Nature and Properties of Materials
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Lecture 24
Smart Materials 2

In the last lecture I have given you a broad overview of all the smart materials, which are generally used. But in this lecture I would like to focus on a very particular part material, which is known as piezo electric material and which works on the principles of piezo electricity. So these are the things that I have planned to cover.

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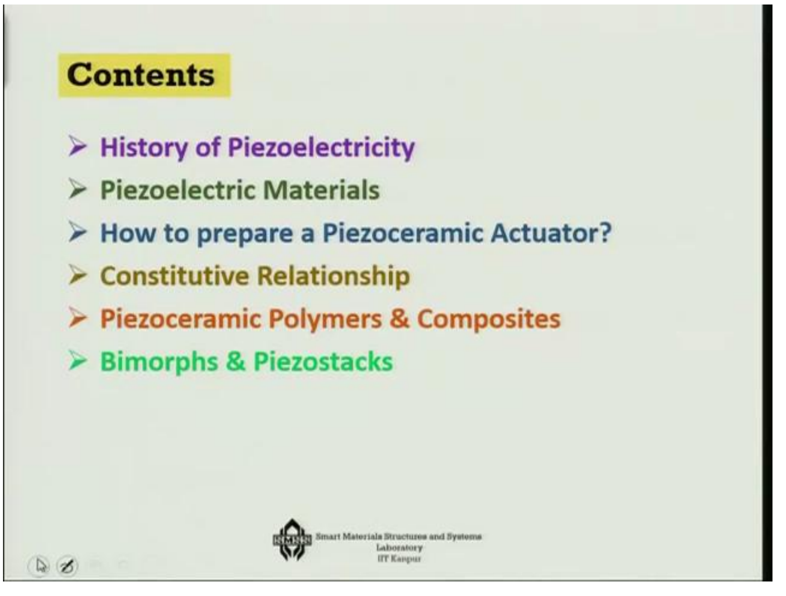

First I will give you a little bit of history of piezo electricity because once the history revolution, then it is easier to keep it in your mind about the how the developments are progressing in this field. Then I will talk about piezo electric materials and I will tell you how to prepare an actuator using one of these piezo electric materials like Piezo ceramic powders.

Also I will talk about the constitutive relationship, which is essentially the stress strain relationship the stress strain relationship of Piezo electric material. And then I will talk about the Piezo ceramic polymers and composites and finally I will talk about Bimorphs and Piezo stacks. So let us 1st start with the history of Piezo electricity.

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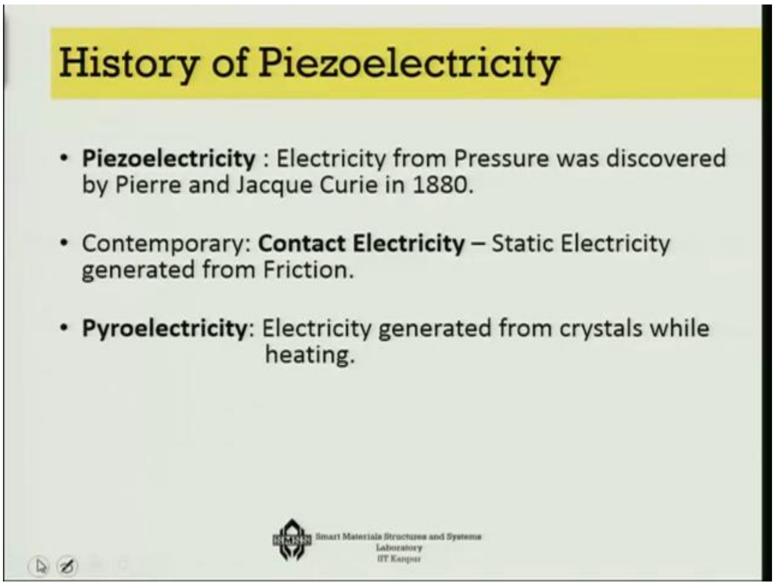

Now, Piezo electricity has a long history, long history in the sense that above all the modern advanced materials that we are today working on and that is very relevant in today, Piezo electric material is actually the oldest among them. And the word Piezo means actually pressure. So Piezo electricity is in other words, it is electricity from pressure which was discovered by Pierre and Jack Curie, we have heard about the Curies in many contexts we have heard of them, their contribution to crystallography, their contribution to Radio activity studies these are all very famous.

So Pierre and Jack Curie worked in 1880, when they were actually working on some of the crystals like tourmaline crystal and they found that you can get electricity out of the Piezo electric material that was the first of this kind of a discovery. Then at that time there were actually two sources of electricity that was known to us, so that is one of them is contact electricity, which is actually so called getting electricity that gets generated from friction. And the other one is actually Piezo electricity which is electricity that is generated from crystal while heating because that Pyro means heating.

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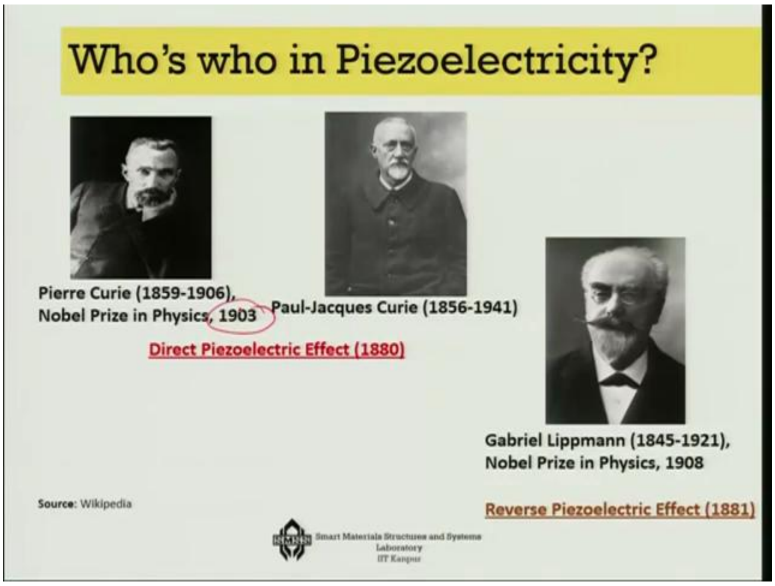

So, contact electricity, heat generated electricity and then in that series they found out pressure generated electricity. Now then that was the first observations experimentally about Piezo electricity. And 1903 Pierre Curie got Noble prize on this particular thing that pressure is generating Piezo electricity, which is also known as direct Piezo electric effect.

After a few years, Lippmann very interestingly studied the same problem and he has proved theoretically that if pressure can be the cause of generating electricity, then electricity can also create deformation or pressure in a crystal that is the reverse is also possible, this brought another Noble prize in 1908, so that is known as the reverse Piezo electric effect. So you should know about these famous names in Piezo electricity Pierre Curie, Jack Curie, Lippmann, Byods, (())(4:13) I will talk about as and when these names will be coming up.

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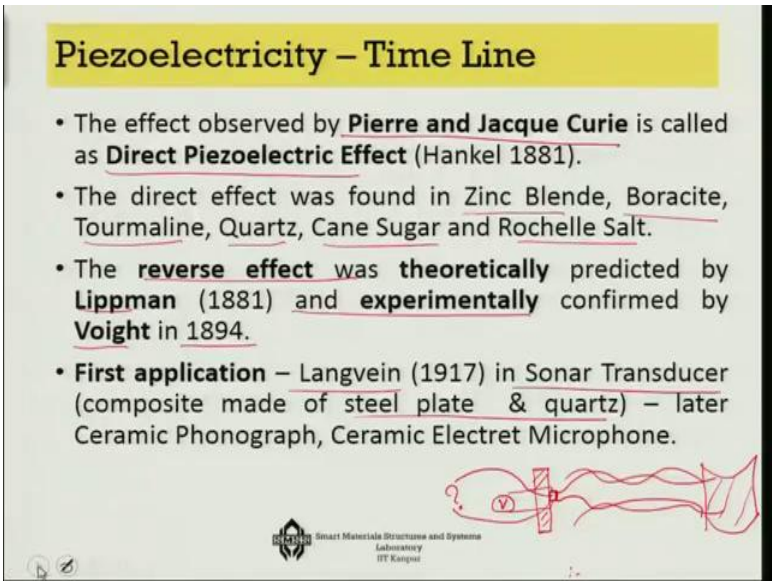

The tagline if you look at it then, the first is the direct Piezo electric effect which observed by Pierre and Jack Curie in which the mechanical force actually generated electric charges. This was found one by one in materials like Zinc Blende, Boracite, Tourmaline, Quartz, Cane sugar and Rochelle salt, so quite a few crystals they found that they show this particular behavior.

In 1881, Lippmann suggested the reverse effect and he got experimentally confirmed by Voight in 1894 however, the engineering application took some more time at least 30 to 40 years when Langvein first used this principle in order to develop a Sonar transducer. So this sonar transducer which is actually made of a composite which is made of steel plate and quartz, so what you can do is that suppose you have a steel plate and you have a quartz at the centre and then you apply voltage to this quartz, so you are applying voltage at a particular frequency, it is not a constant voltage but it is varying.

And as you are varying the frequency, you are getting vibrations in this particular steel plate, so that steel plate gets vibrated. As it gets vibrated, it actually generates waveforms on the water. Now suppose you have something here okay, so enemy submarines which is here at this location and waveform gets hit from here, so it is actually coming back each of the waveforms and some of them are hitting this Piezo electric element back.

What will happen then? This is the electric effect because of the change of the pressure over here, it is going to generate a signal itself, so you can actually trap that and you can find out what is this signal and that signal is going to tell you that whether there is an enemy submarine or enemy ship or anything like that okay, so that was the 1st application that Langvein has thought of the Piezo electric effect.

But starting the journey from there today you have so many applications for example, many of the gas lighters you will see you have this application that as you apply pressure, you will see the gas lighters sparks and generates a little bit of light, which is good enough to actually ignite the gas, like that there are many applications that have come up from this 1881. Now, one of the reasons why all this later on these applications are possible for actually because of the discovery of the Perovskites.

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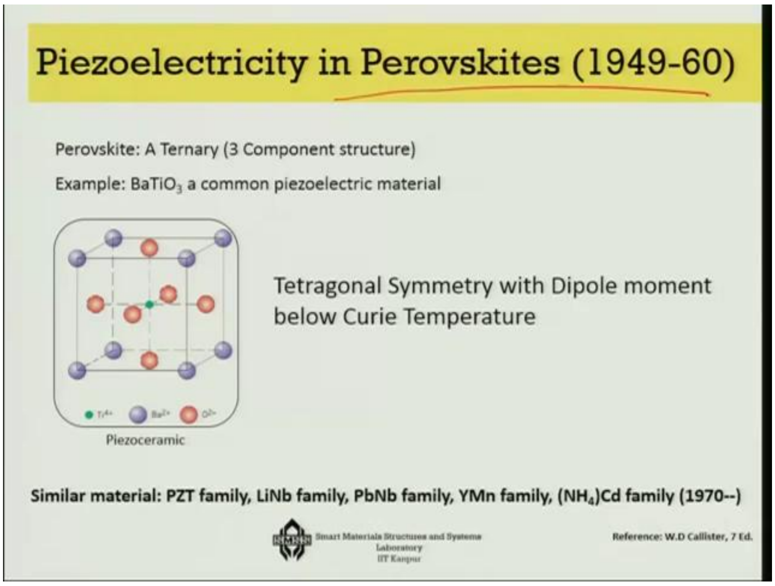

Perovskites of course, it was 1st discovered in nature by scientists Gustav Rose and in Ural Mountains in a small crystal he found that it has a very interesting property that it is not a single oxide, but a ternary oxide, something like Barium titanate. So that means it has 2 of the metallic types and one of the oxides. Now, Perovskites the structure of Perovskites is something like, which has a Tetragonal symmetry with dipole moment below Curie temperature. What is the source of this dipole moment?

For example, if I look at this tetragonal symmetric crystal structure, we will see that the titanium is at the core of it and the Bariums are here at the vertices and oxygens are at all the phase centers. Now, what happens is that this particular structure is stable in a very small margin, the moment you try to deform the structure suppose I am applying a compressive and deforming it and then this fellow will actually get shifted from its location by a little bit because you can never apply very perfect force system, so at that atomic level it will get deformed.

And that small deformation is good enough to disturb the structure, so that you get electricity out of it because you see that titanium is electron giver and oxygen is electron taker, so this titanium at the Centre is just pseudo-stable and it will generate a dipole moment, the moment you actually deform it. It was found later on that it is not only Barium titanate, but materials like lead zirconate titanate, lithium niobium, lead niobium, yttrium magnesium family, NH4 CD family, et cetera, all of them show this kind of Piezo electricity.

And this is the electricity effect is actually much more pronounced than the Piezo electricity that was earlier found out in 1880s in materials like Rochelle salt, et cetera for quartz for that matter. So here the deformation is much more or the voltage generation is much more, we will talk about it in the comparison. But because of the predominant discovery of this Perovskites, this name has come after a very famous Russian geologist whose name is actually Perovski, his name this is done, so the discovery of the Perovskites actually open a whole domain of new technology for smart transducers.

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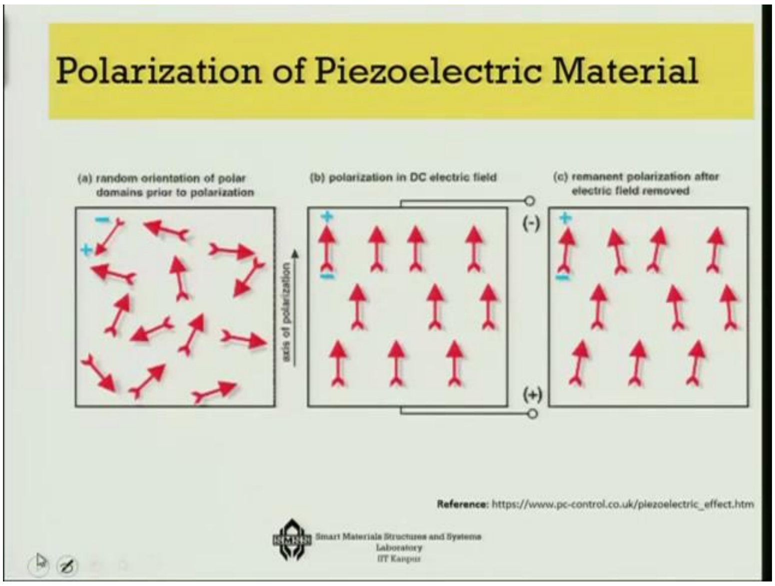

Now the dipole moment in the Perovskites, if it is not polarized, it is always random like this. Very random, each one of the atom will show a random dipole direction, which means that if you apply a voltage because some are oriented, some are not, and you would not get too much of a change in the deformation. On the other hand, if you apply a DC electric field and then at a very high DC electric field and then you remove that electric field, you will get it partially aligned here partially aligned.

And once we do that, we call this to be process of polarization, then if you apply voltage you will see a very sharp effect of Piezo electricity on the system. So how do we define this Piezo electric effect in case in the case of 3 dimensional let us say a system? So we have the core material to be Piezo electric here and you can see.

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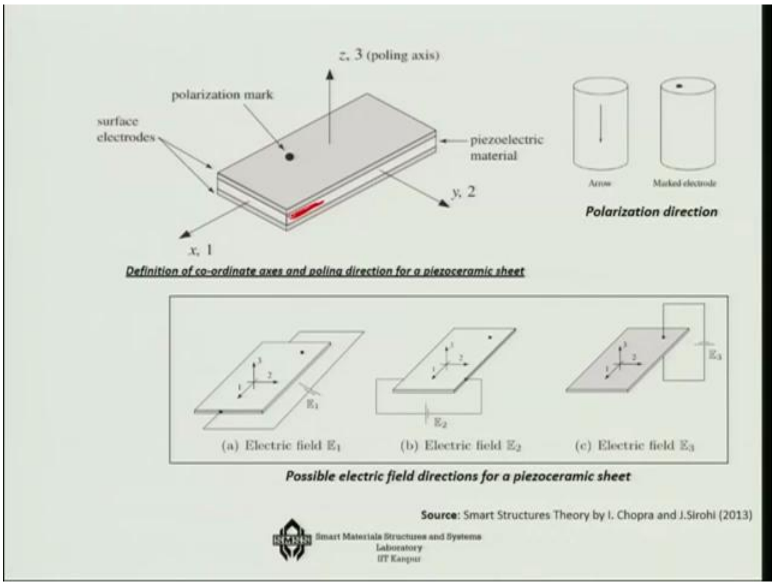

And there are 2 surface electrons where you are actually sort of giving the polarization in order to give the polarization you have to… Every time you actually purchase it in the market you will see a black spot, which gives the polarization mark, this is important and I will talk about it soon. Now, you can define very easily because it is a 3 dimensional object you can define very easily the 3 axis.

So this is suppose the X axis or 1, Y axis or 2 and Z axis or 3 and we have to keep in mind that this point is showing that the poling axis is the Z direction and toward this arrow itself, so that is the polarization direction in this case suppose you see this arrow here, then this is the polarization direction of the system. Now, you can get 3 different types of electric fields, one is that if you attach this to the 2 of the shorter of sides, you get an electric voltage E.

If you attach this to the 2 of the longer side, you get an another electric field E2 and if you attach this across, then you get another electric field which is E3, so thus E1, E2 and E3 the 3 type of voltage generation is possible from a Piezo electric material. So, let us look into now this stress strain relationship or in other words, constitutive equation of Piezo electricity.

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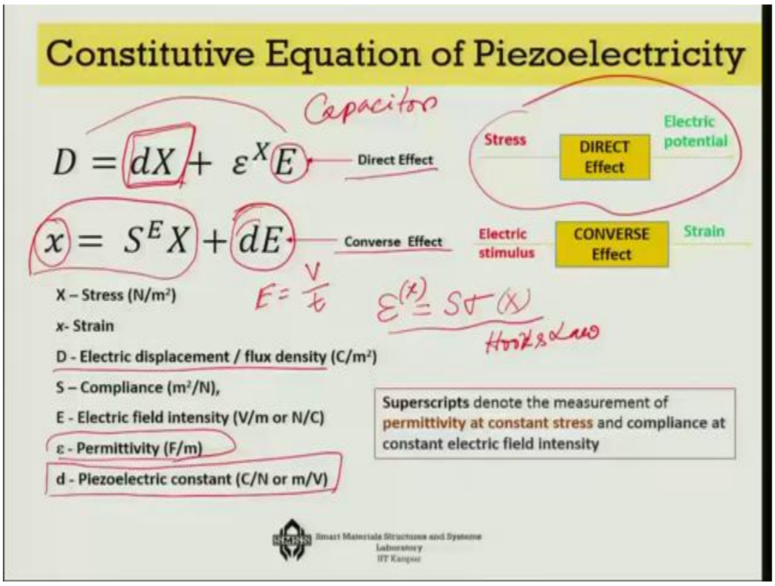

The stress strain relationship that you have here, you may not be able to readily identify it because we have changed the symbols and we have made it compatible with the IEEE way of writing the symbols. However, if I just tell you that the 1st part of the 2nd equation if you look at it x is strain, so you know that you generally show it as Epsilon, in this case it is not. In this case Epsilon is permittivity, but generally you say that Epsilon equals to S Sigma that means the Sigma is the X and Epsilon is the small x here, capital X and small x are the small strain and the as the strain and the stress in a material.

Now this relationship if you know that this is nothing but the Hooke’s law, right in one form or the other. So, the first part of the 2nd equation is actually the Hooke’s law, the only thing that is added here that made it functional, made it smart is that if you add the electric field E in fact, E by definition is actually voltage across the thickness V over T. So if you apply the electric field because of the coupling factor d, small d is known as the Piezo electric constant, you are going to generate strain in the system, so this is an extension of the Hooke’s law which is covered by the converse effect of Piezo electricity.

Now let us look at the 1st equation which is actually discovered earlier that is the direct effect. In this case once again, if you initially do not consider this part then what you are going to get is actually the standard relationship for a capacitor because that the electric field displacement D as the electric field displacement of a capacitor that is proportional to the electric field that you are going to apply and also the permittivity of the field that I had already discussed.

So, this part is a standard equation of the dielectric material, the addition of the dX part, well actually once again capital X is the stress and small d is the electromechanical coupling coefficient or Piezo electric constant that actually says that yes you can generate charge not only by applying a voltage, but also by applying stress that is what is the direct effect. So you have 2 different effects defined by 2 different equations in which part of the equations are already known to you, it is this additional part which when we are considering, we are getting the effect of the piezo electricity.

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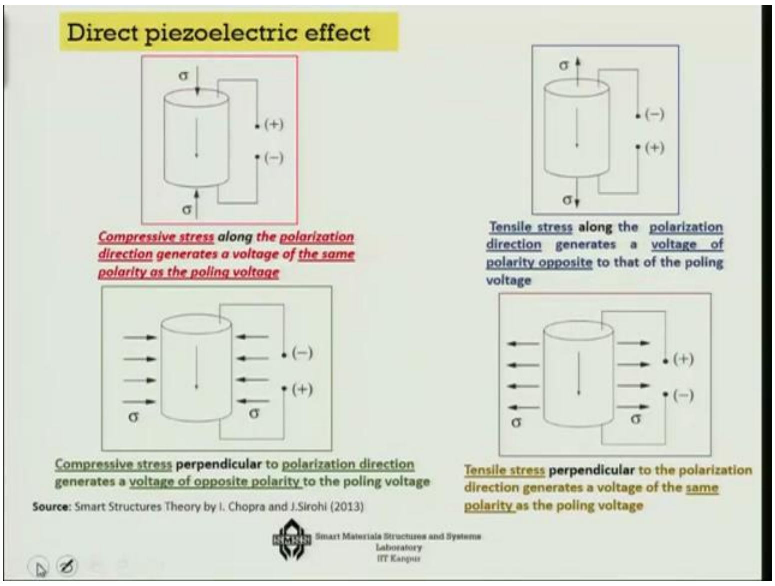

Now there are various ways in which we can actually define this Piezo electric effect in the direct effect and the reverse effect, what is positive, what is negative. One of the convention is like this that suppose this is my direction of polarization that means I have a black spot here and then if I apply actually compressive stress along this polarization direction, then it will generate the voltage of the same polarity as the polling voltage, so this is + and - it will generate the same voltage same polarity of the voltage.

On the other hand, if I apply the same compressive stress not in this direction but in the perpendicular direction, then you are going to get voltage of opposite polarity because now it is - in the top and + in the bottom. Extending the same logic instead of compression if you give here tensile stress, which is opposing the direction of actually polarization, and then naturally you will generate a voltage which is opposite to that of the polling voltage.

And in that case if you apply the tensile stress in the perpendicular direction to the polarization, then what you are going to get is a voltage which is of the same polarity as the polling voltage, so these 2 cases are just an extension of the 1st two logics. If you keep that in mind that the direction of compression match with the direction of polarisation are going to give you positive voltage.

And if it is perpendicular, it is going to give you a negative voltage. And in the case of tension, if it is opposite to the direction of polarization it is going to give you a negative voltage. If it is towards the like a in perpendicular direction tensile stress, it is going to give you the same effect as the direction of polarisation.

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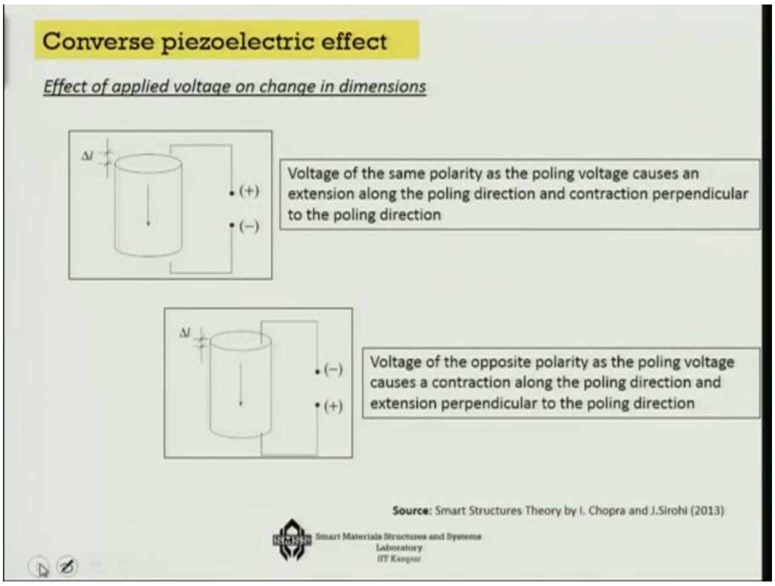

Now, for the converse Piezo electric effect, where you are interested in deforming the system, there what will happen? If I apply + and - following the direction of polarisation then what I am going to get is the voltage of the same polarity as the polling voltage, it will cause an extension along the polling direction, so it is going to expand. On the other hand, voltage of opposite polarity as the polling voltage will cause a contraction in the system, so that is how we will get the direct and the converse effect of Piezo electricity.

(Piezo Application video-Micro Piezo technology The basics)

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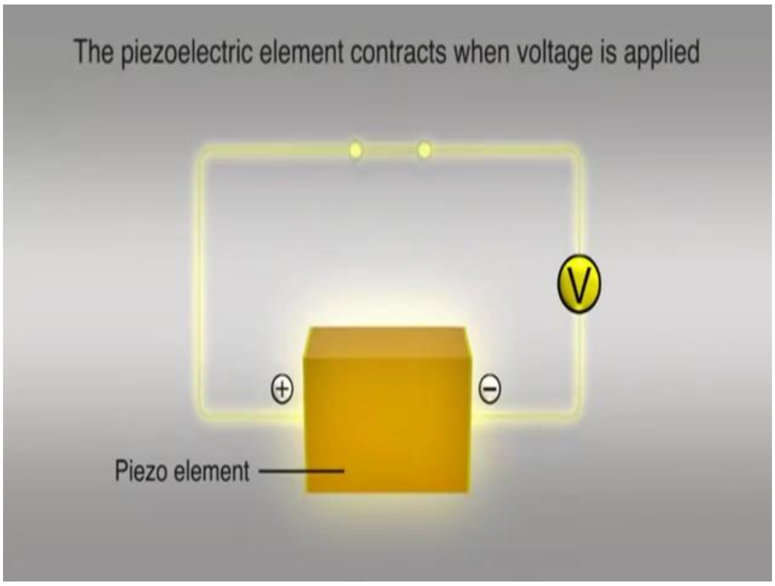
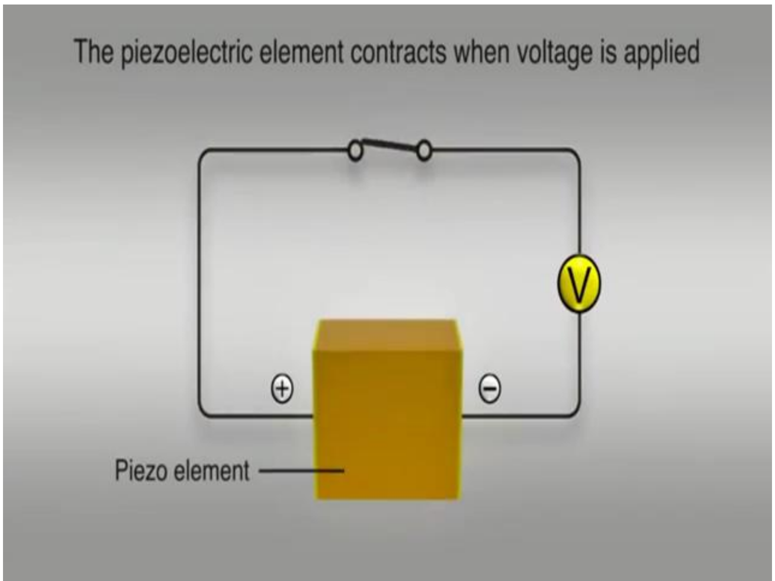
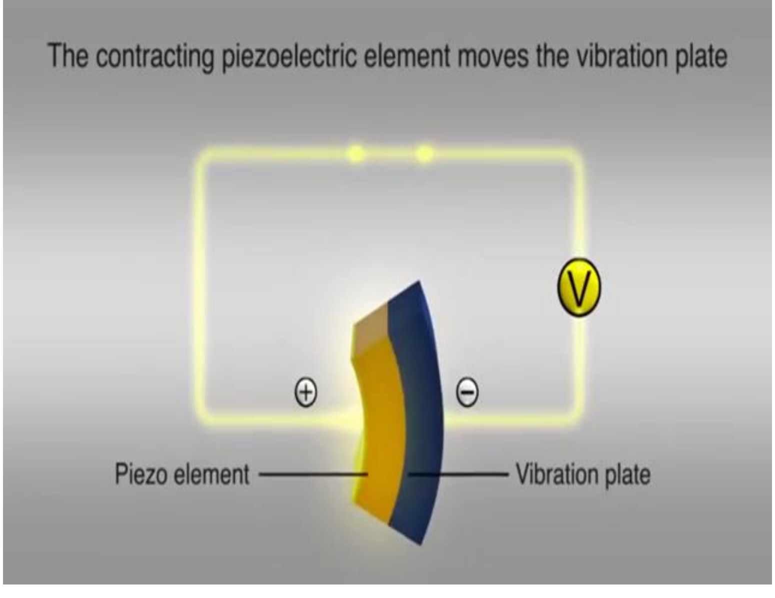
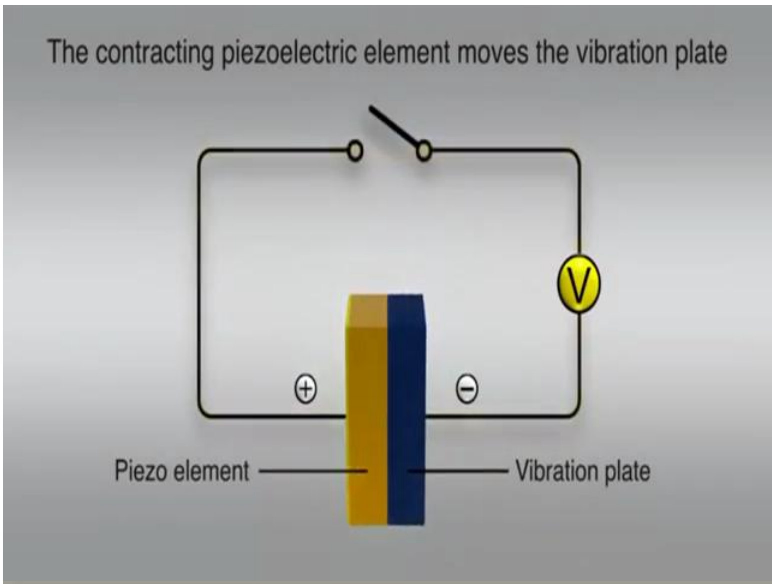
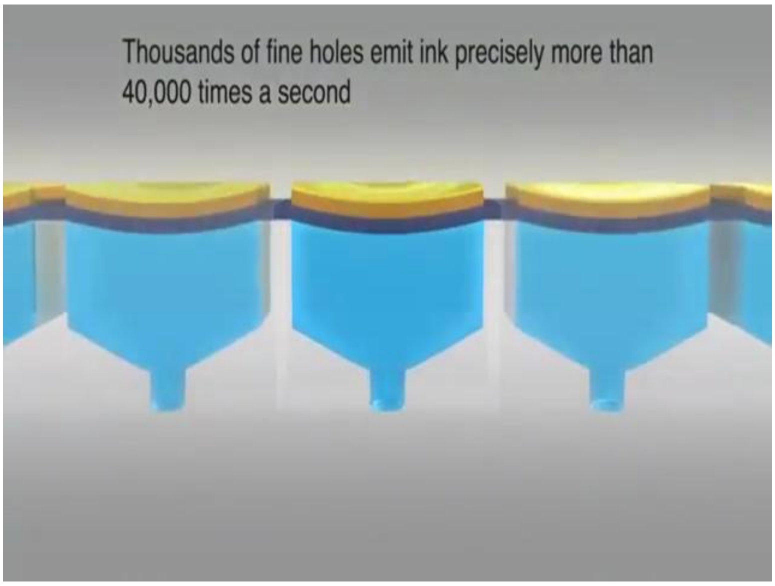







The contracting piezoelectric element moves the vibration plate
V
⊕
⊖
Piezo element
Vibration plate


This mechanical movement emits ink, with no need for heat


Thousands of fine holes emit ink precisely more than
40,000 times a second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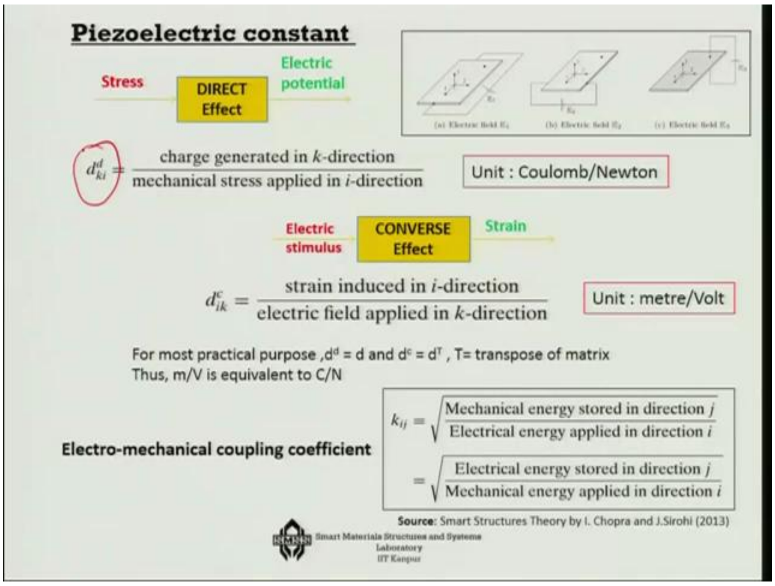

Now, again and again here one particular constant is coming that constant is electromechanical coupling coefficient or Piezo electric constant. Now that constant can be defined in two ways because you have two situations where this d was there, right. If you remember if I go back once again, you just see that in the 1st equation you have d small d and in the 2nd equation also you have small d.

So if we see that there are 2 ways of defining it, the 1st one says that charge generated in the K direction that d ki, charge generated in K direction over when you are applying mechanical stress in i direction that is one measure of d. The other measure of d is that, when you are applying electric field in the K direction and you are getting strain in the i direction. So in one case then the unit is coulomb per Newton and in the other case the unit is meter per volt.

The same constant that is very interesting can be actually described with the help of 2 different unit systems. Now, it is not only this coupling coefficient d that is important, the Piezo electric coefficient d that is important, there is a electromechanical coupling coefficient which is even more important and it basically talks about the ratio of the 2 energy that is mechanical energy stored in direction j over electrical energy applied in direction i or the other way vice versa.

So that actually tells how much of energy is getting transformed from the system, so that is even more important consideration. In fact, coupling coefficient and electoral mechanical constant, they are actually related to each other. Now, how do we prepare a Piezo ceramic actuator?

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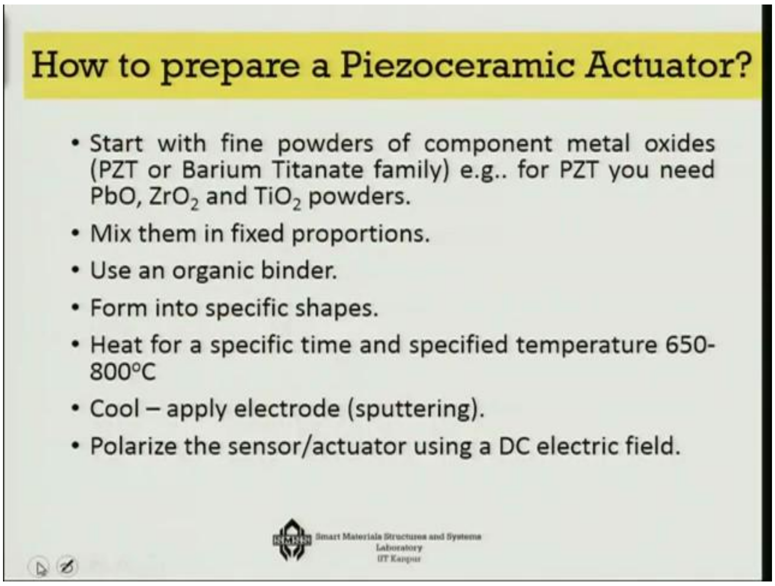

Very simple, we 1st start with a fine powder of its component metal oxides because we have to go through a tertiary like 3 element system ABO3. So you for example for lead zirconate titanate you start with lead oxide, zirconium oxide then titanium oxide powders. Mix them in fixed proportions, use an organic binder otherwise they will get lost, form into specific shapes, make them in a specific shape you call is that give the green shape and then heat for a specific time and temperature about 650 to 800 degree centigrade.

Cool it, apply electrode layers using sputtering, polarize the sensor actuator using a DC electric field, your Piezo electric actuator is ready for use okay. So once again we have to 1st take the all the basic oxide powders, lead oxide, zirconia, titanium oxide and then mix them, use organic binders, apply temperature and pressure in a particular shape and then cool it, apply the electrodes, your material is ready to be used.

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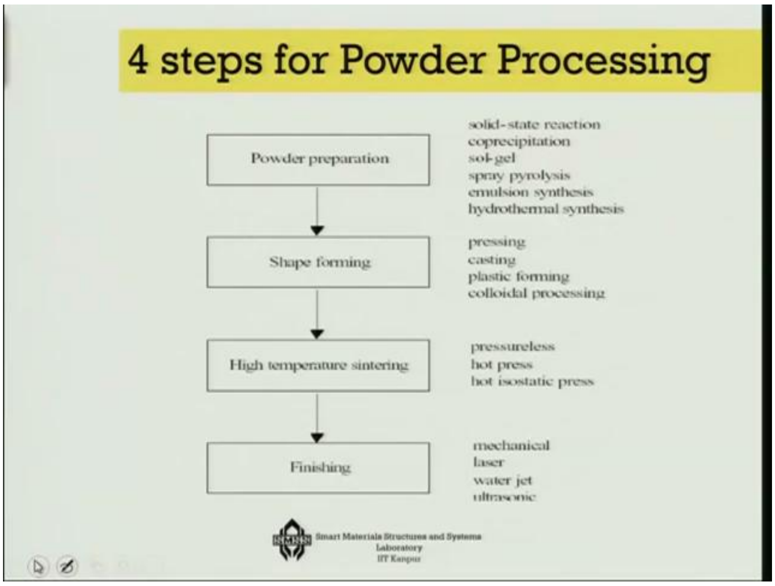

Now, there are many ways in which you can make the powders of course, you can use solid-state reaction, co precipitation, sol gels, which is it does not need heat, spray pyrolysis, emulsion synthesis, hydrothermal synthesis, there are many ways in which you can do the powdering. Also the shape forming, you can use pressing, you can use casting, plastic forming, colloidal processing, so that you can give the required shape of the actuator.

High temperature sintering can be pressure less, can be using hot press, and can be using hot isostatic press. Finally, finishing is very important because it is ceramic material, so this finishing could be mechanical in that case you may not get a good finish, it can be laser, water jet or ultrasonic. Ultrasonic, one of the best finishes that you can get out of the system. So thus you can actually make a Piezo electric actuator.

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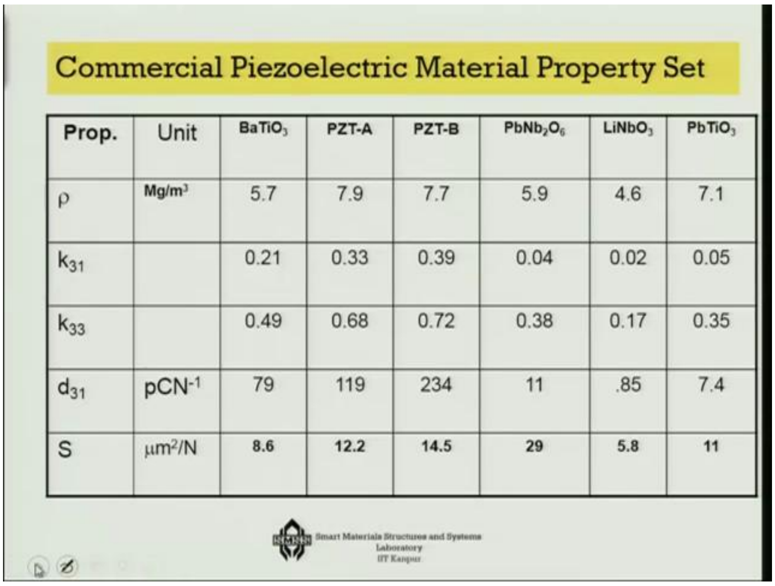

Prop.	Unit	$BaTiO_3$	PZT-A	PZT-B	$PbNb_2O_6$	$LiNbO_3$	$PbTiO_3$
ρ	Mg/m^3	5.7	7.9	7.7	5.9	4.6	7.1
k_{31}		0.21	0.33	0.39	0.04	0.02	0.05
k_{33}		0.49	0.68	0.72	0.38	0.17	0.35
d_{31}	pCN^{-1}	79	119	234	11	.85	7.4
S	$\mu m^2/N$	8.6	12.2	14.5	29	5.8	11

If I will compare the properties of some of the common Piezo electric actuators for example, barium titanate, you look at their d 31, it is 79 Pico coulomb per Newton, compare that with lead zirconate titanate you can get the highest of 234 Pico coulomb per Newton and lithium niobium, et cetera they are very small or possibly they work at a higher temperature, which is what is good for them, so this is an overall comparison of the Piezo electric material properties.

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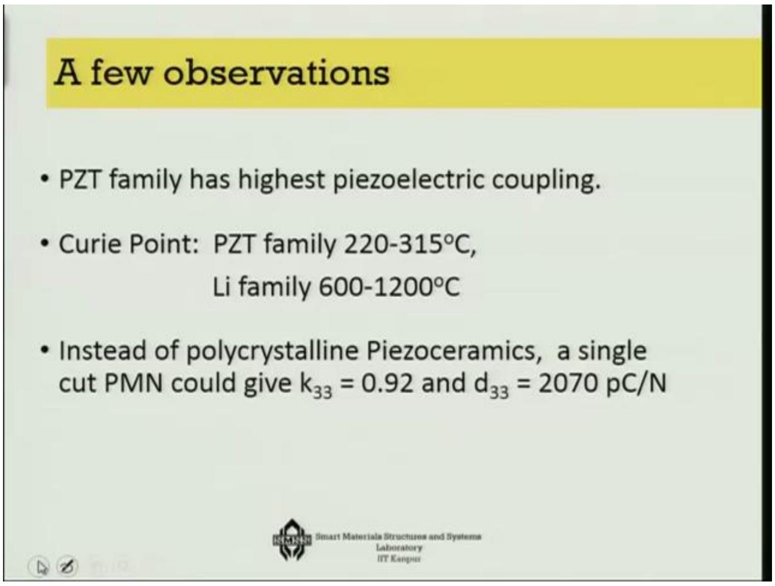

Now a few observations you can actually have from this comparison, one is that PZT family has the highest Piezo electric coupling actually, it is not entirely true but in a poly crystalline phase it is true. And in terms of a single crystal, PMN may give actually even higher and the k 33 value for PMN is about 0.92 and d 33 is about 2070 Pico coulomb per Newton, so this is possibly the best one. The Curie temperature of lead zirconate family is about 220 to 315 degree centigrade and for lithium family about 600 to 1200 degree centigrade.

Its extreme temperature resistance capability because you see beyond curie point, the material is going to lose its property, so this extreme temperature resistance capability makes this lithium families like lithium niobium, etc to be very good candidate smart materials for applications like batteries, the laptop batteries and things like that.

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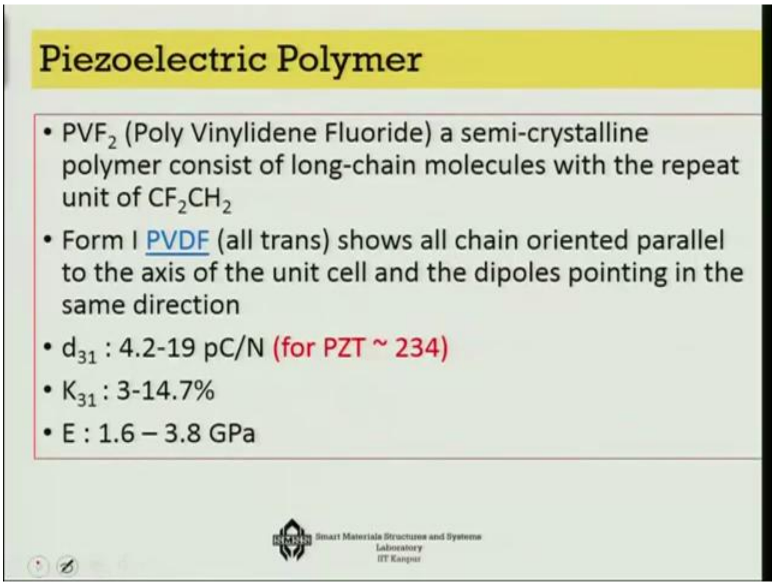

Now, make a Piezo electric polymer so that I can give better shape, you can make you can get a Piezo electric material itself, which has kind of a symmetric distribution from the long-chain molecules with the repeat unit of CF2CH2. And this (())(27:05) is what actually makes it Piezo electric. There are various forms, form 1 PVDF shows all trans, then C 6 trans, et cetera.

The d 31 that you can get is not very high at most about 19 Pico coulomb per Newton, K 31 is about at most 14.7%. But the modulus of elasticity is 1.6 to 3.8, which means it is pretty flexible. And with that flexibility if you use it, you can actually get good use of such a system as sensors.

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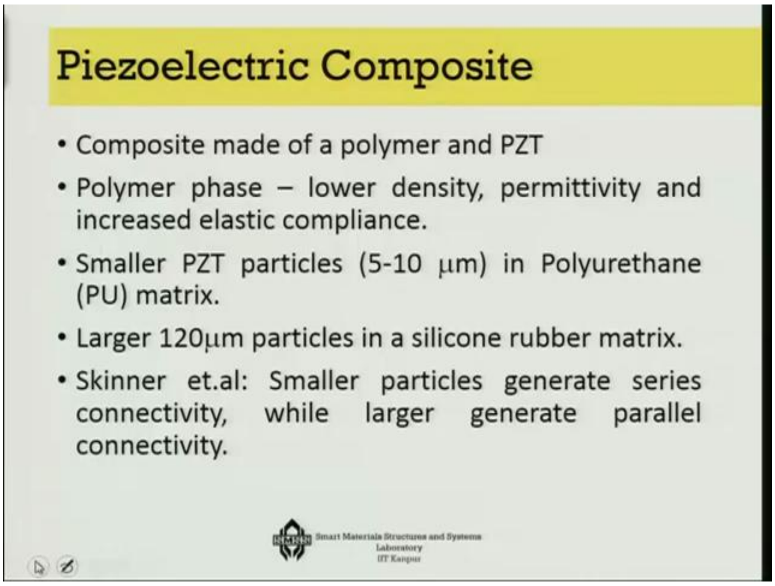

You can also make composites in which you can keep a polymer any polymer and PZT powder, this is even better than a pure polymeric system and you can make smaller particles of lead zirconate titanate for example and put it in PU matrix. And sometimes larger particles are also put in silicon rubber matrix. It has been shown by Skinner etals that by using a racial kind of a configuration you can get a very high connectivity and this composite can ultimately become a very good transducer material.

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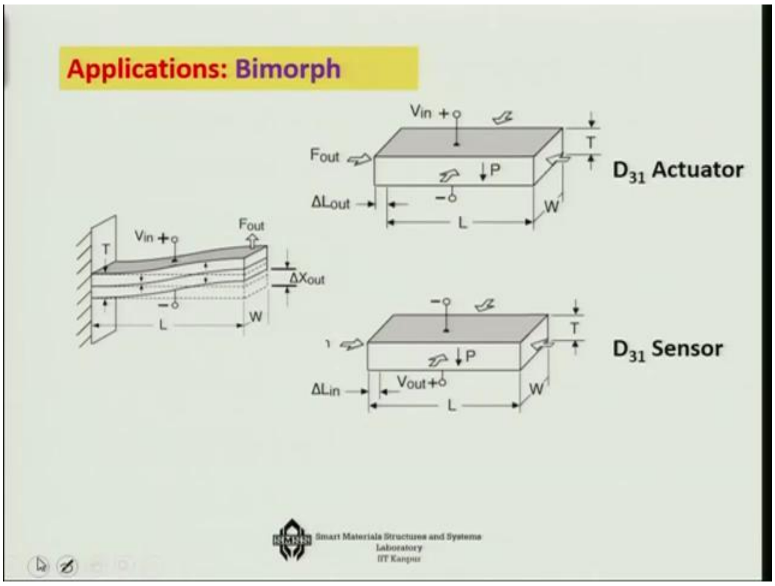

Now there are various applications of it, one is called the D 31 actuator of Piezo electric material. In this actually what happens is, you are applying the current along the 3 direction, this is the 3 direction I have already shown and you are getting the force of the deformation anywhere along the 1 or 2 directions. The sensor does the same thing, but in this case instead of the stress, it has to sense the displacement and then convert it in terms of the voltage.

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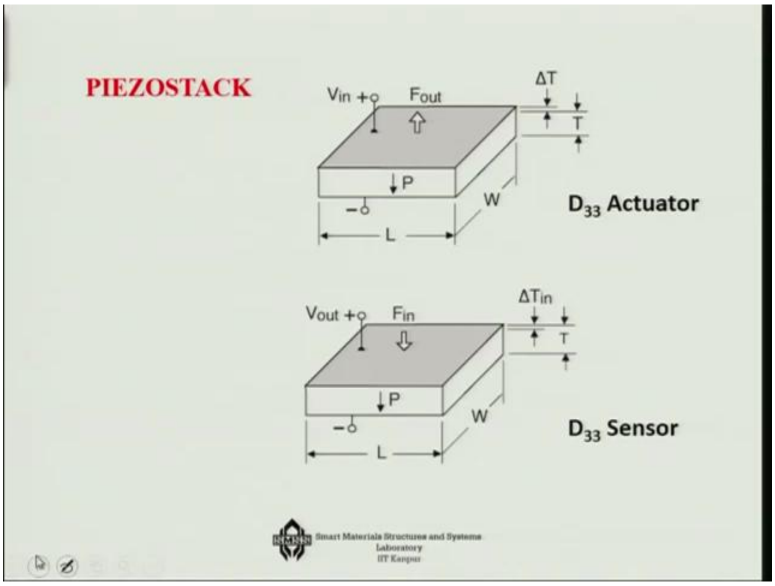

Now this can be done in another manner, it can be done as a stack also. So what you can do in such case is that you apply the voltage over the electrodes and in the same plane you take the force out, this is what is called Piezo electric stacks and this can be done as actuator, this can be also done as sensor, so there are various combinations that you can play.

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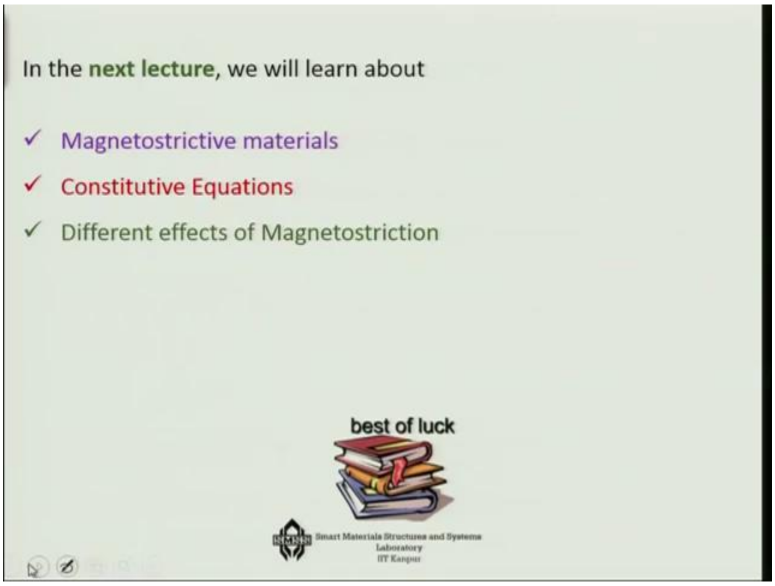

So this is where we will stop today, in the next lecture I am going to talk about magnetostrictive materials, their constitutive equations and different effects of magnetostriction, thank you.