Fundamentals and Applications of Dielectric Ceramics
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Lecture - 28
Piezoelectric Effect

Welcome again to the new lecture of this course, fundamentals and applications of dielectric ceramics.

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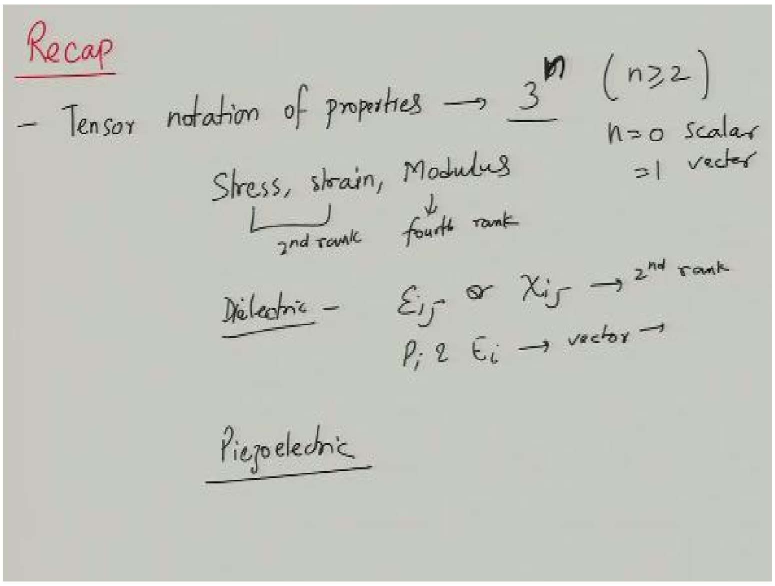

Recap

- Tensor notation of properties → $\underline{3}^n$ $(n \geq 2)$

$n = 0$ scalar

$= 1$ vector

$\underbrace{\text{Stress, strain}}_{\text{2nd rank}}$, $\underset{\text{fourth rank}}{\overset{\downarrow}{\text{Modulus}}}$

Dielectric - ε_{ij} or χ_{ij} → 2nd rank

P_i & E_i → vector →

Piezoelectric

So just briefly recap the last lecture. So in the last lecture we introduced tensor notation of properties, which is important from the perspective of properties in the crystals because the properties of materials are not isotropic. Most properties are anisotropic in nature because stress is a tensor, strain is a tensor and basically tensors are nothing but matrices of components more than 9.

So scalar is a 0 rank, tensor is defined as this formula 3^n. So for a tensor n is greater than or equal to 2, n = 0 will remain scalar and n = 1 will mean it is a vector and n is greater than or equal to 2 will mean it is a tensor. So a tensor will have 9 or more components theoretically speaking and as a result your stress property such as stress, strain, modulus, they are all tensors.

So stress and strain are second rank tensors, and modulus is the fourth rank tensor. Similarly, we look the dielectric properties. You have ε_{ij} with or χ_{ij} which is, so this is ε_{ij}, this is permittivity, χ_{ij} is susceptibility, these are all both second rank tensors and when you look at polarization electric field these are all vectors. So these are second rank tensors and, so in general you will see that the proportionality constant, the property which is the proportionality constant.

Whether it is susceptibility or dielectric constant or modulus or compliance, they will have a rank which is higher than the rank of the stimuli. So if you saw in dielectric properties the stimuli is electric field, the value that you measure is polarization, both are vectors and the proportionality constant is susceptibility which is the tensor okay. Similarly, so you can say that rank 1 tensors are polarization electric filed and accordingly the rank 2 tensor will be the proportionality constant.

And you looked at the stress strain, stress and strain are rank 2 tensors, and correspondingly the proportionality constant which is elastic compliance or stiffness it becomes the fourth ranked tensor. So fourth rank tensor can be very tricky because you have 81 components but life is little easy for us because of thermodynamics and crystal symmetry arguments that we can reduce this number from 81 to 21 or even lower.

So that way we are lucky. So we then started our discussion on piezoelectric properties. So we were not able to get into equations, but we just define what a piezoelectric is.

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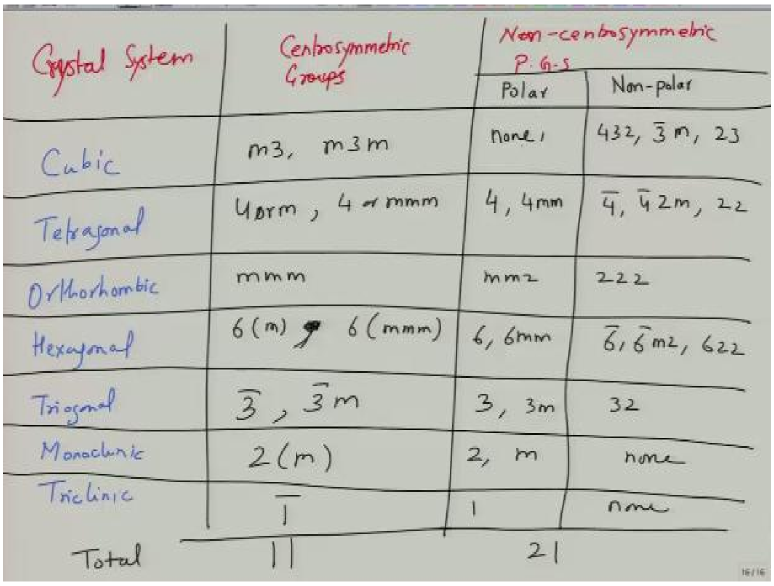

Crystal System	Centrosymmetric Groups	Non-centrosymmetric P.G-S	
		Polar	Non-polar
Cubic	m3, m3m	none,	432, $\bar{3}$m, 23
Tetragonal	4orm, 4 or mmm	4, 4mm	$\bar{4}$, $\bar{4}$2m, 22
Orthorhombic	mmm	mm2	222
Hexagonal	6(m), 6(mmm)	6, 6mm	$\bar{6}$, $\bar{6}$m2, 622
Trigonal	$\bar{3}$, $\bar{3}$m	3, 3m	32
Monoclinic	2(m)	2, m	none
Triclinic	$\bar{1}$	1	none
Total	11	21	

So we will continue on those aspects based on crystal symmetry. First before we look at the piezoelectric properties in mathematical form. So from if you look at the lecture notes of

MOOC in structure of materials you will recall that there are something called as crystal classes and these crystal classes are defined on the basis of 32 point groups okay. So point groups basically we can say they are sort of addressed to the structure of material in some sense.

So point groups are related to space groups and so on and so forth. Space group consider a motive into consideration, so as a result these 32 point groups become some 230 something space groups. We are not going to go into crystography, but basically you can say 32 point groups are 32 representations of points in a space using considering that the distribution of points in the spaces, space filling and symmetric.

And so out of these 32 point groups when you apply symmetry arguments there are 21 which are you can say non-centrosymmetric and remaining 11 are centrosymmetric and what we saw in the last class is this centrosymmetric or non-centrosymmetric. Centrosymmetric will mean having a centre of symmetry, which means you can replicate if you have a centre of symmetry you can replicate a point at x, y, z to –x, -y, -z .

If you do not have centre of symmetry then you would not be able to do this transformation. So basically, the environment at x, y, z will not be similar to environment at –x, -y, -z, which means you cannot perform that symmetry operations. So 32 point groups are based on distribution of points in space, based on symmetry, arguments and so on and so forth, which you can look at in the details related to crystal structure MOOC course, as structure of materials MOOC course.

So the piezoelectric materials belong to those materials which are non-centrosymmetric. So what are these. So let us just define the crystal classes with respect to so let us say we have several crystal classes, crystal system let us say, then we have centrosymmetric groups and we have noncentrosymmetric point groups let us say PGS. So here we write first as cubic then we have tetragonal, then we have Orthorhombic.

Then we have hexagonal and we have trigonal, which is rhombohedral and then we have monoclinic and we have triclinic. Among these let us say we have these point groups, cubic, tetragonal, so among these we have m3, m3m, these are non-centrosymmetric, these are centrosymmetric. Then we can say 4, this is also represented as m, 4 or mmm, then we have mmm in orthorhombic. In hexagonal we have 6 or m as well as 6 or mmm.

Then trigonal we have $\bar{3}$ and $\bar{3}$m. We have 2 or m and then in triclinic we have one $\bar{1}$. So if we count the total number, we have 11 centrosymmetric point groups. In the noncentrosymmetric point groups we have cubic. So we have 432, $\bar{3}$m, 23, then we have 4, 4mm, $\bar{4}$, $\bar{4}$2m and 22. In the orthorhombic we have mm2 and 222.

In the hexagonal we have 6, 6mm and in non-polar we have $\bar{6}$, $\bar{6}$m2 and 622, and then in trigonal we have 3, 3m and 32; 2m and none and 1 and none in monoclinic and triclinic respectively. We will come to the reason why we have drawn them in 2 columns in a minute. So these are all you can see non-centrosymmetric point groups. So we have 21 total.

These have been put in 2 columns because in the non-centrosymmetric there is a further division that some of these are polar and some of these are nonpolars. So ones on the left are polar. Polar means they have, the crystal will have a dipole moment, a permanent dipole moment and nonpolar are the ones that even though they are non-centrosymmetric they are not polar, the crystal does not have a, the dipole moments basically you can say cancel out each other when you put ions on them.

So you can see that in the cubic crystal there is no polar group, but you have non polar group in cubic crystal so you have non-centrosymmetric nonpolar groups, but you do not have any polar non-centrosymmetric. So you can see that polar is a subgroup of non-centrosymmetric. If it is centrosymmetric, it can never be polar. So for something to be polar it has to be non-centrosymmetric, but that is not the sufficient condition.

It can be polar, there is a possibility for it to be a polar, only if it is non-centrosymmetric, but it is not guaranteed that a crystal will be polar if it is non-centrosymmetric alone. As you can see that some of the non-centrosymmetric crystals are cubic crystals are nonpolar, but they are not polar, nothing is polar. Similarly, you can see in tetragonal while 4 and 4mm are polar, $\bar{4}$, $\bar{4}$2m and 22 are nonpolar even though they are non-centrosymmetric.

And similarly, we have these many other crystal systems. So out of these we have 10, which are polar and 11 which are nonpolar. So out of these, so as far as piezoelectricity is concerned.

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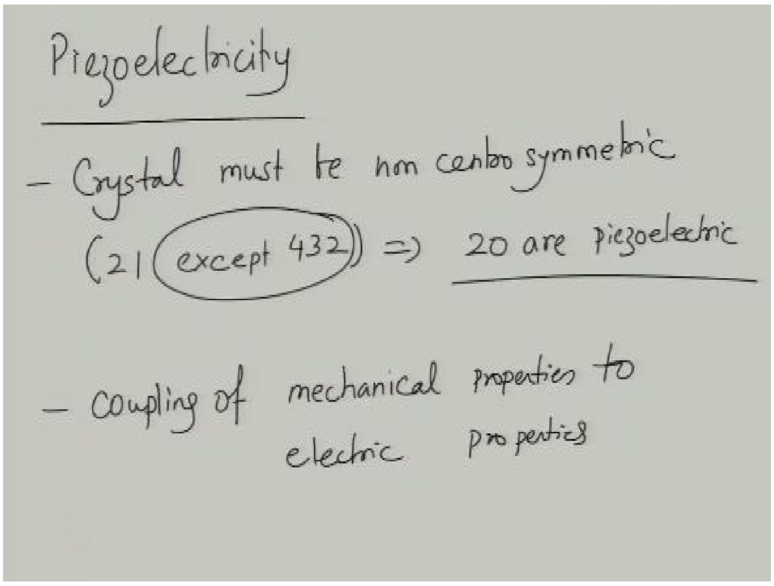

Piezoelectricity

- Crystal must be non centro symmetric
  (21 (except 432)) ⇒ 20 are piezoelectric
- coupling of mechanical properties to electric properties

As far as piezoelectricity is concerned, the requirement is that crystal must be noncentroymmetric, so even though the material is cubic, as long as it is non-centrosymmetric, it will have piezoelectricity. So the only requirement is crystal must be non-centrosymmetric. So it applies to all the 21 point groups except 432. So with the exception of 432 everything else is piezoelectric.

So which means out of 21, 20 are piezoelectric. So as long as your material belongs to these 20 point groups, it will be a piezoelectric material. So this is the must requirement, piezoelectric material must be non-centrosymmetric, it can be polar, it can be nonpolar, it does not matter. So basically piezoelectric properties is coupling of mechanical properties to electrical properties.

And as we will see there are direct and indirect piezoelectric effect. There are 2 effects that we will see them later on. So a piezoelectric material is something which couples mechanical properties to electrical properties upon application of a mechanical stimuli that show mechanical response, electrical response or upon application of electrical stimuli, it shows a mechanical response.

But the main, the fundamental requirement for the material is that it must be non-centrosymmetric that is it must lack centre of symmetry. Build upon this further, we get to what we call as pyroelectric crystals.

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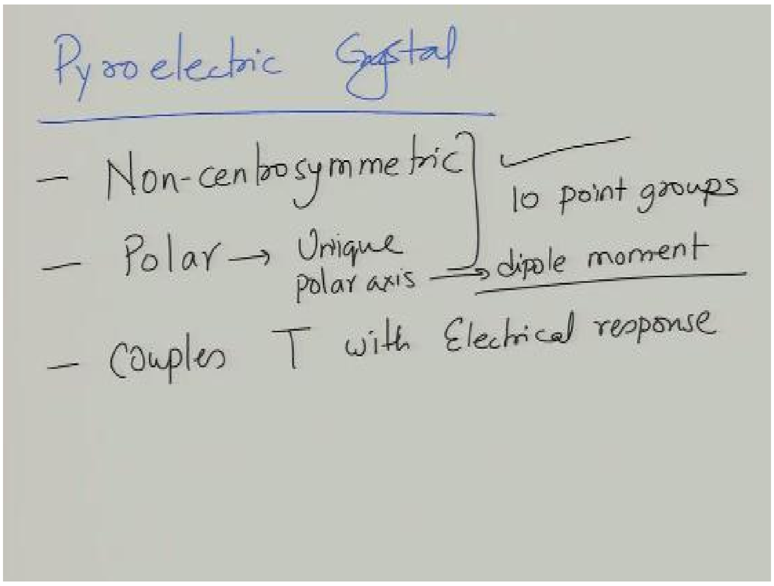

Pyroelectric Crystal

- Non-centrosymmetric ✓ 10 point groups
- Polar → Unique polar axis → dipole moment
- Couples T with Electrical response

Pyroelectric crystal must be non-centrosymmetric and must also be polar. So there are 11, the 10 point groups basically, so we can remove actually this 432 because it is anyway not piezoelectric, so it cannot be pyroelectric as well. So first requirement, it must be non-centrosymmetric and then second requirement must be polar.

So there are 10 point groups on the left that we drew, all of these, these are all non-centrosymmetric and polar. These materials are all pyroelectric. So what is the pyroelectric material? Those who couples temperature with electrical response. So a pyroelectric material is something by definition which is non-centrosymmetric and which must be polar, that is which must have a polar access, unique.

Basically it means that it must have a unique polar axis, which means it must have dipole moment along that axis. So that is what a pyroelectric material means.

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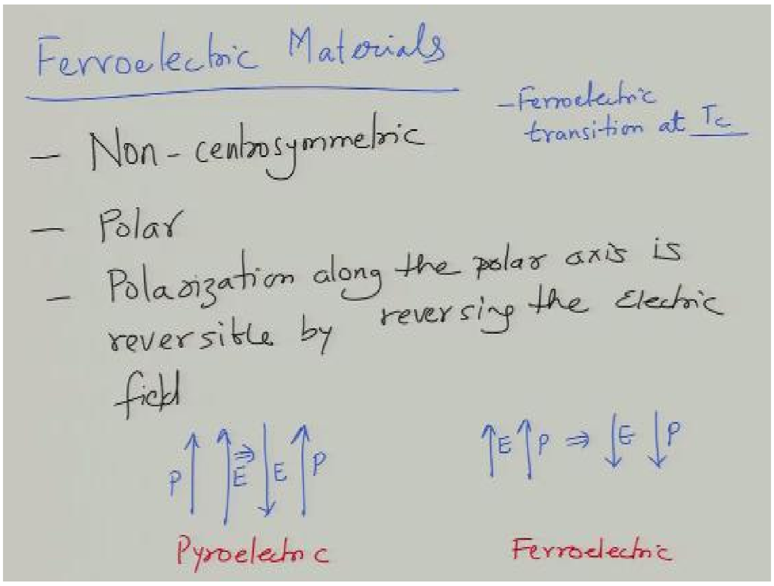

Ferroelectric Materials

- Non-centrosymmetric
- Polar
- Polarization along the polar axis is reversible by reversing the Electric field

- Ferroelectric transition at T_c

Then we come to third class of material, which is called as ferroelectric materials. For a ferroelectric materials the requirement is it must be non-centrosymmetric, it must be polar, which means it must have a unique polar axis. Third requirement is the polarization along the polar axis, is reversible by reversing the electric field. So let me just depict this. So for a pyroelectric this is the pyroelectric.

And here we draw a ferroelectric, so for a pyroelectric, let us say this is the polarization vector. So when you apply electric field in this direction, this remains in this direction, but when you apply electric field in this direction the P remains the same, it does not affect it. So when you change the electric field direction the polarization direction does not change.

In the ferroelectric crystal when you apply electric field in this direction your polarization is in this direction and then you reverse the direction of electric field, the polarization also reverses, it has to happen, the polarization is reversible by reversing the direction of electric field. This is what makes it a ferroelectric, also ferroelectrics are materials which have a transition.

So the ferroelectric material will disappear above a certain temperature called as Curie temperature. So they have a ferroelectric transition, which is typically a phase transition as we will see in the thermodynamic at a temperature called as T_c.

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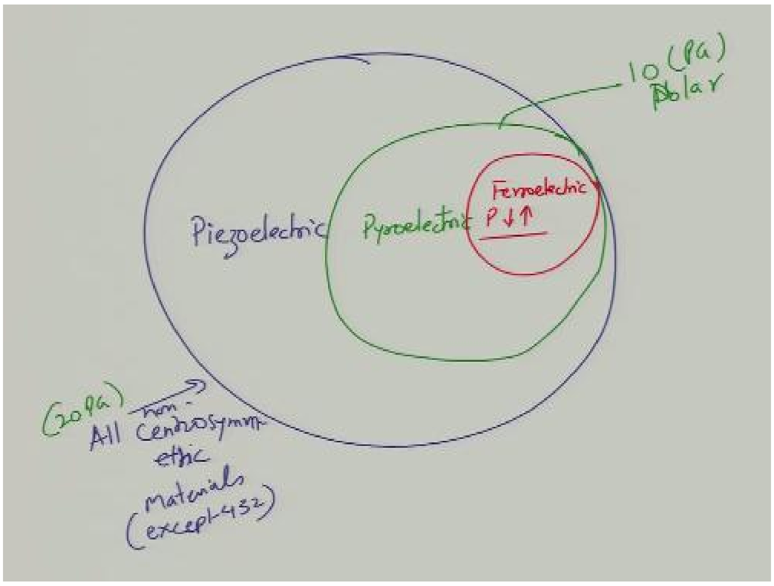

So if you now look at it, there is all centrosymmetric materials are piezoelectric, right, which means all non-centrosymmetric materials are piezoelectric except 432. Within these non-centrosymmetric materials you have 11 of them which are, so this is basically you can say 20 PG, within these you have 10 PG which are polar, these are all pyroelectric. Within these we have another class which is ferroelectric for which polarization is reversible.

This number is not very well defined, so we cannot say what this number is, but basically what we can say is that every ferroelectric material is pyroelectric and piezoelectric by default. Every pyroelectric is piezoelectric by default but not necessarily ferroelectric and piezoelectric material maybe pyroelectric or maybe ferroelectric, but not necessarily. So this is sort of a diagram, Venn diagram kind of you see that piezoelectric is a broader class of materials.

Pyroelectric is a little restricted class of materials from 20 to 10 point groups and ferroelectric is even more restricted class of materials. This is a basic you can say classification of piezo, pyro and ferroelectric materials. So let us get back to the properties of piezoelectric crystals now. So we were talking about the piezoelectric effect.

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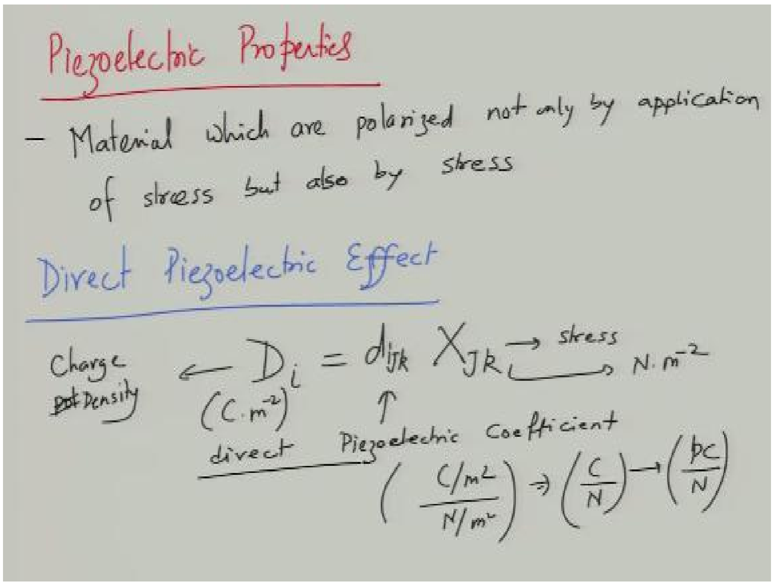

Piezoelectric Properties

- Material which are polarized not only by application of stress but also by stress

Direct Piezoelectric Effect

Charge ~~pot~~ Density $\leftarrow D_i = d_{ijk} X_{jk} \rightarrow$ stress $\rightarrow N.m^{-2}$

$(C.m^{-2})$

$\uparrow$

direct Piezoelectric Coefficient

$$\left(\frac{C/m^2}{N/m^2}\right) \rightarrow \left(\frac{C}{N}\right) \rightarrow \left(\frac{pC}{N}\right)$$

So in the introduction given to you it was necessary just to differentiate between the piezo, pyro and ferro, we will come to that in little bit more detail later on. So piezoelectric materials are basically materials which are polarized not only by application of stress, but also by stress okay. So there is a linear relationship. So there are two kinds of effects, first is called as direct piezoelectric effect.

This direct piezoelectric effect is that D_i, which is the charge density. This is related to stress X_{jk} and the proportionality constant is d_{ijk}:

$$D_i = d_{ijk} . X_{jk}$$

So you can see that D is the basically the charge density. So this is charge density which is nothing but polarization right. Charge density D_i, this is proportional to X_{jk} which is the stress tensor and the proportionality constant is piezoelectric coefficient, which is direct piezoelectric coefficient.

So this is basically you can say this is C/m^2, this is N/m^2 and this will be C/N. Generally values are noted in terms of pC/N, but basic unit is C/N in the SI units. So this is the piezoelectric coefficient, which is the direct piezoelectric coefficient.

So you can say this this direct piezoelectric coefficient d_{ijk} which is the third rank tensor d_{ijk} because it couples stimuli of rank 2 with the measurement quantity of rank 1. So now they also have another property, which is called as indirect piezoelectric effect or converse piezoelectric effect.

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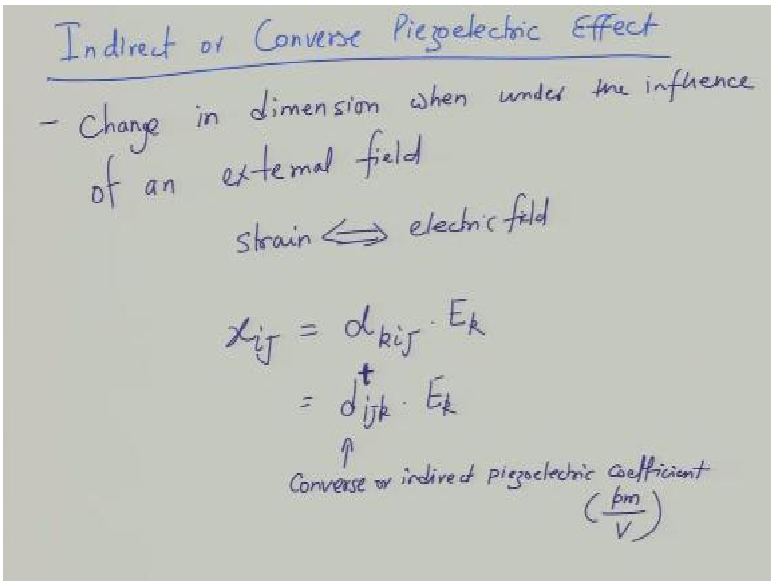

Indirect or Converse Piezoelectric Effect

- Change in dimension when under the influence of an external field

strain ⟺ electric field

$$x_{ij} = d_{kij} \cdot E_k$$

$$= d^{t}_{ijk} \cdot E_k$$

↑

Converse or indirect piezoelectric coefficient $\left(\frac{pm}{V}\right)$

So converse piezoelectric effect is that you have a change in dimension when under the influence of an external field. So when you apply electric field then they show change in the dimension or the strain. So this converse piezoelectric is basically strain is related to electric field. So this is described as:

$$X_{ij} = d_{kij}.E_k = d^{t}_{ijk}.E_k$$

We can write a transpose t. There is a transpose of matrix and this is basically called as converse or indirect isoelectric coefficient. So again you can see the units. This is unit-less and this is V/cm or V/m. So this would be pm/V. So you can see the direct piezoelectric coefficient will have a unit of pC/N.

And in this case the units will be pm/V. Basically, for a volt of voltage what is the displacement that you measure in picometers, it is a very small displacement that is why it is typically in picometre, but you can say it is meter per volt. So it is very small, that is why we generally write in terms of picometer or nanometer, things like that. So these are 2 piezoelectric coefficients we have.

One is the direct piezoelectric coefficient, d_{ijk} and second is the indirect piezoelectric coefficient which is d_{kij} which is transpose matrix d_{ijk}, t. The units are pm/V for indirect one and C/N for the direct piezoelectric coefficient. So there is also something about the sign.

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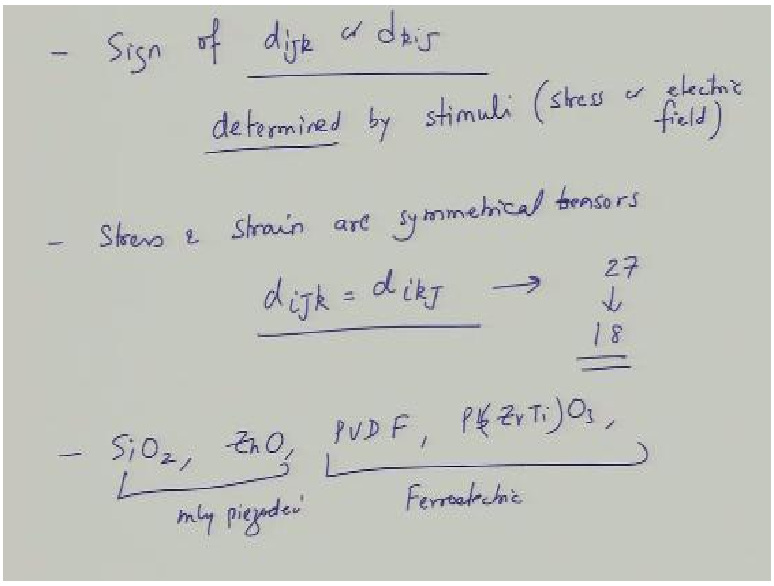

- Sign of $\underline{d_{ijk} \text{ or } d_{kij}}$

  $\underline{\text{determined}}$ by stimuli (stress or electric field)

- Stress & Strain are symmetrical tensors

  $$\underline{d_{ijk} = d_{ikj}} \rightarrow \begin{matrix} 27 \\ \downarrow \\ \underline{\underline{18}} \end{matrix}$$

- $\underbrace{SiO_2,\ ZnO,}_{\text{only piezoelec}}$ $\underbrace{PVDF,\ Pb(ZrTi)O_3,}_{\text{Ferroelectric}}$

The sign of these will depend upon the sign of stimuli. What is the sign of applied, so you can say stimuli, that is stress or electric field. So you may have compressive strain, you may have tensile strain. Similarly, you can have charge density, which has polarity of electric, polarity will change as you change the direction of stress also whether compressive or tensile stress that is applied.

So now essentially in this case if since stress and strain are at symmetrical tensors as we saw earlier, this also makes that the piezoelectric tensors are also symmetrical with respect to similar indices. So for example, d_{ijk} will mean that it will become d_{ikj}. So this is a symmetry argument which is applied to, so you can do again this when you write the matrix of this d_{ijk} and when you make those similarity with respect to what you did in the stress tensor and strain tensor you can work out this as:

$$d_{ijk} = d_{ikj}$$

So this is what we have done today, and so number of piezoelectric coefficient you can see when you do that so for a rank 3 tensor you will have 27 right. So 27 reduces to 18 when you apply this argument that stress and strain tensors are symmetric and these can further be reduced to even lower components when you apply thermodynamic and crystal symmetry arguments.

So they are lowered in general the number is much lower. What are the examples of these materials. Examples are silicon oxide, zinc oxide, PVDF which is polyvinylidene fluoride, lead zirconate titanate, $Pb(ZrTi)O_3$, and so on and so forth. These are all very good piezoelectric materials, of course among these are ferroelectric materials, so they are necessarily piezoelectric and these are only piezoelectric.

So for example, the Quartz watches that we wear they are based on piezoelectric effect and in those materials silicon oxide is Quartz is the one which is used for piezoelectric, as a piezoelectric components. So what we have done is we have basically discussed what is the crystal basis for piezo, pyro, and ferro electric materials and then we have looked into the tensor notations of piezoelectric properties. We will further dwell upon in the next few lectures.