Fundamentals and Applications of Dielectric Ceramics
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Lecture - 27
Basics of Non-linear Dielectrics

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

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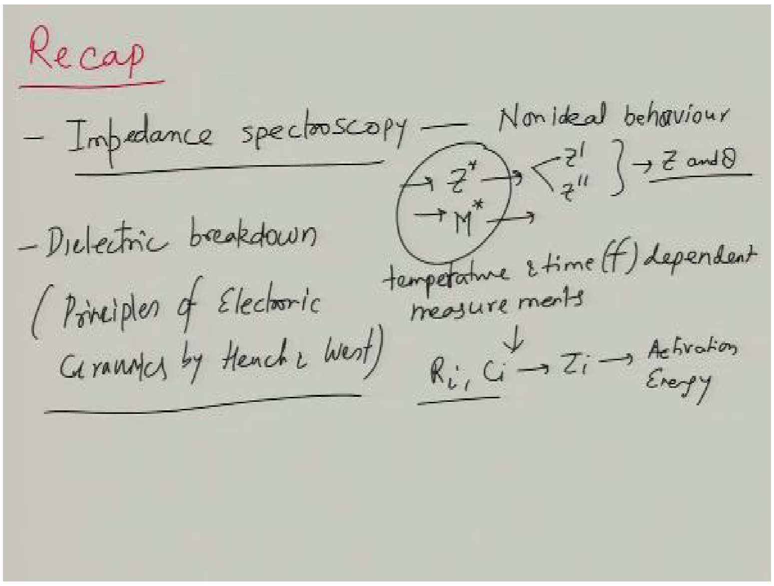

So in the last class we looked at detail little bit further into impedance spectroscopy and this is a very useful tool to determine the dielectric characteristics of the materials. So many materials show non ideal behaviour and as a result their description is incomplete by a circuit. So as a result you would like to evoke other electrical circuits to model them and for this it is useful to measure properties such as complex impedance.

Complex impedance contains real and imaginary part which are basically, calculated by measuring Z and θ. So θ will also allow you to measure that loss tangent and from this modulus electrical impedance you can determine modulus and by combining temperature dependent, temperature and time dependent measurements, time means frequency right. One can determine things like R_i, C_i, i means certain entity.

So resistances and capacitances, you can also calculate what are the time constants and from these temperature dependence of these one can also determine what is activation energy and then one can look into mechanism of electric materials, mechanism for conduction etcetera, so you might have vacancy, you might have interstitials, you might have impurity atom so far and so forth.

So different things will have different entities will have different time constants and they will have different temperature dependence and frequency dependence as a result you can look into different mechanisms a little bit more clearly and by combining this impedance and modular spectroscopy the difference become more amplified you can say clear. So this is one way to characterize electric materials in a very useful way.

And then we looked the dielectric breakdown and dielectric breakdown is basically, when the dielectric materials become conducting or they will stop functioning as the dielectric and this could be because of increase in electron temperature or certain conductivity or because of thermal build up, temperature build up again makes materials conducting and it could also be because of defects in the material such as porosity, grain boundaries etcetera.

So there are multiple mechanism that we briefly discuss, we did not get into details of this, but if you want to get into details of dielectric breakdown, you can read this book, *Principles of Electronic Ceramics by Hench and West*. So this is a very nice book which gives you a good insight into dielectric breakdown. So now what we are going to continue about in this lecture is we will look at, we will now continue our discussion into what we call as nonlinear dielectrics.

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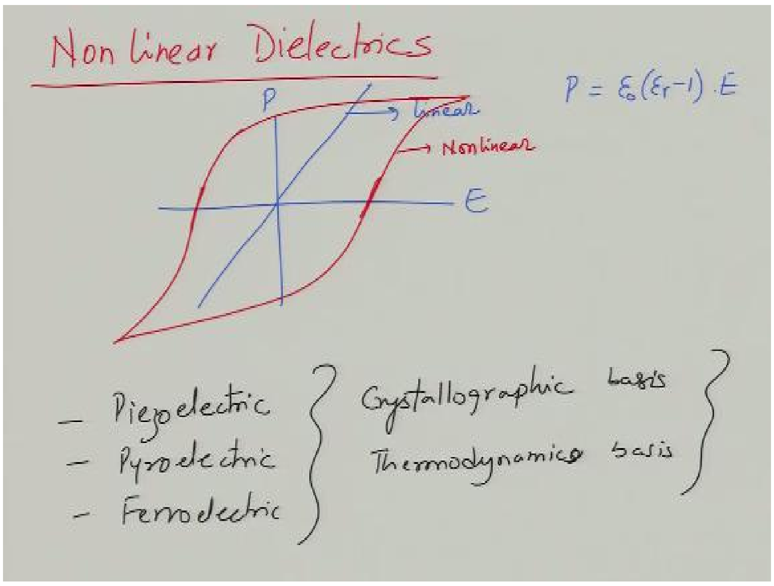

Okay and nonlinear dielectrics we mean, by this what we mean is that when you apply electric field at say polarization, so we saw in case of linear dielectric that:

$$P = \varepsilon_0(\varepsilon_r - 1).E$$

so basically, this polarization increases as a function of electric field linearly. So when the field is zero, the polarization is zero. So as a result you have a linear variation of polarization.

This is what is the linear dielectric, but in case of nonlinear dielectrics especially at higher fields, you might have different effects. So for example, a ferroelectric material will show loop polarization switching loop like this. It has certain linear part at low fields, but the linear part is limited, but rest of the places the curve is pretty nonlinear. So this is a non-linear dielectric.

So these nonlinear dielectrics have special characteristics and generally we classify them in three categories, one is called as piezoelectric, second is called as pyroelectric and third is called as ferroelectric and these have crystallographic basis of distinction as well as thermodynamic bases to understand these. So what we will do is that to begin with so far what we did earlier, we looked at the properties of a dielectric in mostly in scalar form.

But to understand ferroelectrics, piezoelectric and pyroelectric, it is important to invoke the tensor form of these properties. So what we will do is that, first we will introduce the formal notations for these properties in the tensor form okay.

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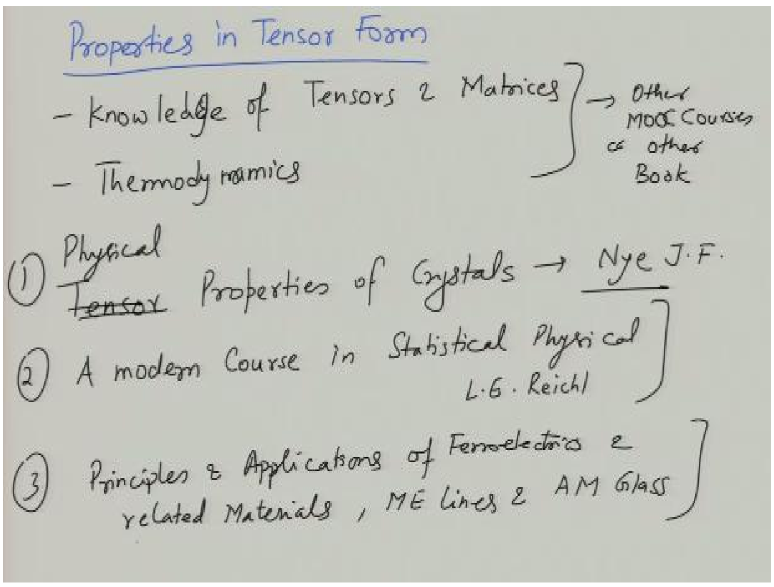

So what we will do first is that we will look at the properties relevant to these materials in tensor forms. So assuming that you have some knowledge of tensors and matrices and you would also have some knowledge of thermodynamics. If you do not have knowledge of these subjects then look at other MOOC courses or other books. So for example, for looking a tensor properties of crystals, J.F Nye is recommended.

This is a very nice book on tensor properties of crystals and let me give you one or two more references. So this is basically, you can say physical properties of crystals. *Physical properties of crystals by Nye J. F.* So this is first book and then to learn about thermodynamics you can read, *A modern course in a statistical physics which is by L. E. Reichl*.

And third recommend book is *Principles and applications of ferroelectrics and related materials*. This is by M. E. Lines and A. M. Glass. This is a classic book on ferro-electricity, which goes a bit into phase transitions and thermodynamics and things like that. This is more about the statistical mechanics, thermodynamics. This is more about tensor properties of physical properties of crystals.

So these are some books, otherwise there are lot of other books you can also look at them. So let us begin with some discussion on this.

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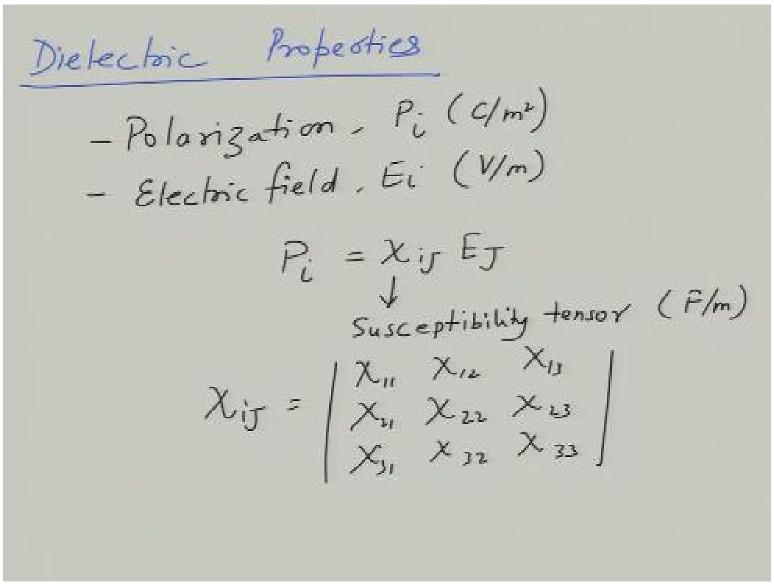

So our discussion will remain on basically, we will use system will be, co-ordinate system will be Cartesian and so we will use x, y, z coordinates and then z will be considered as perpendicular to the plane of the film or plane of the substrate or plane of the paper. So let us first begin with the tensor definition of properties okay. So first let us begin with the dielectric permittivity.

So among dielectric properties, the first thing that we know is the polarization right, which we saw P, but in this case we determine as P_i, so i determines the direction right and the units are coulomb per metre square. So when you apply electric field, vector, let us say electric field is also E_i, it could be E_i, E_j, E_z, whatever. So again this is in volt per metre. So when you apply electric field to a dielectric crystal, you generate a polarization.

And this polarization is written as:

$$P_i = \chi_{ij} . E_j$$

So this is your basically, applied electric field vector E_J and this is the polarisation P_i and so you apply the field in J direction and you measure the field in i direction, polarization i direction and this χ_{iJ} is known as susceptibility, tensor. So just like we have magnetic susceptibility here we have dielectric susceptibility.

So this is dielectric susceptibility tensor, this is Farad per meter and as you can see this is the second rank tensor. So basically, χ_{iJ} you can write as:

$$\chi_{ij} = \begin{vmatrix} \chi_{11} & \chi_{12} & \chi_{13} \\ \chi_{21} & \chi_{22} & \chi_{23} \\ \chi_{31} & \chi_{32} & \chi_{33} \end{vmatrix}$$

So this relation however, is valid only for linear dielectrics or the linear portion of the nonlinear dielectrics. So when you make polarization versus electric field diagram for a nonlinear dielectric you can apply this relation only to the linear region of that plot not to the other plot.

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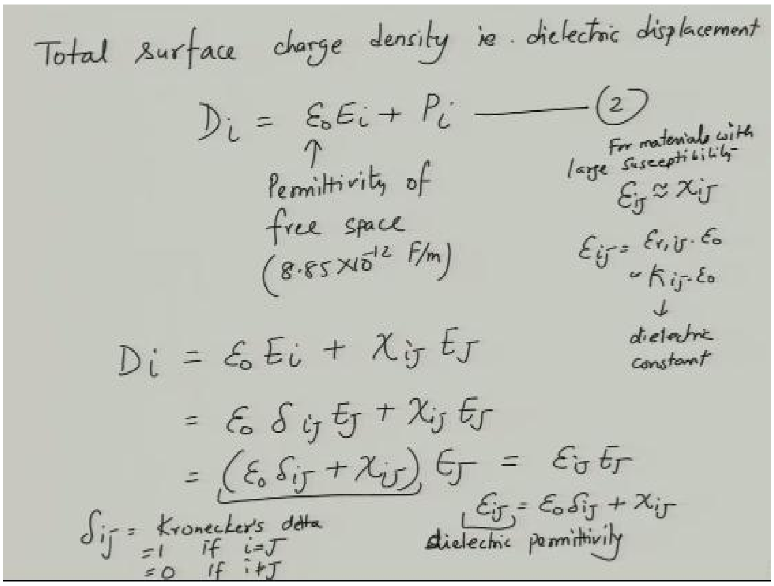

So now let us see what is the total surface charge density. So total surface charge density which is essentially dielectric displacement when you apply electric field. So we can write this as:

$$D_i = \varepsilon_0 E_i + P_i$$

So here ε_0 is permittivity of free space which is 8.85 x 10^{-12} F/m and E_i is the basically, you can say the field and P_i is the polarization that is generated.

So now if you combine the, so let us say if you write this as equation number one and if you write this as equation number 2, we can write this D_i as:

$$D_i = \varepsilon_0 E_i + \chi_{ij} E_j$$

which can be written as:

$$D_i = \varepsilon_0 \delta_{ij} E_i + \chi_{ij} E_j$$

where δ_{iJ} is called as Kronecker's delta which is equal to 1 if i = J and 0 if i $\neq$ J .

And this particular thing is called as basically, you can write this as $\varepsilon_{iJ}E_J$. So:

$$\varepsilon_{ij} = \varepsilon_0 \delta_{ij} + \chi_{ij}$$

and this is basically, the dielectric permittivity, that this is a dielectric, which we were earlier writing in case of, in the form of scalar form.

And this for ferroelectric kind of material for the materials for which the susceptibility is really large, for them for materials with you can say large susceptibility, you can say this is equal to:

$$\varepsilon_{ij} \approx \chi_{ij}$$

$$\varepsilon_{ij} = \varepsilon_{r,ij}.\varepsilon_0 \approx k_{ij}.\varepsilon_0$$

So when you say high K dielectric or low K dielectric, this is the kappa.

And which is also nothing but ε_r. So because this is what is the more useful term ε_r of k, then ε_{ij}. So you can see that here also that ε_{ij} is a second tensor, so which means it has nine components. Often we will see in many of these electric properties or other properties as well of second rank and third rank and say fourth rank is that they although they, let just briefly introduce what tensor is.

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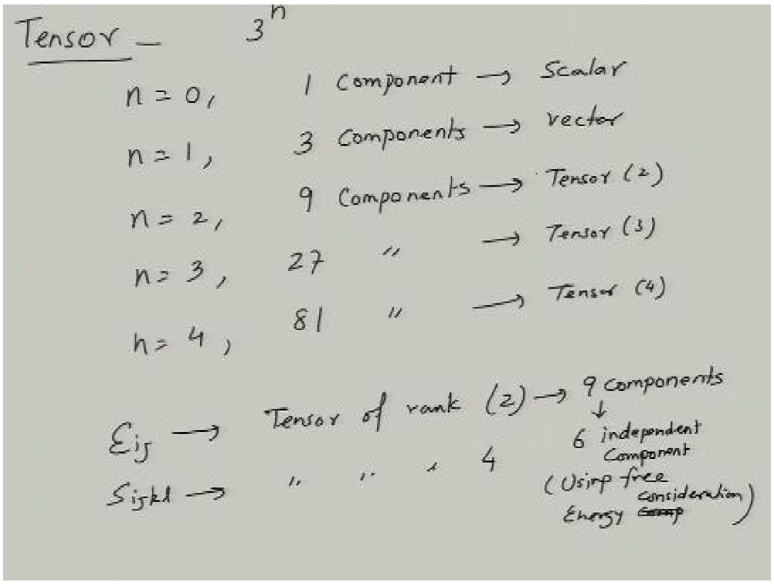

So we know that tensor is defined by a rank by the formula 3^n, so when n is equal to zero, it has one component. So this will become a scalar, when n = 1, it will have three components, so this will become vector. When n = 2, it will have nine components, then it will be second rank tensor. So vector is a rank 1 tensor. So this will have nine components, so this is a tensor of rank two. When you go to n = 3, you will have 27 components.

And then it will be a tensor of rank 3 and generally we will see up to n = 4 which is 81 components and this will be tensor of rank 4. So this is how these will be. So when you see something like ε_{iJ} it is basically, tensor or rank 2. So this is what it will be, so when you write for example, as we will see in case of stiffness if you write S_{ijkl}, then this is tensor of rank 4.

It will have 81 components, but we are fortunate that crystal symmetry and thermodynamic arguments reduce the number of component, but this is how it is this notation means. So this is as we say is the dielectric and in case of dielectric permittivity we say that ε_{ij} is this, so ε_{ij} is tensor or rank 2, so it will have 9 components, but basically, using the free energy arguments this reduces to 6 independent components.

So you could have thermodynamic consideration, you can have crystal consideration and so on and so forth. So 9 is reduced to 6 using thermodynamics considerations and 6 can be reduced to even further if you have, so for example, if you take for a cubic crystal, it will have lesser components. If you go for a monoclinic or tetragonal crystal it will have more.

So more asymmetric the crystal is, more the component you will have. More symmetric the crystal is, lesser the number of components will be, so that is the general guideline. So these 9 components can be reduced to further lower number depending upon the crystal symmetry and thermodynamics.

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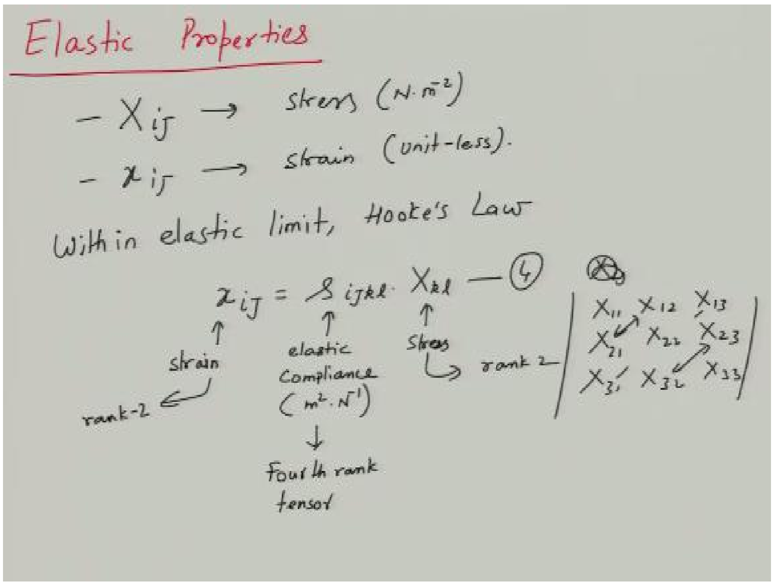

So now let us look at the second aspect that is elastic properties. So in the elastic properties let us first define the stress. So this is stress which is in N/m^2, this is X_{iJ}, so this is the stress that is applied and then you measure the strain which is x_{iJ}, which is strain, which is unit less.

So if you apply stress on any elastic material within the linear region, within elastic limit you apply Hooke's law.

And what does this Hooke's law say, it says:

$$x_{ij} = s_{ijkl} . X_{kl}$$

So this is the stress, this is elastic compliance whose unit is $N^{-1}.m^2$ and this is strain. We can see here that stress is a rank 2 tensor and strain is again rank 2 tensor, the elastic compliance as a result in rank 4 tensor. So this is the proportionality constant basically, it turns out to be rank 4 tensor.

So basically, you can say it is a and stress is rank 2, strain is rank 2 and so you can write stress as:

$$\chi_{ij} = \begin{vmatrix} \chi_{11} & \chi_{12} & \chi_{13} \\ \chi_{21} & \chi_{22} & \chi_{23} \\ \chi_{31} & \chi_{32} & \chi_{33} \end{vmatrix}$$

So it has 9 components but by symmetry it will reduce to 6. Similarly, strain will also reduce to 6 because these 2 are equivalent. This and that is equivalent and these 2 are equivalent. As a result you will reduce them to 6 components because of crystal symmetry.

So this is the relationship between strain and stress using elastic compliance as a proportionality factor. So this is equation number let us say, so you have to use numbering system, so this is 1, this is 2, this is 3 and this is 4.

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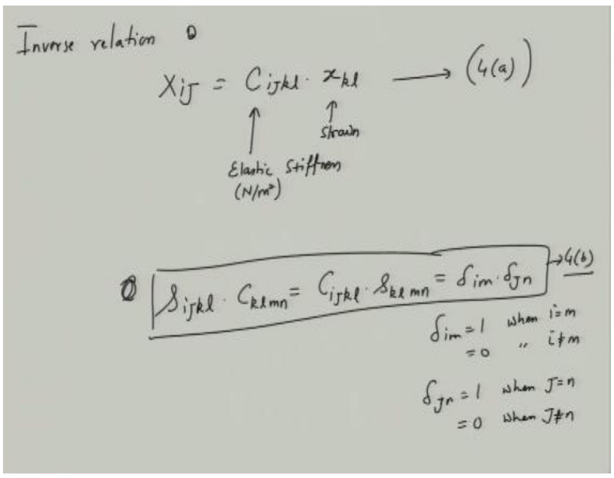

And let us come to equation number, and the inverse form of the above equation, so inverse relation will be:

$$X_{ij} = C_{ijkl}.x_{kl}$$

so this is strain, this is elastic stiffness or elastic modulus, this is again rank 4 tensor, this is N/m^2 and this is stress okay. So now that you have elastic, so this is let us say 4(a). So we know that these two equations are related to each other, so as a result we can relate the stiffness and the compliance using the relation.

So we can relate them as:

$$s_{ijkl}.C_{klmn} = C_{ijkl}.s_{klmn} = \delta_{im}.\delta_{jn}$$

δ_{im} = 1, when i = m and is equal to zero when i $\neq$ m. Similarly, δ_{jn} = 1, when J = n and is equal to zero when J $\neq$ n and this you can write the matrix and prove it. It is not difficult to prove it.

So this is the relationship between the elastic compliance and the stiffness and let us say this is equation number 4(b).

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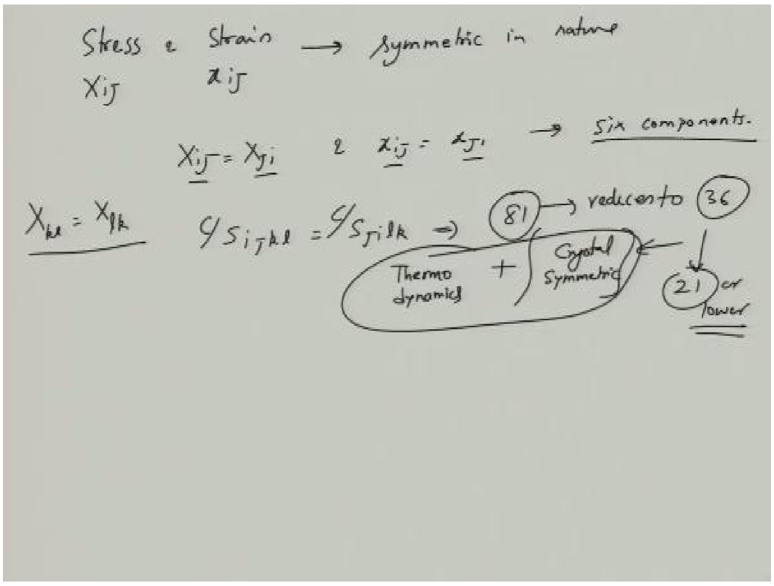

So this stress and strain tensors are, so these are all as we said second rank tensor, but they are symmetric in nature okay and what it means is that basically:

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

$$X_{kl} = X_{lk}$$

so as a result the total number reduces to 6, so basically, 6 components and when this happens as a result since you have a, there is a symmetry in stress strain this also reduces the number of components and stiffness.

So for example, complies becomes S_{ijkl} to S_{jilk}, so number of, similarly, you can write for C/S. So for both together and compliance the number of components in a fourth rank tensor you will have 81. So this 81 reduces to 36. So you can write the matrix and then you can use the symmetry arguments and see which ones are similar because we are saying ij = ji and ij = ji for a strain also, what is also means is that this kl will be equal to lk.

So when you make these combinations you will see that 81 component will reduce 36 and crystal symmetry further reduces these components to 21. So when you apply crystal symmetry because crystals are symmetric. So the crystal symmetry argument further reduces these 2 lower numbers, such as 21 so, when you apply crystal symmetry plus thermodynamics actually we should say both of them.

So both of these arguments reduce to 21 or lower. So we are fortunate that from 81 we get down to 21 or even lower components and for symmetric crystals which we generally deal with have even lower number of components, so it makes life easier. So this is tensor notation for elastic properties. Now we do not look into plastic properties because dielectric materials are ceramic materials as a result they do not have plastic deformation.

So we mostly deal with the elastic properties in these materials. So next we will look at what we call as, we probably are going to run out of time.

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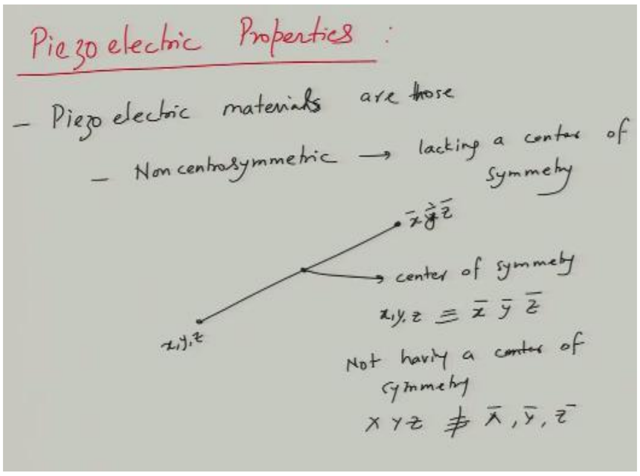

But next is what we called as Piezo electric properties. So let us first define piezoelectric materials. Piezoelectric materials are those which are first of all non-centrosymmetric okay, among crystal classes there are certain classes which are centrosymmetric, there are certain classes which are non-centrosymmetric. Non-centrosymmetric means they do not have lack of, lacking a centre of symmetry.

So for example, what does it mean? It means that let us say you have two points x, y, z and another point –x, -y and –z. If you have a centre of symmetry, so if you have a centre of symmetry then what you see, so if you do an inversion operation then x, y, z can be replicated to –x, -y, -z. If you have a centre of symmetry, but if you do not have centre of symmetry then x, y, z will not be equal to –x, -y –z.

This is a very basic definition of piezoelectric material. So piezoelectric materials by definition have to be non-centrosymmetric that is the must requirement. So we are probably going to run out of time now. So we will just briefly summarise this that we have discussed about some tensor properties of materials, mainly right now looked dielectric properties and elastic properties and we will further discuss the piezoelectric properties and other properties of this nonlinear dielectric materials in the next few lectures.