

Smart Structures
Professor Mohammed Rabius Sunny
Department of Aerospace Engineering
Indian Institute of Technology, Kharagpur
Week 01
Lecture No: 05
Introduction to Piezoelectric Materials (continued)
Part 02

Welcome to the fifth lecture.

Today, we look into 3D point groups, and then we will see the origin of piezoelectricity. So, in three dimensions, the symmetry element also can be combined in various ways, but the combination has to be consistent, which means the combination should give something which is meaningful and realistic. So, with that, there are a total of thirty two combinations possible, and we look into these combinations. Now, here, we will not draw the combinations, but rather, we will look into them with their symbols.

So, there is a Hermann-Mauguin system or Mauguin symbols to define these symmetry elements in 3D point groups. So, this is an internationally accepted notation. There are other systems also, like Schoenflies, but we will here look into only Hermann-Mauguin symbol.

So, in this system, a rotation is denoted by numbers like one, two, three, four, six. Rotoinversion is denoted by one bar, two bar, and so on. A mirror, which means a reflection plane is m, and also elements, which are parallel, are written one after another, like two m, a two-fold axis, and a mirror parallel to the axis. And elements perpendicular, are written with a slash. For example, in a two-fold axis, if there is a mirror which is perpendicular to the axis, then it is two slash m.


(Refer Slide Time: 03:24)

3D Point Groups

Hermann Mauguin Symbols
Internally accepted notation

Rotation: 1, 2, 3, 4, 6
Rotoinversion: $\bar{1}, \bar{2}, \dots$
mirror: m

Elements parallel are written one after another $2m$
Elements perpendicular are written with / $2/m$



Smart Structure

Now, let us look into this. So, at first, we have one. It is just one, means a one-fold axis, and one-fold axis does not mean much. So, it is one, and then comes one bar. It is a one-fold rotoinversion axis. And this is in the triclinic, this is in the category of triclinic. So, these are triclinics. And then comes these two, two, two, and two, these are monoclinics. And then we have three. They are orthorhombic. And here we have tetragonal.

Now, this just means that it has one-fold axis of rotation. And this means one-fold axis of rotation plus inversion. So, it is a rotoinversion, one-fold axis of rotoinversion. This simply means two-fold axis of rotation, and here, there are three two-fold axis of rotation. So, three two-fold axes. Now comes something where we have a mirror and which is perpendicular to it. So, it is two-fold axis and a mirror perpendicular to it, perpendicular to the axis of rotation. Six means, I mean, number six, we have just m . So, m means just it has one mirror. So, it has one mirror plane. And we have two m m . Two m m means two-fold rotation axis. So, number seven is two-fold axis and two mirrors. They are parallel to the rotation axis. Then number eight has triple m . It has three mirrors. Among those three mirrors, two are parallel, and one is perpendicular. Number nine is just four-fold axis. At number ten, we have four-fold axis of rotoinversion, which means inversion plus rotation.


(Refer Slide Time: 07:12)

3D Point Groups

Sr. No.	3D Point Group
1	1
2	$\bar{1}$
3	2
4	222
5	2/m
6	m
7	2mm
8	mmm
9	4
10	$\bar{4}$

Handwritten notes:

- 1 fold axis of rotation
- Triclinic → 1 fold axis of rotation + inversion
- 2 fold axis of rotation
- Three 2 fold axes
- Monoclinic
- 2 fold axis mirror ⊥ to the axis
- 1 mirror plane
- Orthorhombic
- 7. 2 fold axis, 2 mirrors
- 8. Three mirrors
- 9. 4 fold axis
- 10. 4 fold axis of rotoinversion
- Tetragonal



Smart Structure

Then, if we move forward, we have these are all tetragonal, and then these are all trigonal. So, at eleven, we have four-fold axis and two-fold axis. So, it has four-fold axis, here axis means axis of rotation, and two two-fold axes. Then, we have four-fold axis and two mirror planes, which are parallel. Then we have four bar two, which means four-fold rotoinversion and one two-fold axis. Twofold axis, and then one mirror, and this mirror is diagonal to it. Then, we have four-fold axis and one mirror perpendicular to it, mirror perpendicular to it.


Then we have four-fold axis and then, three mirrors. Three mirrors and these are perpendicular to the rotation axis, and we have three-fold axis for sixteen. And for seventeen, we have three-fold axis and two-fold axis. For eighteen, we have three-fold rotation axis and a parallel mirror plane and mirror, which is parallel. Then we have three-fold rotoinversion. And then, we have three-fold rotoinversion and one mirror, this mirror is diagonally placed. And then we have six-fold axis.

(Refer Slide Time: 10:57)

Sr. No.	3D Point Group
11	422
12	4mm
13	42m
14	4/m
15	4/mmm
16	3
17	32
18	3m
19	$\bar{3}$
20	3m
21	6

11. 4 fold axis and 2 two fold axis
 12. 4 fold axis two mirror planes
 13. 4 fold rotoinversion 2 fold axis mirror
 14. 4 fold axis, mirror \perp
 15. 4 fold axis, three mirrors \perp
 16. 3 fold axis
 17. 3 fold axis 2 fold axis
 18. 3 fold axis, mirror
 19. 3 fold rotoinversion
 20. 3 fold rotoinversion, mirror
 21. Six fold axis

Tetragonal: 11, 12, 13, 14, 15
 Trigonal: 16, 17, 18, 19, 20, 21



Now, if we look at the last six, then these are all hexagonal. And these are all cubic. So, number twenty two, it has six-fold rotoinversion, and then number twenty three, we have six-fold axis and two two-fold axes. And two, and two, two-fold axes. And then, we have six-fold axis. Here, we have six-fold axis and two mirrors; they are parallel. And, then we have six-fold rotoinversion, then mirror, and then we have two-fold axis.

Here, we have six-fold axis and one perpendicular mirror, which is perpendicular. And then, we have six-fold axis, and then we have three mirrors. All these mirrors are perpendicular to the six-fold axis and so perpendicular to the axis. And, then we have four bar three m. So, it is a four-fold rotoinversion. Then, a three-fold axis and, a mirror, and a mirror. In twenty nine, we have four three two, four-fold axis, three-fold axis, and two-fold axis. Then we have two three, two-fold axis, three-fold axis. And then thirty one, we have mirror, but this is perpendicular to three-fold rotoinversion. Three-fold rotoinversion. And, here, we have a mirror, three-fold axis, and then, we have mirror. And again, they are perpendicular to each other.

(Refer Slide Time: 15:16)

Sr. No.	3D Point Group
22	$\bar{6}$
23	622
24	6mm ✓
25	$\bar{6}m2$
26	6/m
27	6/mmm
28	$\bar{4}3m$
29	432 ✓
30	23 ✓
31	m $\bar{3}$
32	m $\bar{3}m$

22. 6 fold roto inversion
 23. 6 fold axis, two 2 fold axis
 24. 6 fold axis, two mirrors
 25. 6 six fold roto inversion, mirror, 2 fold axis
 26. 6 fold axis, mirror \perp
 27. 6 fold axis, 3 mirrors \perp to the axis
 28. 4 fold roto inversion, 3 fold axis, mirror
 29. 4 fold axis, 3 fold axis, 2 fold axis
 30. 2 fold axis, 3 fold axis
 31. mirror \perp 3 fold roto inversion
 32. mirror, 3 fold axis, mirror

Hexagonal: 22, 23, 24, 25, 26, 27
 Cubic: 28, 29, 30, 31, 32

So, total, we have thirty two elements here, and so we can see that, out of these thirty two point groups, there are few point groups which has which are centrosymmetric, which are center of symmetry, and they are marked as red here. So, we can see few here. We can see few here. We can see few here. So, they are total eleven in number.

So, out of those thirty two, eleven are centrosymmetric. So, those which are centrosymmetric they do not show any piezoelectricity. Now, the question is, what does centrosymmetry have to do with piezoelectricity that we will talk about after a few minutes. So, out of these thirty two point groups, we have centrosymmetric, which are eleven in number. And then, there are rest twenty one, which has no center of symmetry. And then, out of those twenty one, just one is non-piezoelectric, and there are rest twenty, are piezoelectric.

And then, out of those twenty, ten are polar, or we can call pyroelectric. Now, what it means, we will see it after some time, and ten are non-polar. And again, out of those ten polars, we have some as ferroelectric. So, in ferroelectric, the polarization is reversible, and some are, some has non-reversible polarization.

(Refer Slide Time: 17:55)

Centrosymmetric -

- If it exhibits inversion symmetry.
- Centrosymmetric crystals are not piezoelectric

```

graph TD
    A[32 Point Groups] --> B[Centrosymmetric (11)]
    A --> C[No centre of symmetry (21)]
    C --> D[Piezoelectric (20)]
    C --> E[Non Piezoelectric (1)]
    D --> F[Polar/Pyroelectric (10)]
    D --> G[Nonpolar (10)]
    F --> H[Ferroelectric (Reversible polarization)]
    F --> I[Non reversible polarization]
  
```

Smart Structure

Now, the question is, what does this absence of centrosymmetry have to do with piezoelectricity? That we can understand by these two examples here. Here, we have NaCl. It is centrosymmetric.

So, the center of the positive charge and negative charge are coinciding. Now, if we apply stress to it, suppose, if I compress and suppose it deforms, by deforms into this shape. Then also, because of it is centrosymmetric nature, the center of the positive and negative charge remains coincident. So, they do not separate. They do not form any dipole. So, the center of the negative is here, and center of the positive is here, and they are the same point.

Now, let us look into this ZnS. So, this is piezoelectric, and this is not centrosymmetric. Here, at the beginning, the center of positive and negative charge are same. Now, if we apply stress to it, it deforms in this fashion. And in this situation, the center of the negative charge is here, and the center of the positive charge is here. So, here, the centers of positive and negative charge separate, and then they create a dipole here, and that is how the piezoelectricity originates. So, if it is not centrosymmetric, after deformation, the center of positive and negative charges separate, and a dipole is created.

(Refer Slide Time: 19:42)

Single crystal Piezoelectric Materials

Lithium niobate (LiNbO_3), lithium tantalate (LiTaO_3), bismuth germanium oxide (Bi_2GeO_7), and bismuth silicon oxide (Bi_2SiO_7), quartz or silicon dioxide (SiO_2), zinc sulphide (ZnS) etc.

The diagram illustrates the piezoelectric effect in two materials: NaCl and ZnS. In the NaCl example, a square unit cell is shown with Na^+ ions (red) and Cl^- ions (green) in a centrosymmetric arrangement. When stress is applied, the ions displace, breaking the symmetry and creating a net dipole moment. In the ZnS example, a similar unit cell is shown with Zn^{2+} ions (red) and S^{2-} ions (green). Stress causes these ions to displace, also resulting in a net dipole moment. Both cases show the initial state with $P = 0$ and the state after applying stress with a net dipole moment.

Smart Structure

Now, let us look into the different types of dielectrics. We have seen various other terms like paraelectric and ferroelectric, pyroelectric, and so on. So, now, let us define them. In paraelectric materials, they are centrosymmetric, and they are non polar. So, electric field, it leads to a dipole, and then deformation comes.


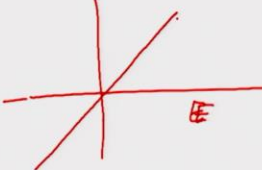
So, electric field leads to dipole, and because of those dipoles, the material deforms. Now, here, the relation between the deformation and electric field is proportional to square. So, if we plot the electric field and the deformation, it looks like this. It should look kind of symmetric with respect to the vertical axis. So, it looks like this. And we have seen that this is seen in materials which are electrostatic. So, it is a phenomenon of electrostriction. So, we have seen that all the dielectrics show some kind of electrostriction, but in some of the materials, it is quite less. In some of the materials, it is quite high. Piezoelectrics they do not have center of symmetry. Here due to stress dipole moments can be generated. Just we saw how it generates.

In piezoelectric materials, if we look at the relation between electric field and the deformation. It is like this. So, when the field is changed, the deformation reverses.

So, in this case, in case of electrostriction, the deformation is somewhat proportional to the square of the electric field. In this case, the relation is linear. But in high, but in very high electric field, the linearity does not hold. The relation starts becoming non-linear.

(Refer Slide Time: 22:00)

Four types of Dielectrics

- Paraelectric:** Have centre of symmetry and non polar
electric field \rightarrow dipole \rightarrow deformation
electrostriction

- Piezoelectrics:** Don't have centre of symmetry. Due to stress dipole moments can be generated
 

Smart Structure

Then comes pyroelectric. Now, in pyroelectric, they do not have center of symmetry, but they have spontaneous polarization. So, even if we do not apply any pressure here, they already have some polarization. So, these materials are pyroelectric materials. Now, why is it called Pyro? Pyro means it has something to do with heat or temperature. So, here, temperature causes expansion or contraction, and which changes the dipole. And when the dipole is changed, a surface charge is generated. So, temperature indirectly leads to surface charge generation. So, that is why it is pyroelectric. And this expansion or contraction due to temperature has opposite effect of surface charge generation.

Ferroelectric, they have center of symmetry, and they have spontaneous polarization, but here, by applying electric field, the field of orientation, field orientation of the polarization can be changed, and there are some materials where it cannot be changed. So that is why some materials within pyroelectrics are ferroelectrics, and some are not.

(Refer Slide Time: 23:50)

The slide features a dark red header with icons of books and a lightbulb on the left, and a circuit diagram on the right. The main content area is white with a list of bullet points. Handwritten red text is added to the first bullet point. At the bottom, there is a black footer with logos on the left, the text 'Smart Structure' in the center, and a video inset of a man in a grey suit on the right.

- **Pyroelectrics:** Don't have centre of symmetry. Have spontaneous polarization
*Temperature → Expansion/Contraction changing the dipole
surface charge generation*
- **Ferroelectrics:** Don't have centre of symmetry. Have spontaneous polarization. By applying electric field orientation of polarization can be changed.

Now, piezoelectric materials are available in various forms. We have seen that piezoelectricity is there in single crystals like quartz, berlinite, and so on.

And there are piezo ceramics, which are polycrystalline in nature. Examples are lead zirconate titanate, PZT. So, PZT is the most commonly used piezo ceramics, barium titanate, and so on. And there are polymers also, polyvinylidene Fluoride. So, PVDF and other polymers.

Now, we have looked into their relative merits and demerits. They have strong piezoelectricity, but and here, it is more flexible, but they have less piezoelectricity. So, depending on the application, some are used, and some are not. And also, there is something called piezoelectric composite, which is made of more than one material. So, to harness the benefit of one material over another, and also with piezoelectric composites, directional actuation sensing is also possible.

(Refer Slide Time: 25:08)

• Piezoelectric materials are available in the following forms

Single Crystal – quartz, berlinite etc.

Piezoceramic (Polycrystalline) - Lead Zirconate Titanate, Barium Titanate etc.
PZT

Polymers - Polyvinylidene Fluoride, Vinylidene fluoride-Trifluoroethylene Copolymer etc.
PVDF

Piezoelectric composites

Smart Structure

The slide features a dark red header with icons of books and a lightbulb on the left, and a circuit diagram on the right. At the bottom left, there are logos for various institutions and a stack of books. A presenter in a grey suit is visible in the bottom right corner.

Now, we will understand what piezoceramics are. To understand piezo ceramics, we have to see what perovskites are. So, perovskites is a structure which is shown here, and these are exhibited by materials like lead zirconate titanate, barium titanate. So, they are rhombohedral tetragonal or orthorhombic. And they show spontaneous polarization below a temperature called curie temperature. So, each of these perovskites below a temperature called curie temperature shows a spontaneous polarization, which can be understood here.

In the structure, we can see that this barium and ions are positive. So, they are sent. So, their net charge is here. Oxygen is negative. So, the net negative is here. However, this titanium ion is shifted a little up or down, that creates a dipole. So, below the curie temperature, because of this kind of structure, it is polarized. However, above the curie temperature, this titanium comes at the center. So, now, there is no dipole. So, this is the same thing when we see it from one side. The above and below the curie temperature.

(Refer Slide Time: 26:31)

Pervoskites

Has a certain crystal structure - Lead zirconate titanate ($\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$), barium titanate (BaTiO_3) etc Rhombohedral, tetragonal, or orthorhombic Spontaneous structure with spontaneous polarization below Curie temperature
Centrosymmetric cubic structure without polarization above Curie temperature

Below Curie Temperature Above Curie Temperature Below Curie Temperature Above Curie Temperature

Smart Structure

Now, as we saw at the beginning that the polycrystalline materials have different domains, and within different domains, orientation can be different. So, we have seen that these perovskites have dipoles, and if we just go back. So, here, the polarization direction is P. This, because it is going from negative to positive. Positive is up here. So, negative to positive, that is the direction of polarization.

Now, in polycrystalline materials, each of these domains have different domains of polarization because the individual domains have their own orientation or distribution. But when we look at the full picture, the net effect is zero polarization because of these diverse orientations. Finally, they balance each other, and we do not see any net polarization. If we look at the full polycrystalline material. So, that is why something called poling is done. So, this material is put under a very high electric field, and that reorients these dipoles and brings it in this form. So, each dipole is now oriented depending on how we apply the electric field. So, if we apply the electric field, plus here, minus here, the dipoles are oriented in this direction, in this way. So, once they are polarized, now they can be used as piezoelectric crystals. However, the relation between the electric field that is applied to polarize and the amount of polarization that we get is not very straightforward. So, if we plot the electric field in this direction and polarization in this direction, suppose we start from here. It increases like this, and after a certain electric field, it saturates. So, beyond this, if we increase the electric field, we do not get any more polarization.

And then, if we bring it back. Here, we get something called residual polarization. So, here it is, we can call polarization in the saturated form. Here, we get polarization, which is left after the field is made zero. We can call it P_s , and then the graph looks the same at the other side also. If we start from zero, the if we start from zero, here the graph would gradually

come here and go back. So, in this hysteresis diagram, these are the arrows: it increases like this, and it decreases like this.

Now, when the electric field is very small, then P is assumed to be proportional to the electric field, and that we will do when we find out the constitutive relation of these piezoelectric materials.

(Refer Slide Time: 29:55)

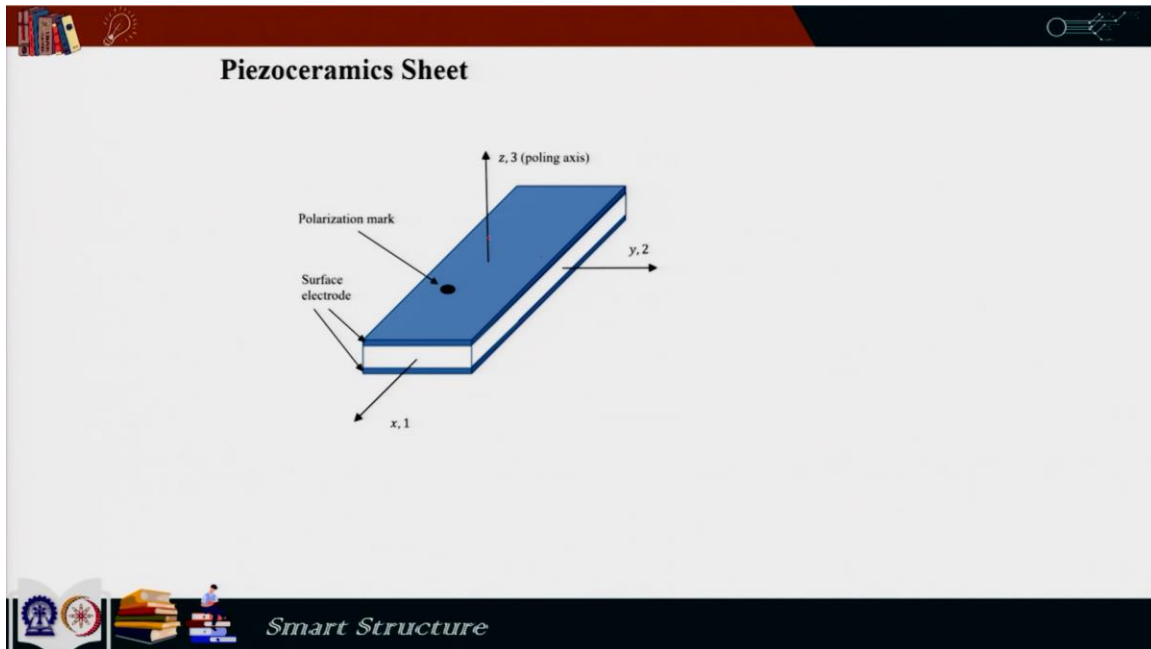
• Below the Curie temperature these materials are divided into domains when there is no electric field. Within each domain poles are oriented in a certain direction.

Polycrystalline structures

The slide includes a diagram of polycrystalline structures showing domains with different orientations of dipoles. To the right, a handwritten hysteresis loop graph plots polarization P against electric field E . The graph shows a loop with a saturation polarization P_s and a linear region near the origin. A handwritten note $P \propto E$ is present. Above the graph, a small diagram shows a rectangular material with positive charges (+) at the top and negative charges (-) at the bottom, with arrows indicating the direction of polarization.

So, this is a piezoelectric material, that is a view of the piezoelectric material that is available commercially. So, it is poled. So, for poling, electrode is applied at the top and bottom, and using this, it is poled. And this polarization mark shows the direction of polarization. It is not necessary that it has to be polarized along the Z axis, electrodes can be put at the other surface also, and it could have been polarized in other directions also. But for most of the practical applications, the piezoelectric sheets that we get are polarized along the thickness direction.

(Refer Slide Time: 30:41)



Piezoelectric ceramics are generally obtained in two different forms: PZT ceramics, hard and soft. Now, PZT ceramics are solid solutions of lead zirconate and lead titanate. They are often doped with other materials to obtain specific properties, or depending on the constituents, the properties can vary. Hard ceramics are better for high-force actuation, and soft ceramics are better for sensing applications. Here are some characteristic comparisons: piezoelectric constants are larger for soft ceramic and smaller for hard ceramic. Permittivity is higher for soft ceramic, lower for hard ceramic. Dielectric constants are larger for soft ceramic and smaller for hard ceramic. Dielectric loss is higher for soft ceramic and lower for hard ceramic. Electromechanical coupling factor is larger for soft ceramic, smaller for hard ceramic. Electrical resistance is very high for soft ceramic and lower for hard ceramic. Mechanical quality factors. They are low for soft ceramic and high for hard ceramic. Coercive field is low for soft ceramic and higher for hard ceramic. Linearity is poor in soft ceramic and in hard ceramic. It is better, and polarization and depolarization is easier in soft ceramic and more difficult in hard ceramics. This comparison can be found out in the book.

(Refer Slide Time: 32:14)

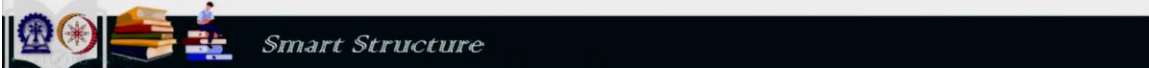


Soft and Hard Piezoceramics

- PZT ceramics are solid solutions of lead zirconate and lead titanate.
- Often doped with other materials to obtain specific properties.
- Depending on the constituents the properties of piezoceramics vary.
- Hard ceramics are suited for high force actuation and soft ceramics are suited for sensing applications.

Characteristic	Soft Ceramic	Hard Ceramic
Piezoelectric Constants	Larger	Smaller
Permittivity	Higher	Lower
Dielectric Constants	Larger	Smaller
Dielectric Losses	Higher	Lower
Electromechanical Coupling Factors	Larger	Smaller
Electrical Resistance	Very High	Lower
Mechanical Quality Factor	Low	High
Coercive Field	Low	Higher
Linearity	Poor	Better
Polarization/Depolarization	Easier	More Difficult

Smart Structures Theory by Inderjit Chopra and Jayant Sirohi, Cambridge Publications



Now, suppose we have a piezoelectric sheet which is poled along the thickness direction. And then, if we apply the voltage in such a way that the actuation electric field matches with the electric field that was used for poling. Now, here, the direction of polarization is shown as negative, which means to get this kind of polarization, the electric field that was used for poling should have been also like this. It should have been plus up and minus up, minus down.

Now, we are applying the electric field in the same sense. So, we are applying the voltage like plus up and minus down. If we do that, then the material thickens, the material thickens. So, its dimension increases along the thickness direction, and accordingly, it reduces along the other two directions. This can be understood again from this perovskite structure. So, now, because the polarization is like this, which means the structure is in this form. The titanium is here shifted down.

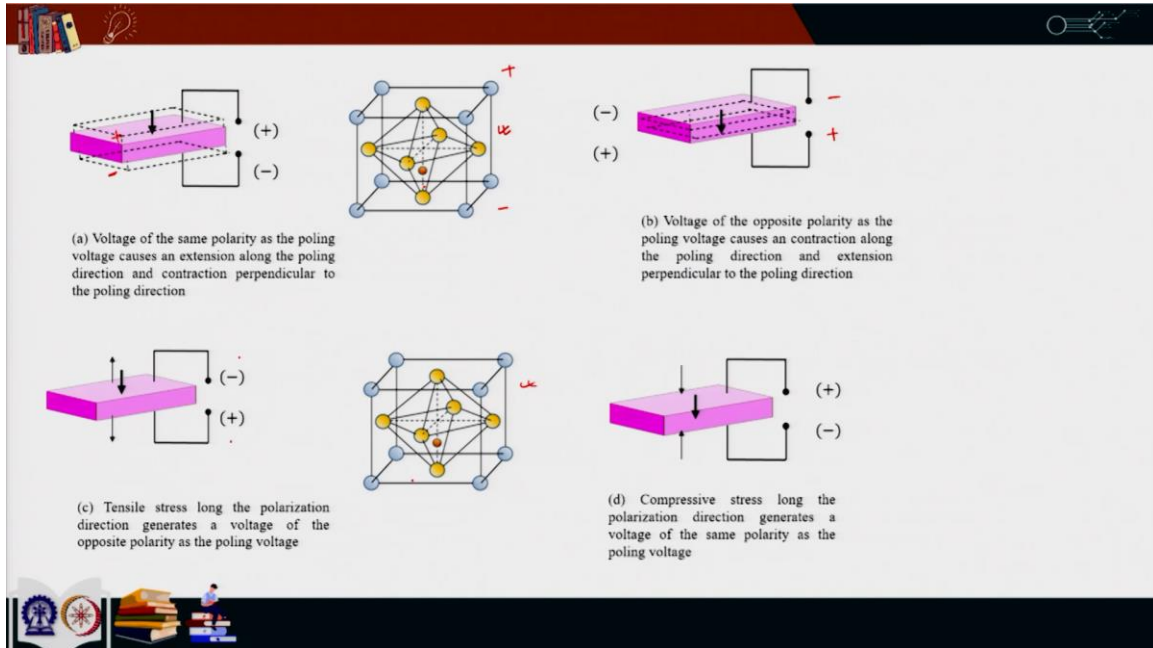
Now, if an electric field is applied in such a way that it is plus up and minus down, so, this is further shifted down. When this is further shifted down, the thickness increases and accordingly, the other two dimensions decrease. Reverse thing happens if we reverse the applied electric field. So, that was about the inverse effect.

Now, while doing the direct effect, again, assume that the polarization is from positive to negative, which means the titanium is at the lower side.

Now, if we want to, if we want to apply tensile stress along the thickness direction, if we want to increase this dimension, in that case, what happens is: if you want to increase it, the distance between this titanium and the center further increases, and that creates an electric field which is plus at this side and the minus at this side. And again, the reverse thing happens when we apply compressive stress along the thickness direction. So, with

the help of this perovskite structure, we can explain these phenomena. The direct and indirect phenomena, when it is: where it is stretching, where it is contracting, or when it is applying a positive voltage, when it is generating a positive voltage, when it is generating a negative voltage, and so on.

(Refer Slide Time: 35:20)



Thank you.