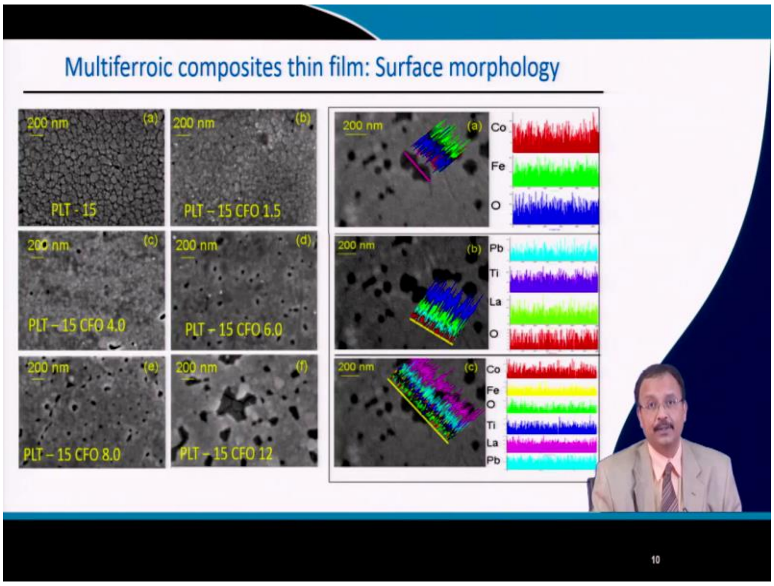

Now, if you see the actual photograph of this material. So, PLT film it is having very small grain size as you can see that and inside that this cobalt oxide grains are individually dispersed. So, for very small volume content you cannot readily identify it, but has progressively it increases from initially from 1.5 volume percent that is too small then 4 volume percent then 6 volume percent then 8 volume percent.

And once you go above 10 volume percent then you can start seeing the cobalt iron oxide they are pretty well distributed inside the matrix. So, how do you know that this one is cobalt iron oxide and this one is your ferroelectric material?

So, in order to do that I told you, I thought that by the way these are actual surface morphology of scanning electron microscopy of this composite film and then you can do the EDS analysis.

So, if you suspect that this one these two are from cobalt iron oxide then you do a line scan so here electron is showered and X ray is generated so constituent elements is carbon sorry cobalt iron and oxygen. So, you should get if you do the line scan here only this three elements. So, then you can confirm that this is indeed cobalt iron oxide.

Similarly, if you suspect that this is your matrix phase then you do a line scan on the matrix and you get lead titanium lanthanum oxygen. So, indeed then this one is your matrix and then indeed that this is matrix and these are disperse. So, you do a line scan the whole range so you get all the elements. So, that will tell you that whatever you are suspecting that this one is lead this one is lanthanum indeed it is true. So, that part is done first.

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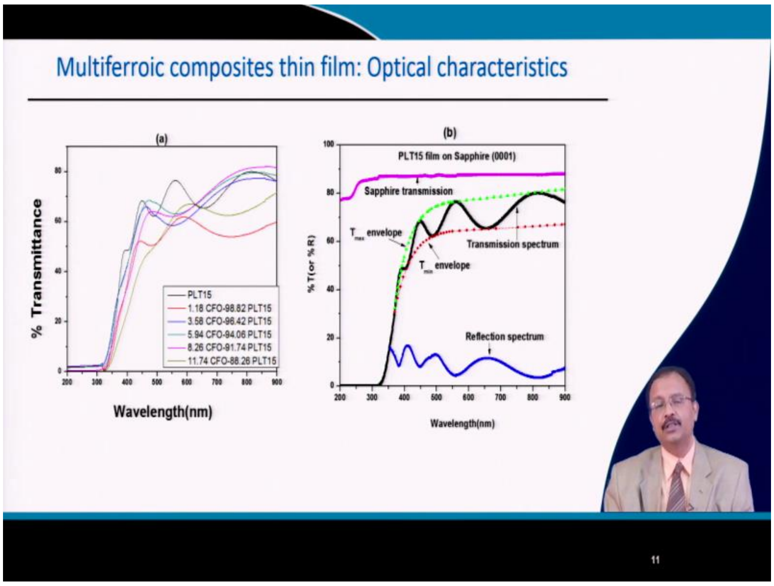

Then, we talked about the optical evaluation of the constant and already in one of my lectures I told you that once you have a relatively thicker film then it will have this interference pattern and this is the transmittance pattern from the film and which is less transmittance is a bit less from the deposited the substrate on which it is deposited which is sapphire.

And the reflectance spectra is exactly reverse you see that wherever the peak is there the crest is here and wherever the crest is here the peak is there so it is a perfect reflection spectra. And in fact this data are available this data are available if you get this original PPT and you click it and this will open an origin file.

And you will get the reflectance spectra R versus lambda you will get the T versus lambda and you can go ahead and do the calculation I mean I in one of the lectures I showed how you can get the extinction coefficient the refractive index the film thickness you can do, you can do that part for this particular film.

And the composite film will have different types of transmittance spectra for different volume content of CFO and that will if you analyze all the optical constant you can see how they can vary with the change in the CFO, for certain other application the optical based applications that is required. So, then this is required to be done to characterize the film.

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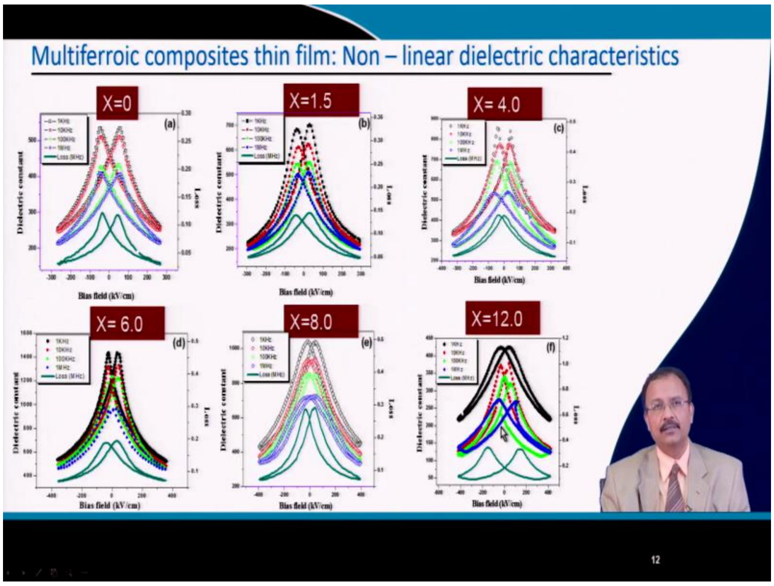

And then the third characterization which is important is non-linear dielectric characteristics you know the PLT is dielectric, but CFO is not a well known dielectric material. So, once you have start mixing it for a very high relatively high CFO content the non-linearity of the dielectric constant is a bit effected. And this is the well shift butterfly loop which is very characteristics to the ferroelectric nature because ferroelectric material they have reversible polarization.

So, if you measure the dielectric permittivity or dielectric constant as a function of a DC biased field then this butterfly field kind of loop that will tell you that indeed it is ferroelectric in nature. So, that needs to be characterized and not only the dielectric permittivity you see the loss tangent also exhibits this kind of butterfly loop so that exhibits the non-linear ferroelectric characteristics of this material.

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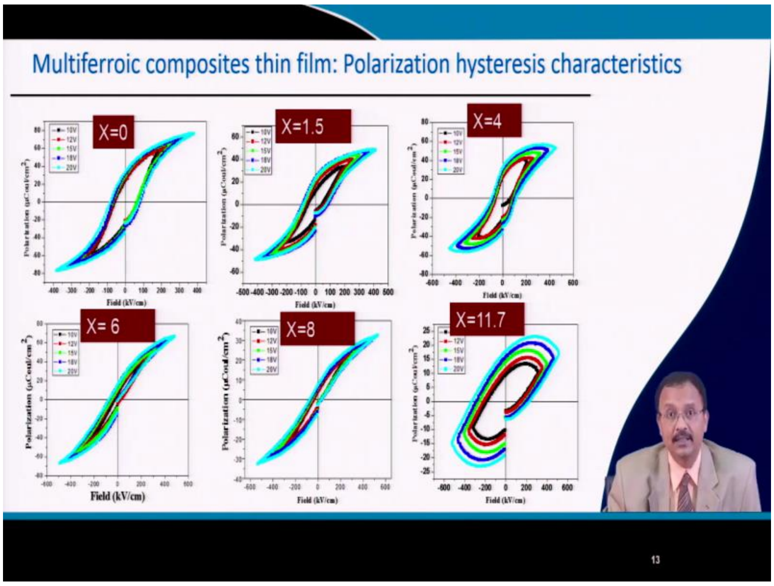

Then their hysteresis behavior also should be there. And as you can see pure material is nicely ferroelectric and already in the last lecture we talked about the ferroelectricity so they exhibit good ferroelectric loops and this each of this loop they are taken in progressively higher applied field. So, we call this is the nested hysteresis loop.

So, you get this kind of nice hysteresis, but as the content of CFO is increased and CFO is relatively higher conductivity then lead lanthanum titanate then the leaky nature of the loop is apparent when it crosses 10 volume percent or more. So, that is perfectly expected.

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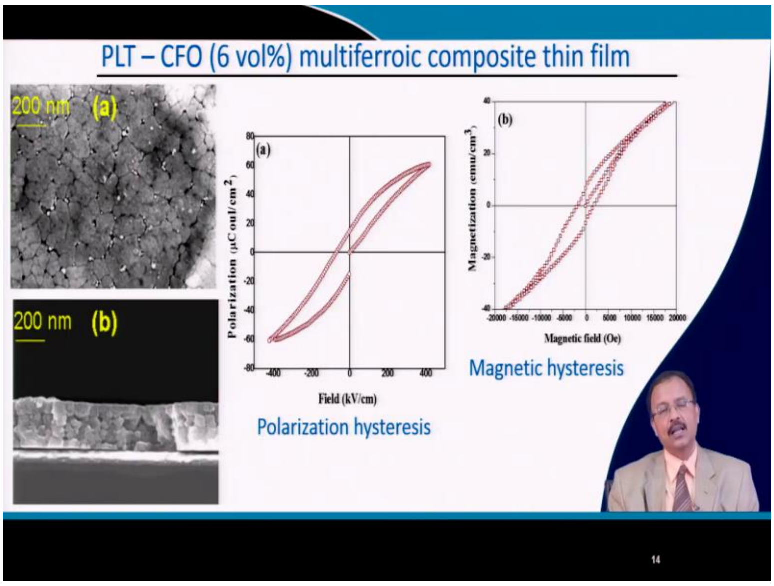

Then you would like to see that how uniform is this film. So, for that you will have to do a cross section this is the surface of the film which is analyzed by the scanning electron microscope once again. And you can see a good granular structure of lanthanum titanate and the dispersion very small dispersion and very homogeneous dispersion of cobalt iron oxide mostly along the grain boundary of this film.

And the cross section also you can see that it is a dense nature of the film and the film is having a substrate and then a layer of this diffusion barrier and then a conducting layer. So, you get a very uniform film which is typically about 350 nano meter thick and this thickness you can measure by scanning electron microscopy by the cross sectional analysis and also the optical trans fringe pattern of the transmittance spectra you can also measure it so and cross verify your thickness.

And this same composite you can see that it is exhibiting a ferroelectric behavior ferroelectric loop as well as ferrimagnetic loops. In the same phase it is ferroelectric and magnetic as well. So, your purpose is solved that the composite is exhibiting both polarization hysteresis and magnetization hysteresis characterize characteristics in the same phase.

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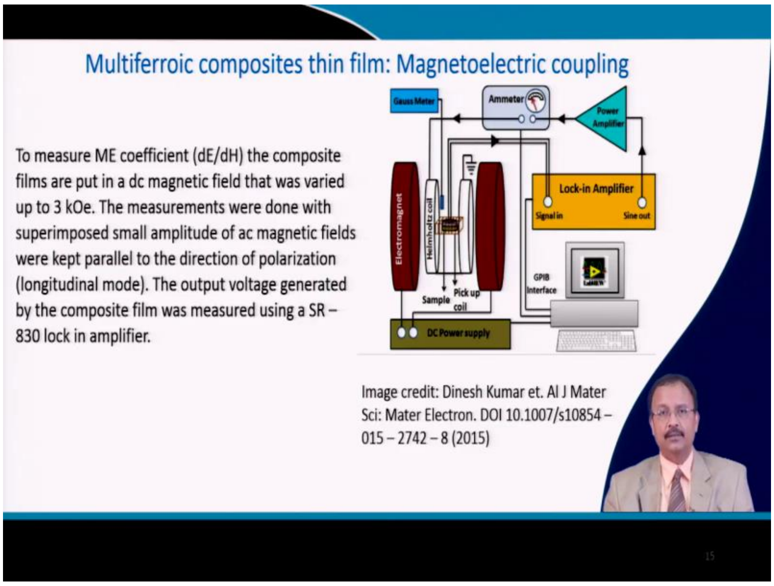

Now, you will have to measure the coupling coefficient between this polarization and magnetization behavior. So, no commercial device if I understand correctly is yet available except one company they have now this multiferroic magnetoelectric coupling measurement commercialize. But usually something similar that can be used which is which is used in this particular paper. So, they have used also something similar. So, the magnetic coupling coefficient is basically the d E by d H.

This is this composite is put a in a magnet where a DC magnetic field can be applied across. And the DC magnetic field can be varied in this particular case about 3 kilo ore state. For the film you need less field for the bulk composite you need more field and the measurement was done with a superimposed small amplitude of AC magnetic field as well through a Helmholtz coil.

So, it is basically a longitudinal kind of measurement. So, that magnetic field were kept parallel to the direction of the polarization in the longitudinal mode. So, you need to pool the composite the way I explained in my last lecture apply a DC field and pooled the film. And then the output voltage generated by the composite because of this action of magnetic field that was measured usually by a lock in amplifier.

So, this is the whole characteristics I mean the whole measurement setup that is needed to measure the magnetoelectric coupling.

In a simple form also you can use if you do not use this coupling coefficient measurement setup in the presence of a magnetic field you can also measure the hysteresis loop or the dielectric constant. But that will not you can see the change the application of magnetic field will change the polarization behavior or the non-linear dielectric characteristics, but actually coupling you cannot measure. So, for measurement of the coupling this is the setup that is basically used.

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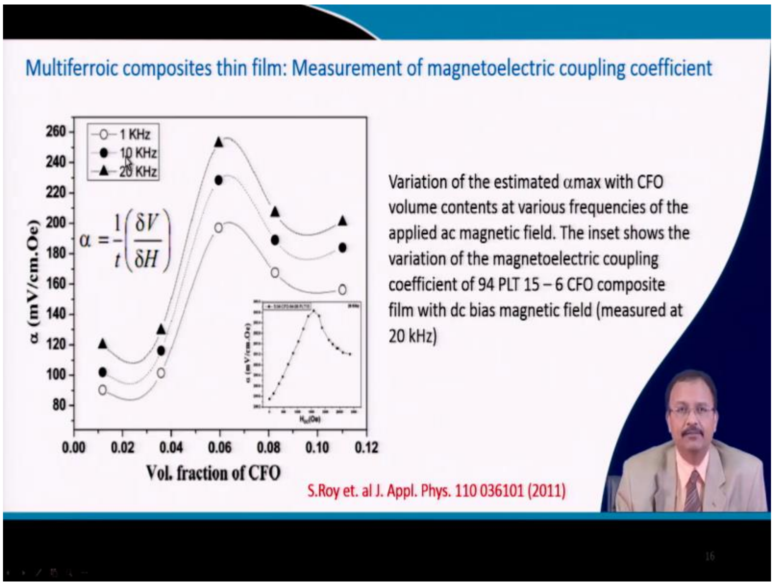

So, based on that this value of alpha that was measured, so you can change the frequency of the field that you are applying at different frequencies. And then this alpha you can measure or estimate from the measured voltage and the field the voltage and field this del V by del H and knowing the thickness of the film.

So, for this different CFO content you can see at one particular content you have the highest value of the alpha. So, this is the optimized composition for your composite film where the magnetoelectric coupling is maximum and roughly about 6 volume percent of the ferrimagnetic phase is sufficient for PLT lead lanthanum titanate type of ferroelectric to give you the maximum coupling coefficient, so that is one example.

And this two things this ferroelectric thin film and multiferroic I decided to include this in this lecture; because my group my research group has and personally I am myself as a student we did lot of research on this. So, this whole study was a part of the results of one of my PhD students. So, I decided that I should introduce this exotic field to this particular course.

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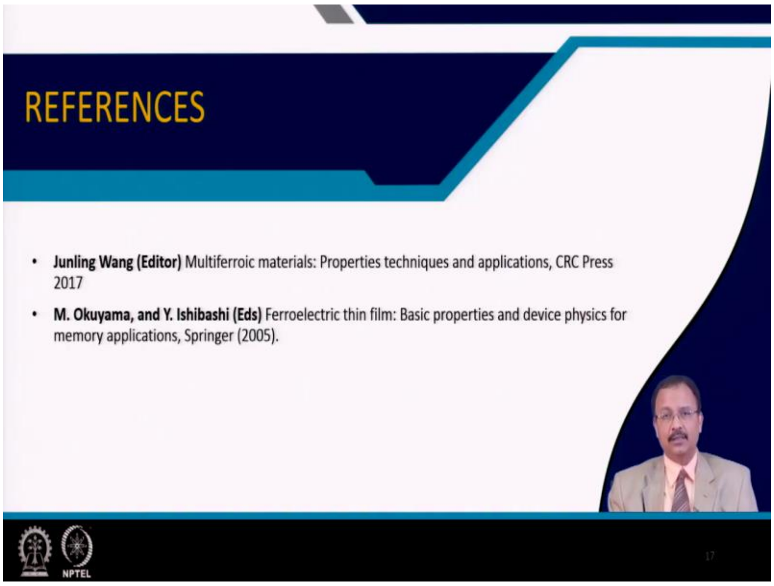

So, there are two good books which you can study if you are particular interested in multiferroic materials one is by the Wang the he is the editor of this book so series of papers are there and the other book on ferroelectric thin film memory that also talks about the concept of multiferroic composites.

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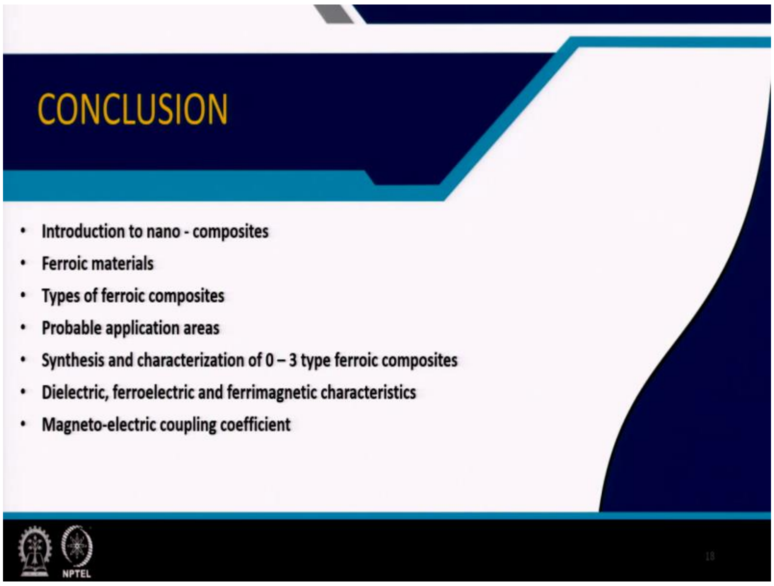

So, in this particular lecture we talked about the nanocomposite then we talked about the ferroic materials in general, then types of ferroic materials, the probable application areas, then synthesis and characterization of particularly 0 - 3 type of ferroic composites and their dielectric ferroelectric and ferrimagnetic characteristics and finally, the magnetoelectric coupling coefficient.

Thank you for your interest.