Fundamentals and Applications of Dielectric Ceramics
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Lecture – 30
Thermodynamics of Piezoelectric and Pyroelectric Materials

Welcome again to the new lecture of fundamentals and applications of dielectric ceramics, so let us just briefly see what we did in the last lecture.

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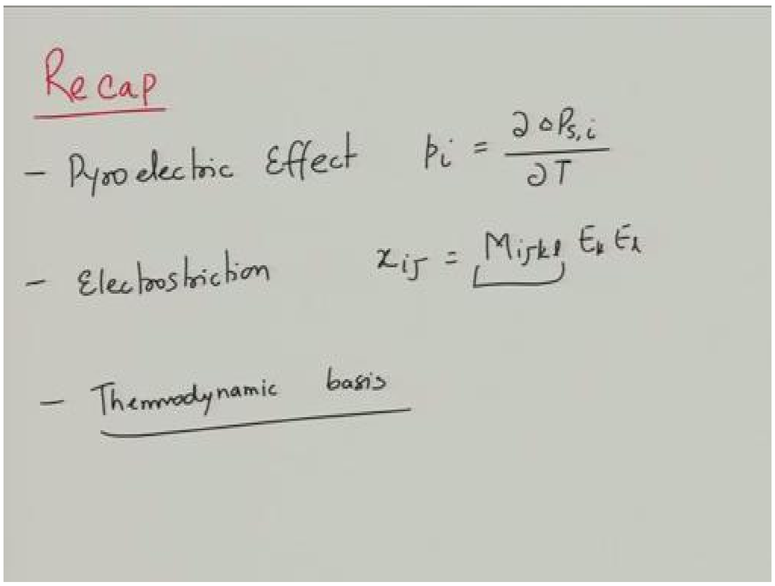

From the last lecture, we wrote equations in the vectorial form for pyroelectric effect, where we described quantity P_i which is nothing but change in spontaneous polarisation vector upon change in the temperature, so:

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

pyroelectric effect is very useful effect as we will see later on in terms of various applications and then we also looked at would we called as the electrostriction which is very similar to piezoelectric effect which again correlates the strain as:

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

So, this is again, change in the dimension or strain generated as a function of pyroelectric field, the proportionality constant is the electrostriction coefficient which is a fourth rank tensor and this is sort of related to piezoelectric effect, so but it is present in all the materials and respect to their symmetry, so even a piezo, non piezo electric material will show this effect, so that is why there is a distinction between the two.

Because one occurs in non-centro symmetric materials which is piezoelectric effect, whereas this effect purely occurs in the; this effect occurs in all sorts of materials and then we looked at; we started looking at the thermodynamic basis of how these properties are coupled to each other, and that is very important to understand if you want to make; if you want to evaluate them and make measurement in a correct fashion.

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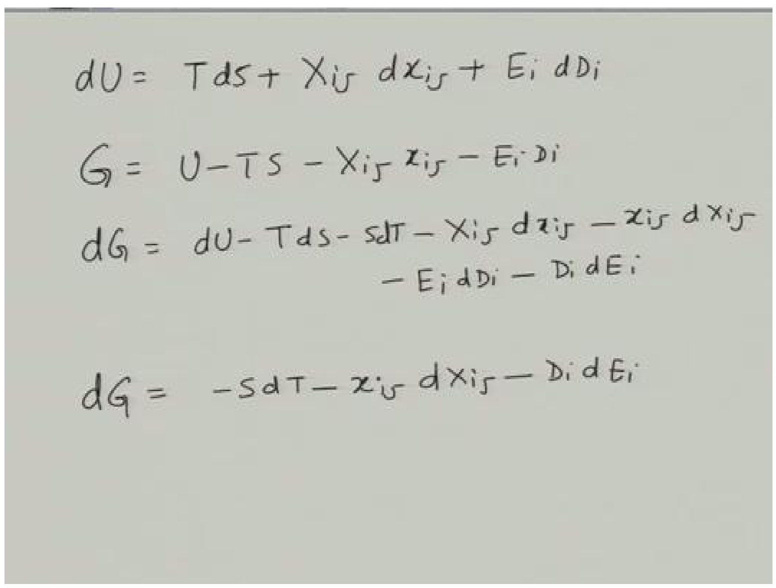

So, what we wrote was the change in entropy, dU was:

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

and then we wrote the free energy expression:

$$G = U - TS - X_{ij}x_{ij} - E_i D_i$$

and then we differentiated this function to calculate the to work out the differential dG and this is:

$$dG = dU - TdS - SdT - X_{ij}dx_{ij} - x_{ij}dX_{ij} - E_i dD_i - D_i dE_i$$

So, when you put in now, dU in the expression, so we get dG as:

$$dG = -SdT - x_{ij}dX_{ij} - D_i dE_i$$

So, from this equation we obtain a few things and what are those few things?

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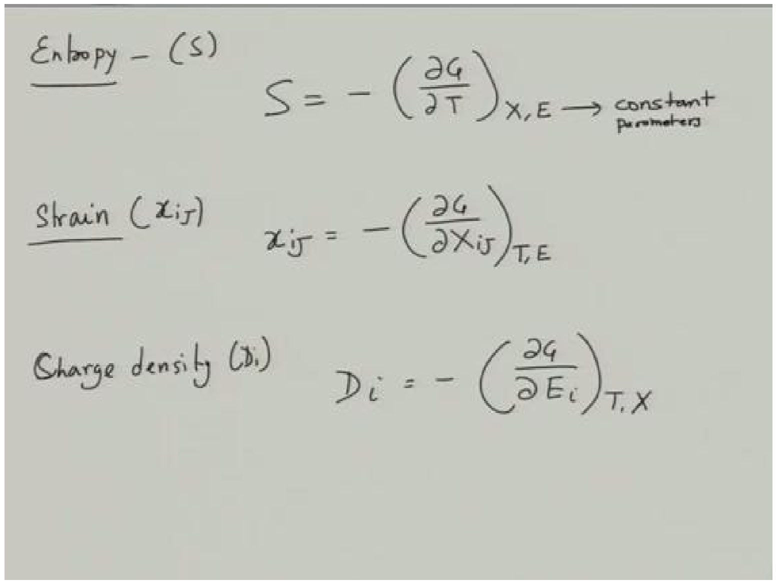

We first obtain entropy, S and what it means is that when you take constant stress and constant electric field which means these two terms will vanish and we can correlate entropy as:

$$S = -\left(\frac{\partial G}{\partial T}\right)_{X,E}$$

Similarly, when you have temperature as constant, electric field is constant, then we can calculate the strain and the strain is nothing but:

$$x_{ij} = -\left(\frac{\partial G}{\partial X_{ij}}\right)_{T,E}$$

so that will give you the strain at constant temperature and constant electric field. At constant temperature and constant stress, what we will obtain is the surface charge density or charge density:

$$D_i = -\left(\frac{\partial G}{\partial E_i}\right)_{T,X}$$

so using these expressions, we can obtain S as:

$$S = -\left(\frac{\partial G}{\partial T}\right)_{X,E}$$

so all these subscripts are basically constant parameters. Second we obtain for strain that is x_{ij} and this x_{ij} can be written as:

$$x_{ij} = -\left(\frac{\partial G}{\partial X_{ij}}\right)_{T,E}$$

at constant temperature and electric field. And third we can obtain is the charge density, D_i which can be written as:

$$D_i = -\left(\frac{\partial G}{\partial E_i}\right)_{T,X}$$

at constant temperature and stress, so these are partial differentials of free energy at with respect to temperature or stress or electric field at other two parameters being constant, which are related to; which depict the entropy, the strain and charge density and you can also write the total differential form.

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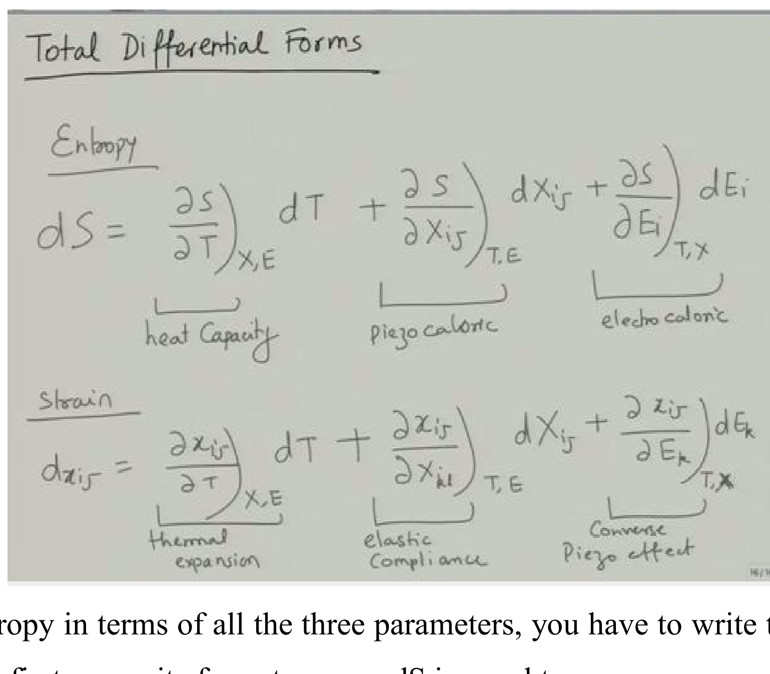

So, to express entropy in terms of all the three parameters, you have to write the total differential form, so let us say first, we write for entropy, so dS is equal to:

$$dS = \left(\frac{\partial S}{\partial T}\right)_{X,E}.dT + \left(\frac{\partial S}{\partial X_{ij}}\right)_{T,E}.dX_{ij} + \left(\frac{\partial S}{\partial E_i}\right)_{T,X}.dE_i$$

Now, what is this term, (∂S/∂T)? It is C, what is the C? You call it, this is heat capacity. What is this (∂S/∂X)? This is called as a change in entropy upon change in the stress, this is called as piezocaloric.

So, this term depicts piezo caloric effect, this term is change in entropy upon electric field, this is called as electro caloric effect. Now, if you look at the strain in total differential form, we can write:

$$dx_{ij} = \left(\frac{\partial x_{ij}}{\partial T}\right)_{X,E}.dT + \left(\frac{\partial x_{ij}}{\partial X_{kl}}\right)_{T,E}.dX_{ij} + \left(\frac{\partial x_{ij}}{\partial E_k}\right)_{T,X}.dE_k$$

Because elastic properties are different as compared to entropy. So you have to take the coupling and measurement and the response in an appropriate directions otherwise, it will not be right, so what is strain versus temperature?

What is the parameter which is of K^{-1} value or dimension that is thermal expansion, what is strain divided by stress, elastic compliance and what is this, there is sort of indirect piezoelectric effect, converse piezoeffect.

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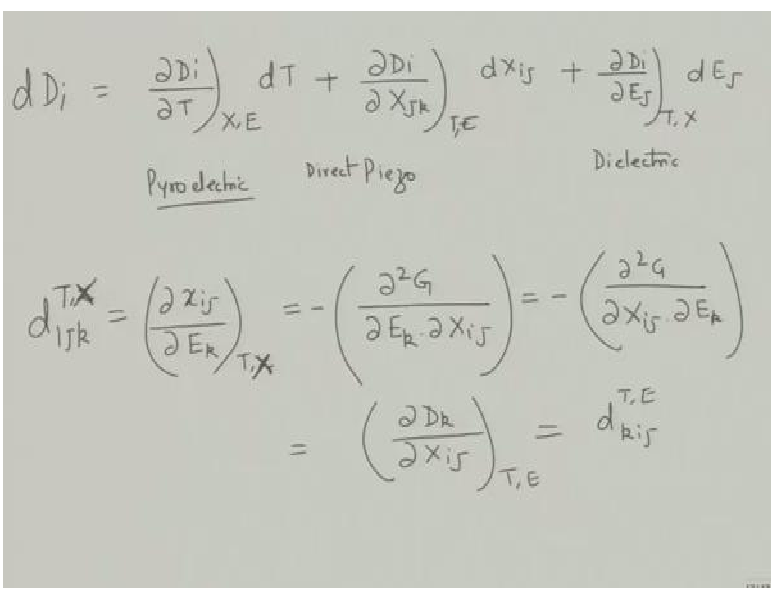

And when you write the similar expression form for the charge density, we can write dD_i to be equal to:

$$dD_i = \left(\frac{\partial D_i}{\partial T}\right)_{X,E} .dT + \left(\frac{\partial D_i}{\partial X_{jk}}\right)_{T,E} .dX_{ij} + \left(\frac{\partial D_i}{\partial E_j}\right)_{T,X} .dE_j$$

This is change in surface charge density as a function of temperature.

What is the change in surface charge density as a function of stress? Direct piezo, and what is this change in dielectric? surface charge density as the function of electric field? This is just an electric effect, plane linear electric effect, so these are basically, each partial derivative is basically a physical phenomena as we see each of them, all nine of them show one or other kind of physical effect that we have just seen in past few lectures.

And many of them can be also correlated using various other arguments for example, if you now want to express d_{ijk} at constant temperature and stress, so how can you write this:

$$d_{ijk}^{T,X} = \left(\frac{\partial x_{ij}}{\partial E_k}\right)_{T,X} = -\left(\frac{\partial^2 G}{\partial E_k . \partial X_{ij}}\right) = -\left(\frac{\partial^2 G}{.\partial X_{ij} . \partial E_k}\right) = \left(\frac{\partial D_k}{\partial X_{ij}}\right)_{T,E} = d_{kij}^{T,E}$$

this becomes $d^{T,E}_{kij}$, so basically what it says is that thermodynamically speaking, indirect and direct effect are nothing but the same, this is sort of equivalence of direct versus indirect piezo electric effect although, they are manifested in different forms.

Thermodynamically speaking, they are nothing but the same whether you see you know pm/V or whether you see pC/N, the manifestation is different but the effects are the same. So, this is what it is, you can correlate other properties as well which we will be not going to do here. In reality in practice, they are represented in slightly different forms.

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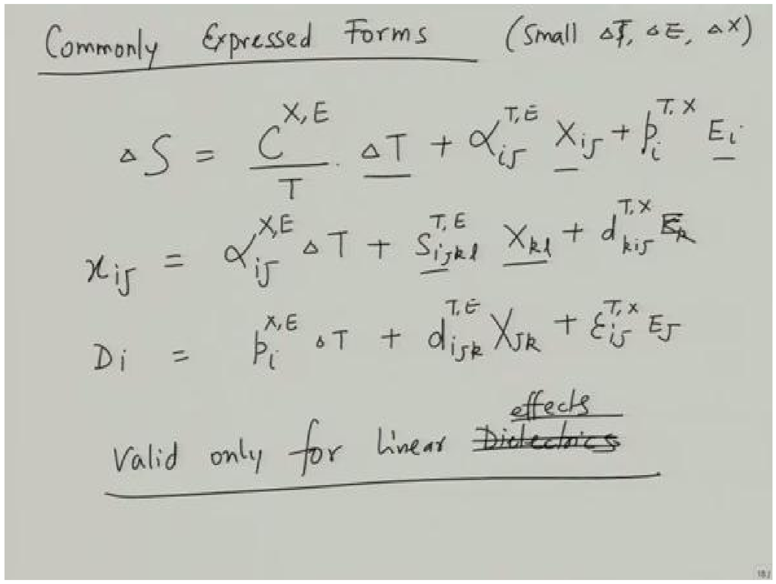

So, for example, let us say commonly expressed forms for, so basically if a small, you can say these are for small changes in ΔS or ΔE or Δx, very small changes. So, for these small changes we see ΔS as:

$$\Delta S = \frac{C^{X,E}}{T}\Delta T + \alpha_{ij}^{T,E} X_{ij} + p_i^{T,X} E_i$$

If you look at it now, we wrote earlier dS as heat capacity into dT, piezo caloric coefficient multiplied by d_{xij}, electro caloric coefficient multiplied by dE_i and the form in which we are writing them now is this, so this is the small change in temperature, stress and electric field and these are the coefficients, so this is $C^{X,E}$ /T.

α_{ij} is basically, you can say thermal expansion tensor and then this is $P^{T,X}{}_i$, so this is for change in entropy, similarly you can write for x_{ij}; xij can be written as:

$$x_{ij} = \alpha_{ij}^{X,E}\Delta T + s_{ijkl}^{T,E}.X_{kl} + d_{kij}^{T,X}.E_k$$

similarly, you can write for Di:

$$D_i = p_i^{X,E}\Delta T + d_{ijk}^{T,E}.X_{jk} + \varepsilon_{ij}^{T,X}.E_j$$

So, these are basically sort of integrated forms that we write, for earlier we wrote the differential forms now we have written what we call as integrated forms of these, and these are the commonly written forms, so here we can see that alpha's are all thermal expansion coefficients, C is the specific heat, okay, S is elastic stiffness right or and S was is compliance.

And then we have pyro electric coefficient and then we have piezo electric coefficients, so all these parameters written in these integrated and the superscripts in all the cases; XE, TE and TX, they mean that these are the constant variables, they cannot be variable. So, in the first; you can see in the first column, temperature is varied, stress and electric field are kept constant, in the second column stress is varied, temperature and electric field are kept constant.

In the third column, electric field is varied and the temperature and stress are varied, now these relations are basically for generally, linear materials only, when you go for nonlinear effects such as ferroelectrics, then they consist of higher order terms which are not present here. So, essentially these are valid only for linear dielectrics, linear effects, you can say non-linear effects, dielectrics but we will say linear effects only in the linear region.

But with the moment, you go to non-linear region; they become slightly different, you have to include higher order terms which we have not.

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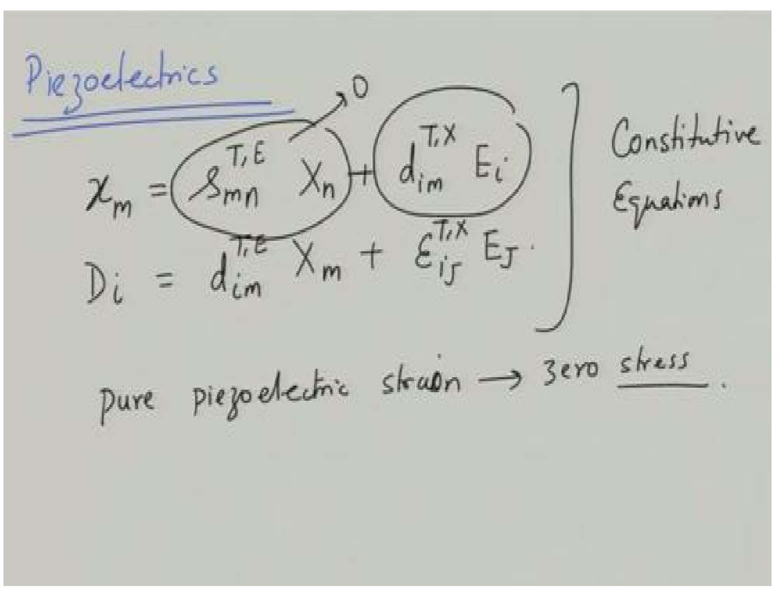

So, these equations when you write in the matrix notation, for piezoelectric let us say these are called as constitutive equation, so for piezoelectric, this strain:

$$x_m = s_{mn}^{T,E}.X_n + d_{im}^{T,X}.E_i$$

there are two notations you might be aware in the linear; matrix notation, the wide notation. So, basically if we write them in the matrix notation, this is how you write them, so you can see that instead of x_{ij}, you are writing x_m, when $i \neq j$.

So, this was strain and then for dielectric displacement, you write this as:

$$D_i = d_{im}^{T,E}.X_m + \varepsilon_{ij}^{T,X}.E_j$$

so basically you can see that if you want to have pure piezo electric strain, then you need to have zero stress, so pure piezoelectric strain which is because of only electric field, then this component must be equal to zero because you can see that strain here as stress term as well as electric field term.

Whereas, we define it to consist of only stress, only electric feel by indirect effect, so if you want to measure the pure piezoelectric strain which means the stress must be equal to zero, you are only taking as if similarly, if you want to measure the charge; pure charge then the electric field must be equal to zero and your stress must be finite. So, these are called piezoelectric constitutive equations.

So, if you read any book on piezoelectricity, they will use these equations, so you can write them in details, if you combine all the thermodynamic potentials, you can write various constitutive equations, total of 6, if you include all the combinations of thermodynamic potentials etc., you will get 6 more such equations, we have written just two which are of most importance but we can write many others as well.

So, what we have done until now is basically to sort of provide you a feel of mathematical framework in which these properties are expressed.

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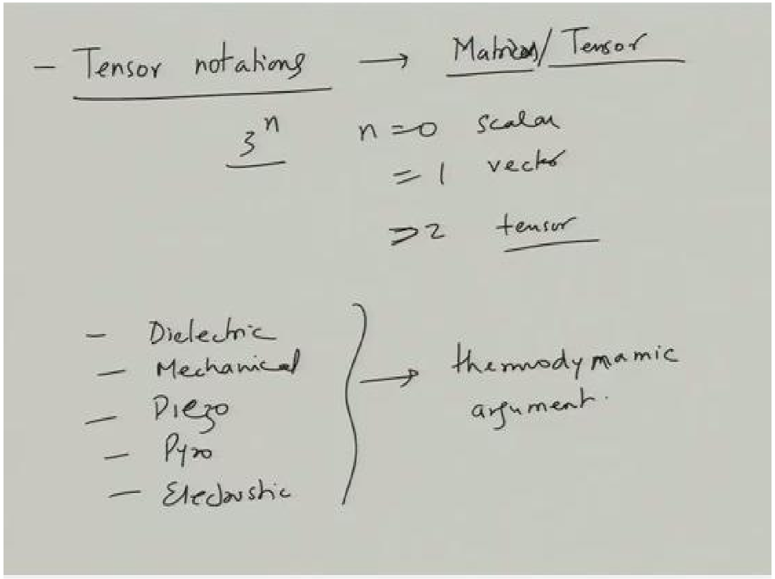

So, we started with basically tensor notations and these tensor notations are basically, you need to read little about matrix and tensors, so as said earlier, if you have a tensor is expressed as the formula 3^n, so n = 0 will mean it is a scalar, 1 will mean it is a vector, and greater than 2 it will mean it will a it is a tensor, so of course the life becomes very difficult as you go to 9, 27, 81 components.

But things are made easier by thermodynamic considerations and symmetry considerations and other factor such as stress and strain tensors being symmetric in nature, as a consequence the total number of independent components in each tensor reduces substantially for example, modulus which is the fourth rank tensor will contain 81 components, it reduces too much lower numbers determined by symmetry and thermodynamic arguments.

Similarly, in case of susceptibility and piezoelectric coefficients, the numbers go down dramatically because of for example, in case of piezoelectricity because of symmetry of stress, the numbers go down from 27 to 18 and they can be further lower depending on the crystal symmetry and thermodynamic arguments. So, essentially we look that as said various properties, dielectric properties, then we looked at mechanical properties.

Basically, elastic properties, we looked at piezo electric properties, we looked at pyroelectric properties and we looked at electrostrictive properties and in the end, we coupled them together using thermodynamic arguments, right in the form of free energies and those equations are partial equations that we develop, they are called as Maxwell equations, many of them, there are total of 27 Maxwell equations, you can write, we have written just few of them.

Any book on classical thermodynamics will take you through 27 expressions, we wrote just a few which will useful to us in the context of this course, it is far more difficult topic then we have just in this case but we just want to you to get introduced to how they are written in exact forms. So, in the next lecture, now we will continue with the discussion on ferroelectrics because we have not discussed about them.

So, we look at what ferroelectrics are, what is the temperature dependence, what can be the phase transition ferroelectric associated with, what is ferroelectric switching like, what is the ferroelectric hysteresis loop, what is the effect of domains and things like that and then finally, we will look at the applications of all the three materials, we will take up a few cases where we will see how these effects are practically used in making devices.