Fundamentals and Applications of Dielectric Ceramics
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Lecture – 29
Pyroelectric Effect and Electrostriction

So, welcome again to the new lecture of this course; fundamentals and applications of dielectric ceramics, so let us just briefly recap what we did in the last class.

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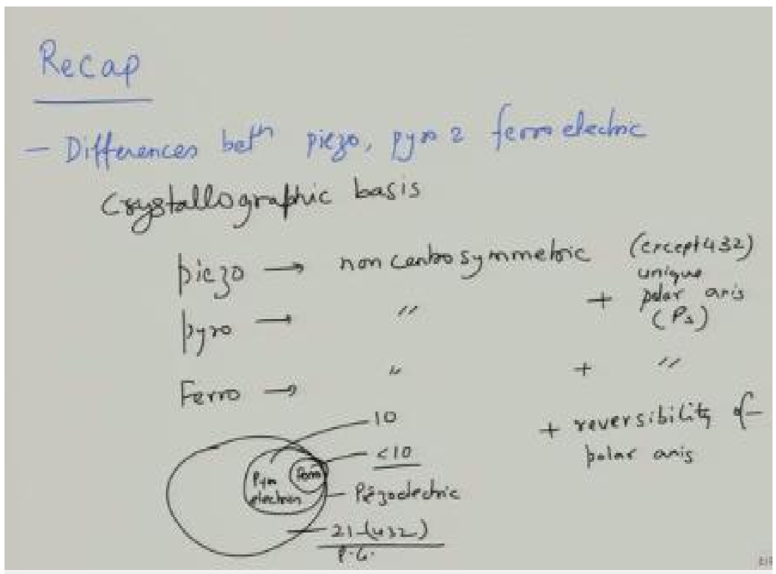

So, in the last class we looked at the differences between piezo electrics and; piezo, pyro and ferro electrics and the underlying basis was crystallographic basis, so as we said that piezo electric material is something which is non-centro symmetric except 432, all the non-centro symmetric point groups are piezo electric and pyro electrics are those which are non-centro symmetric plus they have a unique polar axis.

As a result, they have a spontaneous polarisation and then ferro electrics are which are non-centro symmetric plus unique polar axis plus reversibility of polar axis. So, as a result you know, you can look at the Venn diagram, where piezo electric is the biggest class of non-centro symmetric materials, some of the piezo electric are also pyro electrics and some of the pyro electrics are ferro electrics.

So, ferroelectrics is the most restrictive class of materials, so out of these 21 except 432 that is the point group which are non-centro symmetric , so 21 PG is except 432 and then here you have 10 of them and here less than 10. So, this is what we did and we also looked at the piezoelectric tensor.

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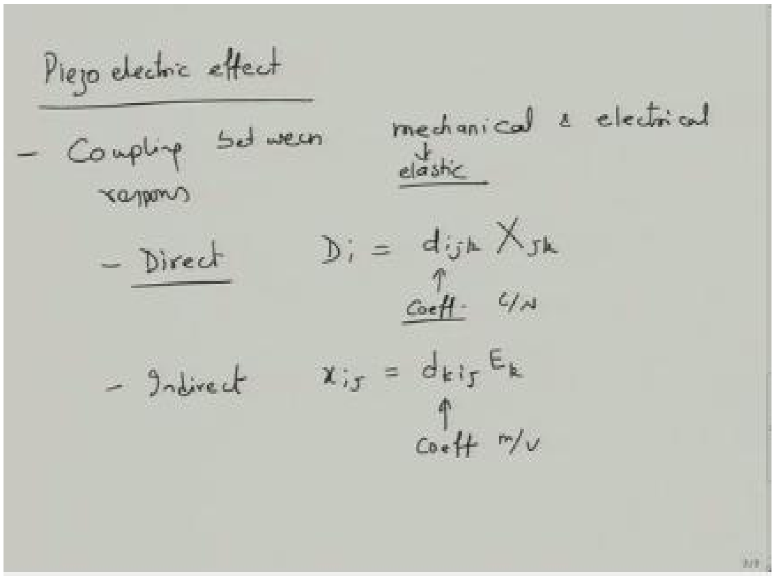

So, piezoelectric effect is basically, coupling between mechanical and electrical response, so by mechanical we mean it is mostly elastic in nature, it is elastic in nature and this is; so we have a direct piezoelectric effect. In direct piezoelectric effect, you have charge density produced as an outcome of applied stress, so this is the direct piezoelectric coefficient whose units are in C/N.

And then we have indirect effect, where we relate the strain with respect to d_{kij} and your stimuli is basically electric field and this is your indirect coefficient, which is the essentially in m/V.

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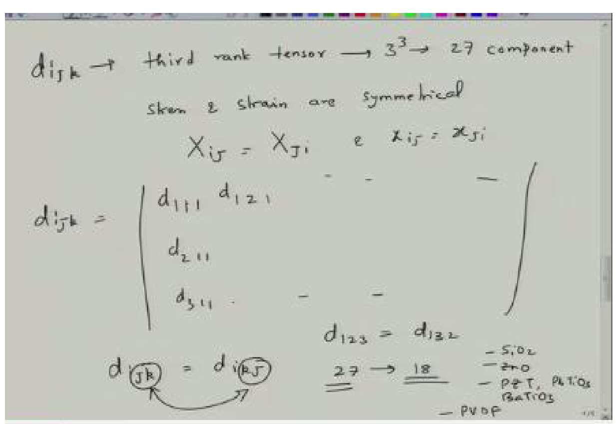

So now if you look at this d_{ijk}, this is the third rank tensor, or third rank tensor will have 3^3 which means 27 components but since we know that stress and strain are symmetrical tensors, so as a result you have:

$$X_{ij} = X_{ji}$$

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So, as a result when you expand it, so d_{ij} can be expanded in the form of metrics as:

$$d_{ijk} = \begin{vmatrix} d_{111} & d_{121} & .... \\ d_{211} & .... & .... \\ d_{311} & .... & .... \end{vmatrix}$$

if you have d_{ijk}, this will be equivalent to the d_{ikj}. So, as a result because of this correlation between the stress and strain, you will reduce the number of components to; so basically, something like d_{123} will be equal to d_{132}.

So we can say that total number of components reduced from 27 to 18, so this is what and they can further be reduce by crystal symmetry depending upon the type of crystal and so on and so forth, so essentially, and we also looked at the examples of materials, so examples such as you know silicon oxide is the best known; one of the best known and simple piezoelectric.

Then, you also have zinc oxide, then you know materials which are ferroelectric will always; so things like PZT, or $PbTiO_3$ or $BaTiO_3$, these are all ferroelectric which are naturally piezoelectric and then of course, polymeric materials like PVDF, polyvinylidene fluoride, CH_2-CF_2, based materials, they are also piezo electric in nature by the virtue of being ferroelectric in nature.

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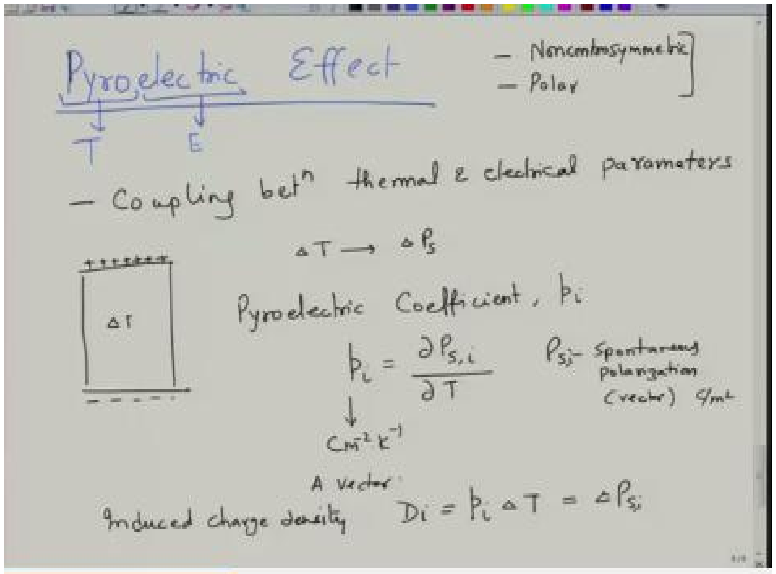

Now, let us move towards what we call as pyroelectric materials; pyroelectric effects, so pyro electric effect as we say that basically, pyro means this term, pyro will mean it is related to temperature and electric will mean it is related to electric field, so basically, pyro electric effect is nothing but coupling between thermal and electrical parameters. So, as we said that the requirement for a pyroelectric material that should be non-centro symmetric and it has a polarisation.

So, when this pyroelectric material is subjected to a temperature difference ΔT, as a result it has certain charge density change in, you can say since it is polar it will always have charge density, but as you change the temperature, there is a change in charge density, so when you apply a gradient ΔT, which means it results in change in ΔP_s, so change in the P_s which is ΔP_s.

And this ΔPs is nothing but the you can say surface charge density that you have induced as a result of making temperature change, so we can correlate value called as pyroelectric coefficient which relates as:

$$p_i = \frac{\partial P_{s,i}}{\partial T}$$

where P_s is the spontaneous polarisation.

And we know that it is a vector, it has a unit of C/m^2, so as a result, p_i will have unit of $C/(m^2.K)$ and this is also a vector. Now, alternatively you can also write that induced charge density let us say D_i, this is related as:

$$D_i = p_i \Delta T = \Delta P_{s,i}$$

change in the spontaneous correlation that you observe upon P_{si}, upon applying a thermal gradient.

So, these materials as we said, they are non-centro symmetric necessarily, non-centro symmetric and necessarily, polar. So, basically all the ferroelectric materials are pyroelectric materials and most of the commercially available pyroelectric materials are nothing but ferroelectrics themselves.

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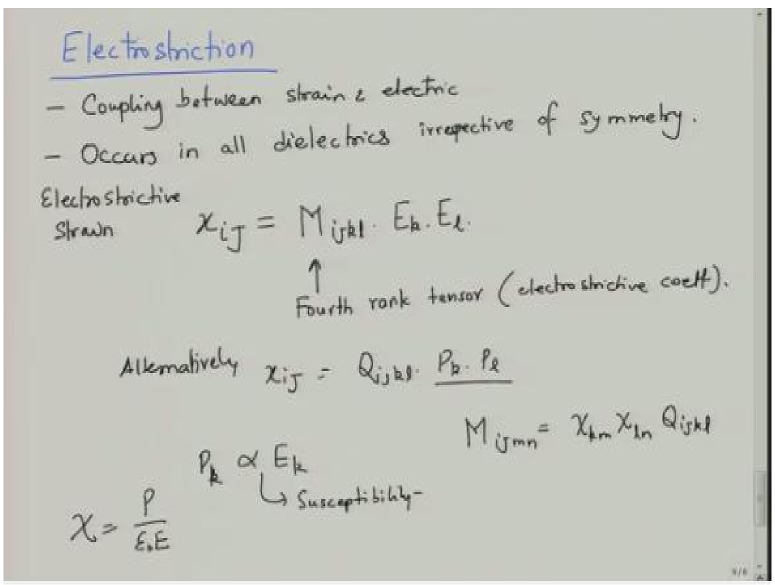

So, now let us move to another effect which is which may be which you must know is called as electrostriction, electrostriction is very much similar to piezoelectric effect except that electrostriction; and it is basically, you can say coupling between the electrostriction, to coupling between you can say its strain and electric field, same as piezoelectric effect except that piezo electric effect occurs in non-centro symmetric materials.

Whereas, electrostriction occurs in all dielectric materials irrespective of symmetry, so it is an effect that occurs in all dielectrics irrespective of symmetry, so this is where when you make piezoelectric measurement, it is important to distinguish between what you are seeing as an electrostrictive effect and the purely piezoelectric effect and this; so the electrostrictive strain that is generated by applying an electric field is depicted as x_{ij}, this is electrostrictive strain.

This is depicted as x_{ij} is equal to:

$$x_{ij} = M_{ijkl}.E_k.E_l$$

so you can see that M_{ijkl} is the fourth rank tensor and concerned open and the this is basically, electrostrictive coefficient. So, you can also write in terms of polarisation, so we know that polarisation is related to electric field by susceptibility:

$$P_k \propto E_k$$

So, if you can do that transform then, alternatively we can say x_{ij} can be written as:

$$x_{ij} = Q_{ijkl}.P_k.P_l$$

where P_k and P_l are the polarisation vectors, so instead writing in terms of electric filed vectors, you can also write them in terms of polarisation vectors and these polarisation vectors are related to electric field by susceptibility, because we know that susceptibility is nothing but:

$$\chi = \frac{P}{\varepsilon_0 E}$$

So, basically the proportionality constant will be susceptibility, so we can sort of write this as:

$$M_{ijmn} = x_{km}.x_{\ln}.Q_{ijkl}$$

so this will be electrostrictive effect, so we are not going to get into details of electrostriction but basically, it is something which is present in all the materials and it can be present in addition to piezoelectric effect on the materials.

And sometimes, piezoelectric effect and ferroelectrics may also be interpreted; may also be explained as sort of electro restriction which is based on spontaneous polarisation, so there is a possibility that polarisation that is present in the material that gives rise to electrostriction which is manifested in the form of piezoelectric effect.

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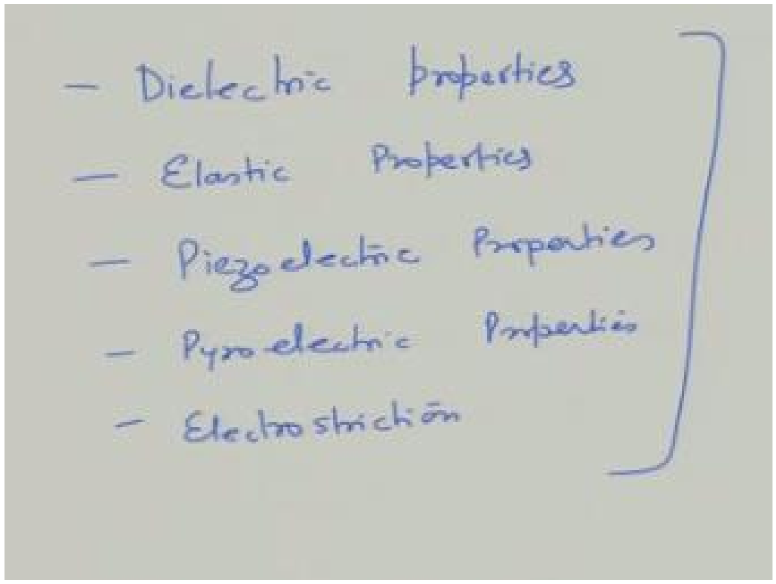

So, this is basically a brief introduction to the tensor notation of these typical properties, which are so what we have looked is; looked at is; we have looked at dielectric properties, we have looked at elastic properties and we have looked at piezoelectric properties and we have looked at pyroelectric properties and finally we have done electrostriction. So, these are all basically, vectorial, tensorial properties which are related to the stimuli which could be you know stress or it could be the electric field, it could be ΔT; temperature difference.

So, basically we have this proportionality parameters which are in the form of stiffness in the form of susceptibility, in the form of piezoelectric coefficient, in the form of pyroelectric coefficient or in the form of electrostriction coefficient, which all are you know, second rank, third rank, or fourth rank tensors depending upon the properties we correlate. Now, let us do a little bit analysis of these properties in terms of thermodynamics.

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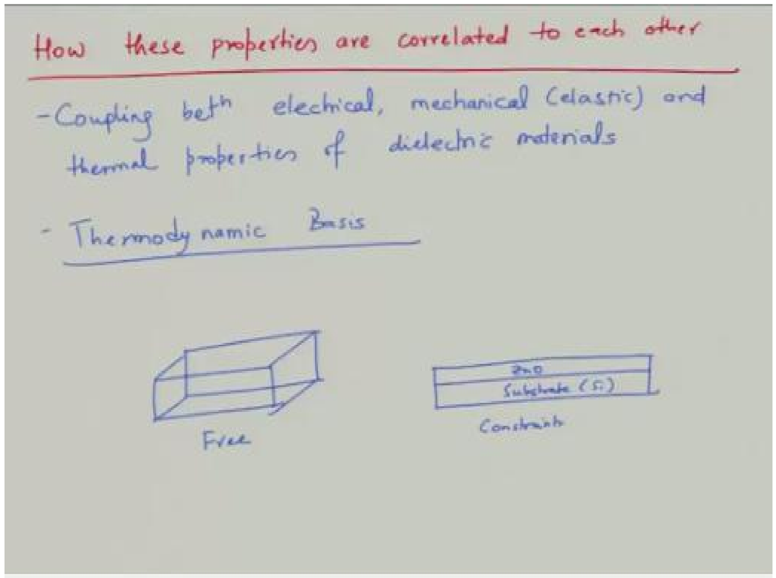

So, basically what we want to now look at is how these properties are correlated to each other because we have seen you know when you have a thermal gradient, you have a polarisation change, change in polarisation will change to change in the electric field. As a result, you will have; you may have strain, so you know all these thermal properties, electrical properties, elastic property they are all correlated to each other.

So, we must understand the coupling between these properties, so coupling between electrical, mechanical and by mechanical we mean elastic and thermal and for this, we will establish what we call as the first thermodynamic basis. For example in a piezoelectric effect, you have direct piezoelectric effect, when you apply stress and you get a response in terms of change in; we can have polarisation for example, induced polarisation.

Similarly, in the converse effect when you apply electric field, you will get strain, and this and then you have pyroelectric materials when you apply ΔT, you get ΔP, which is nothing but D and it is important because these properties are correlated to each other, we need to evolve formalism, so that they are useful in making us understand how experimental determination has to be done.

So, for example, let us say you make piezoelectric effect material for a free material, free material means, it is ready to expand, contract in other directions freely, there is no external constraint on it but let us say, so this is a free material but let us say you have a material in this form, you have a substrate which is let us say silicon.

On the silicon, we have put a layer of let us say, zinc oxide, now in this case, this becomes a constraint media, because the strain in the thin film is going to arise as a result of clamping with the substrate because they are atomically bonded with respect to each other. So, in this case when you apply electric field, you have a strains of different kind, they are all free strains.

Whereas, the strains that are generated in this case are going to be determined by boundary conditions, how the material is clamped with respect to substrates, so as a result it is important to understand the effect of various variables on the calculation of these parameters, so that we exactly decouple various effects for example, whether the piezoelectric strain is because of stress only or is it also because of does it also have a contribution from substrate inducer strain or because of difference in coefficient thermal expansion between film and the substrate and so on and so forth.

So, basically you would like to decouple these effects and to decouple these effects and understand them and also it also allows you to choose parameters, which parameters to allow which parameters to; which parameters can be allow to change and which parameter should be kept constant. So, that is what it helps us to determine a formalism in terms of let us say.

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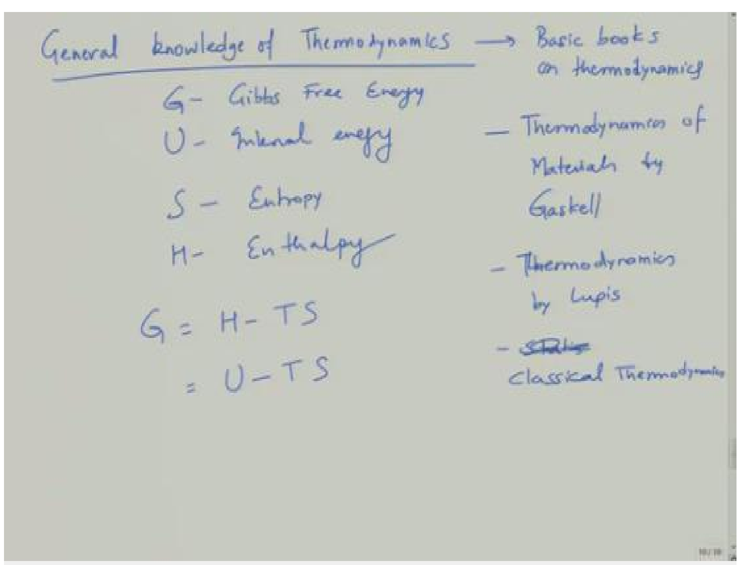

So, basically these are all thermodynamic expressions. We assume that you were aware of terms such as G, which is Gibbs free energy, U is given as internal energy, S is given as entropy and H is given as enthalpy, these are certain thermodynamics parameters and we all know that you know:

$$G = H - TS = U - TS$$

depending upon where you are looking at constant pressure or constant volume.

So, you can have various scenario but we are not going to do thermodynamics discussions hoping that you know, if you do not know thermodynamics, then you should go to any basic books on thermodynamics, there are plenty of books, for example you can read this *Thermodynamics of materials by Gaskell*, there is a book by *Thermodynamics by Lupis*, then you can also look at some classical thermodynamics.

So, thermodynamics of materials is slightly different as compared to thermodynamics of mechanical systems like engines etc., so but the terminology remains the same, so concepts of entropy free energy, enthalpy that remains the same. So, you can go through any basic books on thermodynamics, if you are not aware of thermodynamical parameters. So, let us say, so thermodynamics have three laws as we know first law of thermodynamics, second law of thermodynamics and third law of thermodynamics.

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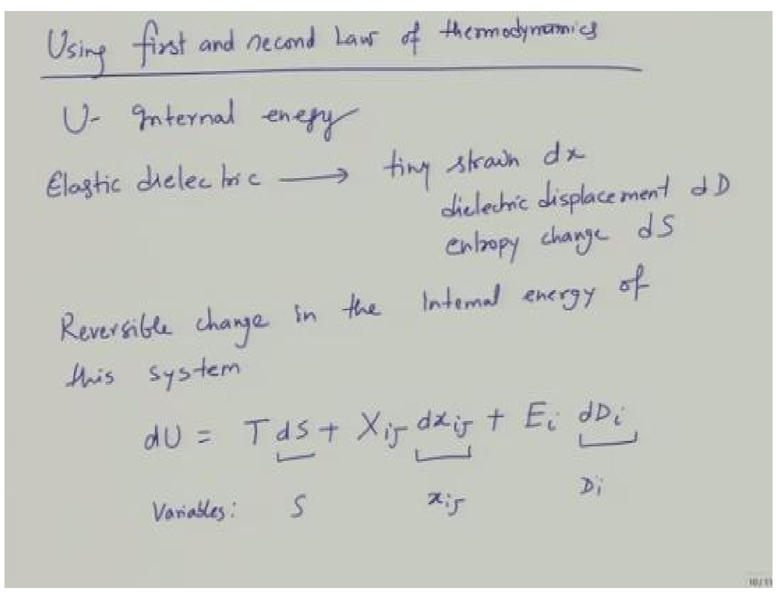

So, using the; using first and second law of thermodynamics, we can write that reversible, let us say U is internal energy, so you have consider a; so you have a elastic dielectric, which is subjected to let us say tiny strain, if it experiences a tiny strain let us say dx, it experiences the dielectric displacement dD, and as a result and it also has a change in entropy which is dS, so for such a system, the change in the; reversible change in the; so we can write the reversible change in the internal energy of this system can be written as dU is:

$$dU = TdS + X_{ij}dx_{ij} + E_i dD_i$$

So, x_{ij} is the strain, dD_i is the change in the directive displacement and dS is a change in the entropy where T is the temperature, capital X_{ij} is the stress and E_i is the electric field, so most of our measurements as we see although, we make temperature dependent measurements but the at each temperature, certain measurements are made, so most of the measurement that we make electrical measurements or directive measurements, they are all isothermal in nature.

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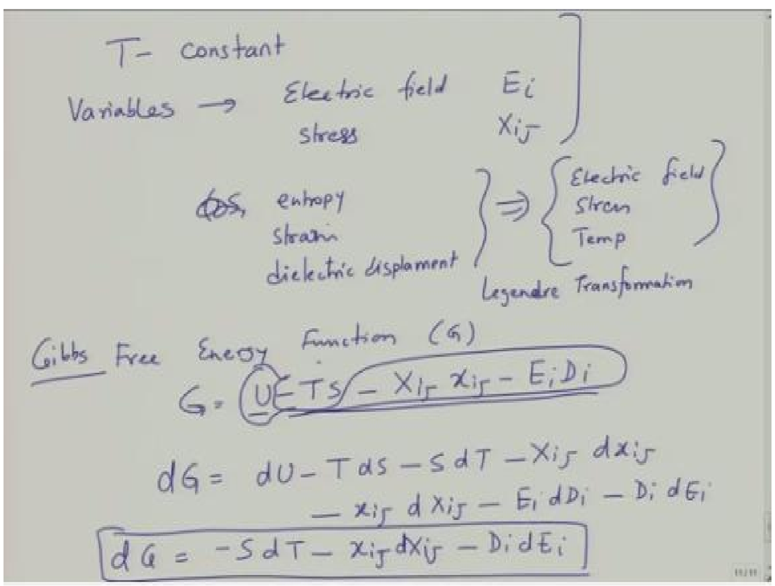

So temperature is generally kept as constant, whereas other variables are you can have electric field or you might apply change in stress, these are all; these are the variables that you; these are the parameters that you independently vary, so as a result by independent variables that we have in the first, so in this case the first slide, the independent variables is; so what are the variables here; the independent variables are S, x_{ij} and D_i.

But however since the measurements are made in the form of by keeping electric field as a variable or a stress as the variable, temperature is kept constant but it can also be variable, so we generally make our measurements in this fashion, we would like to change these parameters, so right now we have a set of parameters entropy, strain and dielectric displacement, we would like to transform them to electric field, stress and temperature.

And these are all related to each other, so they are not sort of independent of each other, so for this what we call as we make a transformation in the thermodynamic parameters and this is basically done by what we call as legendre transformation, so legendre transformation which; if you have done basic engineering mathematics, you would know what legendre transformation is, so as a result, when you apply this transformation that free energy function; free energy is G, basically, Giffs free energy function can be written as:

$$G = U - TS - X_{ij}x_{ij} - E_iD_i$$

This is capital G now, if you want to look at the differential of G that is the free energy change, so dG will be equal to:

$$dG = dU - TdS - SdT - X_{ij}dx_{ij} - x_{ij}dX_{ij} - E_idD_i - D_idE_i$$

so this is the free energy function that we get in the form of all the parameters. So, we include this, U is the internal energy, and these are the terms which need to change in these are the thermodynamics changes.

So, basically S is the entropy term and you can take rest of the terms, this is the next term which is basically, the net internal energy you can say, so do the subtraction of dU, so when you subtract dU here, you will get rid of TdS, you will get rid of this term, dx_{ij} and you will get this:

$$dG = SdT - x_{ij}dX_{ij} - D_idE_i$$

This is what we will get in terms of the change in free energy, it is related to negative of SdT negative of x_{ij} differential of X_{ij}, negative of D_i multiplied by change in electric fields. So, now we have stated the change in free energy in the form of parameters that may vary and from this, we will calculated the properties independently, we will stop here.

What we have done is basically, we have looked the pyro electric properties in this lecture and also we have started the thermodynamic basis to understand the properties and before we get into material applications and some other features.