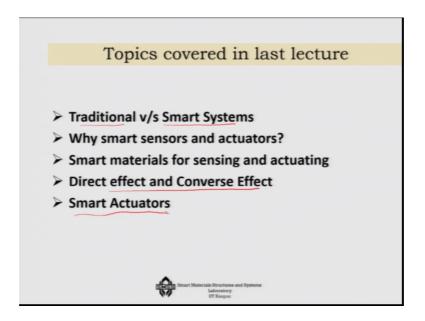
Smart Materials and Intelligent System Design Prof. Bishakh Battacharya Department of Mechanical Engineering Indian Institute of Technology, Kanpur

Lecture – 02 Piezoelectric Material

Welcome to the second lecture of module 1, in the overview of smart materials.

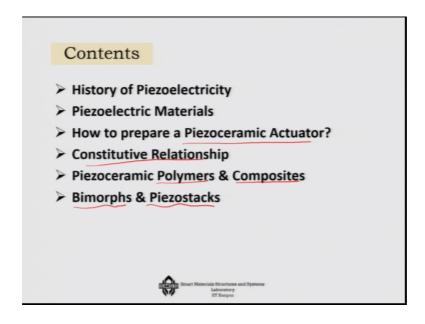
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So, our focus today is Piezoelectric Material, now what we have covered in the last lecture very very briefly, we have talked about it lot about traditional system versus smart system, we have also emphasize that why smart sensors and actuators are important for us, then we have talked about smart materials for sensing and actuating. And we have talked about the direct effect and the converse effect you know in terms of sensors and actuators. If you remember that we have said that direct effects are generally used for sensors and converse effects for the actuators, we have also talked about the smart actuators.

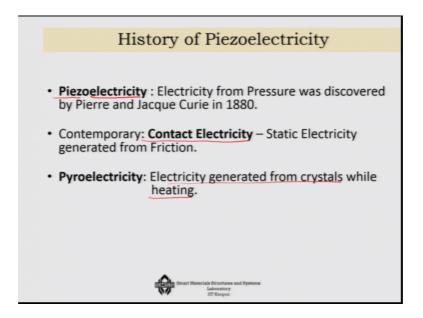
Now, today our focus will be the piezoelectric materials, which is the most widely used smart material and it has a legacy of its own.

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So, that is why I first want to talk about the history of piezoelectric material, the piezoelectricity itself piezoelectric materials how to prepare piezoceramic actuator what is its constitutive relationship Piezoceramic polymers or Piezoceramic composites, and then how you can device an intelligent system like bimorphs and Piezostacks by using piezoelectric materials, this is what is our goal in this particular lecture.

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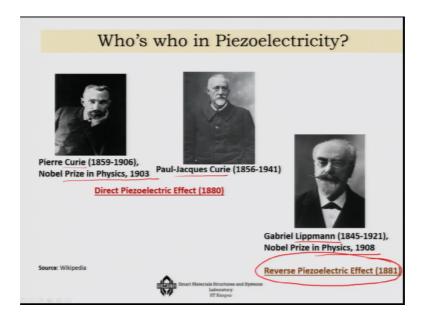


Now, let us talk a little bit about the history of piezoelectricity. So, the when these term piezoelectricity was coined at the time there was this term called pyroelectricity; that

means, it was known that some crystals if you heat it up they generate actually charges and that means, electricity can be generated from crystals while heating up that was known.

And also it was known from the static electricity that there is something called contact electricity; that means, if there is a friction that can generate charge. So, when these you know <u>eurie_Curie_brothers</u> Pierre and Jacque <u>eurie_Curie_in</u> 1880, they found out that pressure can also generate charge the word pressure is called Piezo you know Greek these things. So, they thought that let us give this as a new name in terms of electricity the source of electricity is pressure here. So, it is a piezoelectricity so, that is how the piezoelectricity term get coined.

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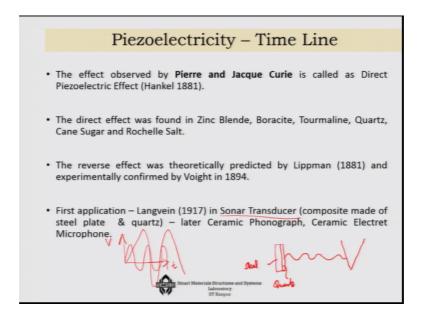


And who are the people behind this? this This 1880 direct piezoelectric effect in which pressure was generating the you know this voltage; or the charge in the system. So, that was actually discovered by Pierre eurie Curie and Jacque eurie Curie, they got in fact, Nobel prize in 1903 for this very important discovery. And interestingly Lippmann have gone through the whole thing and he was the first person to develop actually the crystal structure, the analytical relationships and he has theoretically predicted, that if pressure can generate charge then voltage can also generate in this materials deformation.

So, that was his prediction and that was experimentally verified, as a result he received the Nobel <u>prize Prize</u> in 1908 for the <u>reverse Reverse piezoelectric Piezoelectric</u>

effectEffect, in which as you are applying the electric field then you know he is showing that there is a change in the mechanical property that is happening to the system. So, eurie Curie brothers are responsible for piezoelectric say sensor development. And Lippmann's analysis responsible for say piezoelectric actuator development. So, that is how the entire field started.

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However, this all happened long before even the <u>first_First_world_World_warWar</u>, because it was you know in 1880s etcetera we are talking about. it at At that the time this piezoelectric effect was only found in certain materials like say zinc blendes, like boracites, like tourmaline and quartz cane sugar see. So, many materials people tried that what are showing it and Rochelle salt. In fact, sugar crystals if you can manage to get a big sugar crystal, keep it in a dark room and apply a sudden thrust on it by a hammer.

You will see the strike of light in it. So, that you know is the point that proves that cane sugar contains this piezoelectric effect. Now, the reverse effect was actually theoretically predicted by Lippmann, as I told you and experimentally confirmed by Voight and that came at a later stage. The application; however, first came was in the first_world_war_War_ as usual war, you know forces people to develop some cutting age of technologies. So, in this particular case this sonar transducers were actually developed in which the idea is that, if you can have a composite made of steel plate and quartz, then

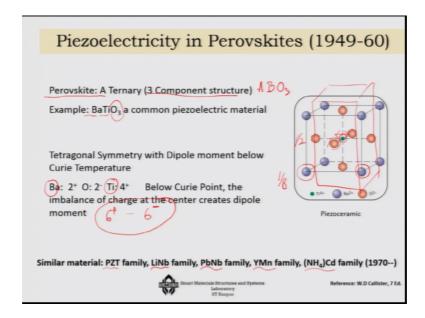
you consider that you have a composite ok, which has a steel plate and a small level of quartz in it.

So this is a steel plate and then a small quartz, you know over it. Now, whenever you are using it a you know for transducers sonar transducer mostly for submarines. So, as the you know as a ship is say passing by ok, it is producing mechanical wave, that mechanical force variation that is coming up here, on the system that is creating in this particular system, a particular variation in terms of a voltage in the system. If you look at this that in this composite system, as a ship is passing by it is producing actually a mechanical wave which is hitting this quartz quartz part.

Now, this-quartz part being piezoelectric in nature, then a as the wave is hitting it will be you know getting expanded and compressed and as it gets expanded and compressed, this quartz stream, it is going to actually produce what you call a voltage in the system. And the because it is with the steel we will later on show that for bimorph kind of systems, it actually increases this bending effect, and And hence this you know bending that is happening you know is called actually helping it to create charge further.

So, mechanical bending is actually creating charges in the system; and that charge is used as sonar transducer. So, you can actually essentially analyze in a particular you know oscilloscope, that with respect to time if you look at the charge in terms of the voltage, how this voltage signal is happening. And suppose you know if it is a normal wave it will be like this and suddenly if there is the ship entering, then you know this voltage is increasing. So, you know that you know you can that there is a presence of a ship or enemy ships etcetera. So, that is how first this transducers were actually you know coming into picture and that was the first application of this piezoelectric materials.

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Now, this kind of applications after you know finding it in terms of Rochelle salts and sugar cane sugars, and quartz etcetera people started getting interested that, exactly what kind of crystal structure produces this kind of piezoelectric effect. And it was found that a broad group of crystal structures which shows, this they are actually Perovskite in nature, is named after a Russian famous geologist who first found out this type of materials. Now, Perovskites are actually a ternary ceramic, which has three component structure and we normally call it as A B O 3.

So, the first two components are for example, two metals like say barium and titanium so, it can be metallic oxides along with a metal nonmetals and or two metals, but it has to have these two elements of oxides. So, there A Bs and along with that you have the oxygen there. Now, how they are arranged that is also very interesting, they are generally arranged in a tetragonal structure, as you can see here that the bariums are all sitting at each one of these corners of the tetragon. And oxygen is there at the face centers and, titanium is at the very root of the whole thing.

Now, this crystal structure is arranged in such a manner, that they are inherently balanced. So, that inherently there is no charge in it as long as they can maintain this tetragonal symmetry. So, for example, if you look at barium, it has 2 plus charges but also each barium is actually shared among 8 such you know crystal structures surroundings so; it becomes one eighth of it.

So, essentially you will see that considering the barium and titanium together, you are getting 6 plus ok, on the other hand if you look at oxygen's they are actually shared with another ok, such system in the adjacent crystal structure. So, they will become half of it. So, if you consider all these oxygen's together like 1 2 3 4 5 6 here. So, that will be equivalent to 6 minus so, this 6 plus and 6 minus cancels each other. So, that it actually gives you a neutral charged system.

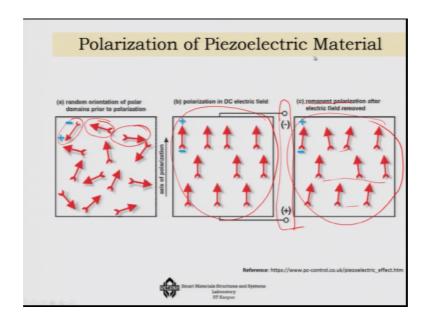
However as long as the symmetry is maintained. Now, let us say I am just deforming this structure ok. So, I am applying a mechanical force to this structure, the moment I do that you can very easily see that the titanium at the center with respect to these oxygen's, they are actually far away in comparison to this oxygen's. So, they are closer to some oxygen atoms and, they are farther from some other oxygen atoms.

So, these immediately discharge, because you know that the Coulomb force is inversely proportional to the distance. So, this immediately discharges the position of the titanium atom. So, they may try to move in one of the directions. And the moment they try to move you in one of the directions immediately, there will be charges that will be happening to the system.

So, thus you know this systems actually if you think of it that in reality the in a crystal structure, there are hundreds thousands or millions of all these single cells that are arranged. So, at any particular time every cell is having in a some kind of a stressed state. So, every cell is not in its pure tetragonal state so that means, there will be a spontaneous piezoelectricity that will be present in such a system. And this not only happens for this barium titanate A B O 3s, but also for other materials like lead, zirconate, titanate, lithium, niobium lead niobium yttrium and manganese based system or NH 4 cadmium based system all this things are later on found out.

In fact, the most of the development happened towards the end of the last century. So, as a result we get materials where this effect is more and more pronounced. So, you can use it for real engineering applications.

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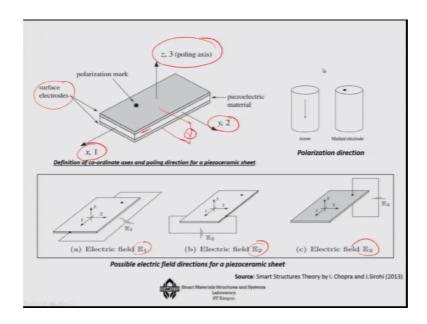
Another interesting thing is that imagine that, you have the a block of this smart material. Now, it will be having as I told you that millions of this crystals and, each crystal there is a state of stress which is creating you know charges from it, which means it has a particular dipole directions positive negative in it inherit.

So, each crystal is having its own dipole moments and a dipole vector signifying it and at any particular point they are randomly oriented. As a result the whole system will hardly show any piezoelectric effect, but if you apply a high voltage then these dipoles will actually align themselves towards the voltage. And then if I remove this voltage there will be still remnant polarization, which will be happening this remnant polarization would mean that, they will not entirely lose their directions to some extent they will lose, but they are still a sense of alignment in them.

And that would actually make them piezoelectric. So, in order to make this is very crucial a smart sensor or a smart actuator, a from piezoelectric material you have to first check the piezoelectric material its natural state. And then you have to apply a high voltage across it and, we generally electrode it because otherwise how will you apply high voltage. So, you electrode it at the top and bottom and apply the high voltage, then these kind of polarization would happen to the system, then I will be withdrawing the voltage and then it will be useful as a sensor or actuator, because it will be still having

this remnant polarization in it. So, that is the way we generally develop piezoelectric you know actuators.

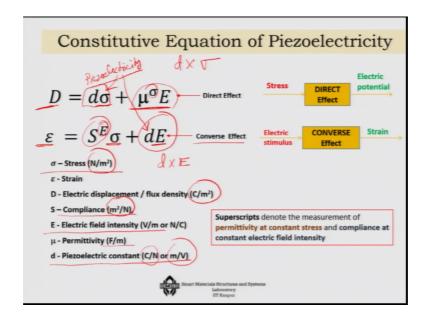
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Now, there are some sign conventions that are related to it. So, as you can see here that the base material here, this is piezoelectric and whereas, there is the surface electrodes at the top and the bottom. And also there is a polarization mark which shows that which size is positive you know how it is to be connected between the positive and the negative terminals of a voltage. Now, in the in plane part we have the axis which will be interchangeably we will call it x axis or 1 and y or 2 so, 1 2 or x y are actually in plane direction and out of plane direction is actually z 3, which is also known as the poling axis.

So, if you consider this piezoelectric material to be a plate, then it is across the plate that is how it is across these plates we are applying the voltage, you know to the system so, that is what is the polling direction. So, if you look at it that in this particular case, if you apply it along the plane along x direction, then electric field E 1, then this direction electric field is E 2 and if it is across which is what is generally done is electric field is E 3. So, you have to keep this sign convention in our mind while actually getting the constitutive relationship of the system.

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Now, what is the constitutive equation of piezoelectricity, where there this equation is developed in such a beautiful manner that there are always two parts in it ok, if I consider only the non smart part for example, in the first equation if you look at it which is on the direct effect and in the direct effect, if you remember if you apply stress you are getting charges. Now, you know that charges can also be developed in any dielectric material by applying the electric field itself. So, if I consider the relationship between d and mu E this is for any general material this will happen ok, there is no smartness in it.

If it is a dielectric material if you apply electric field, you will be getting charges ok; however, if you are applying mechanical stress and getting charges then this part comes into picture and this is what is due to piezoelectricity. So, that is the additional smartness in the whole system ok. So, that is what we have to keep in our mind and this d sigma, there is basically two term in it one is the D, which is known as electro mechanical you know coupling coefficients sometimes we call it as piezoelectric constant and sigma is nothing, but the d time sigma and sigma is nothing, but the stress ok.

But this is in vectorial you know vector notations. So, we will come to the vector notations and these are all you know matrix equations, we have to keep it in our mind. Only in very special cases, they will become linear equations, then this is you know that is one part of it ok. If I look at the converse effect if you see then here epsilon is the strain and strain, we know can be generated by stress which is related by the Hooke's

law, where S E is the compliance and that part there is no smartness in it, but if strain can be produced with the help of the electric field, or you know so; that means, as an actuator. So, that is the part which is piezoelectric in the second equation.

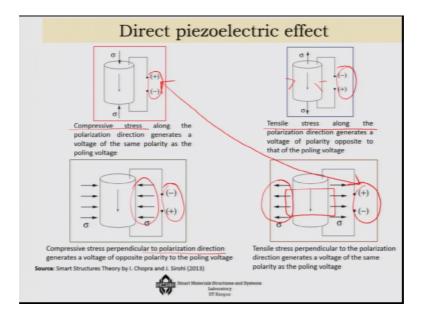
So, in the direct effect this part is giving me piezoelectric nature and in the reverse effect, it is this part which gives me the you know piezoelectric part into this particular governing equation. Now, if you look at d it here it is d times E. So, again d is the piezoelectric constant and E is the electric field intensity, which is generally in terms of voltage per meter or Newton per coulomb.

So, the units are important stress unit is Newton per meter square strain in unit less as you know electric displacement is coulomb per meter square compliance is meter square per Newton electric field I told you already permittivity, which comes into picture for this particular part, permittivity you know farad per meter and piezoelectric constant coulomb per Newton or meter per voltage.

So, and another thing you would be noting that there are some superscripts, we have given here this why this superscripts are there, when I will be measuring the charges at that time these permittivity may change by the application of stress. So, that we should not allow so; that means, you know in each of this constituent and in this case also the compliance may change by the presence of the electric field, that we should not we have to assume that to be constant.

So, in each of the cases the superscript means is that the mechanical properties assumed to be constant against, either in this case electric field and in this case against mechanical stress that, we have to keep in our mind while applying this particular you know set of equations in the constitutive relationship.

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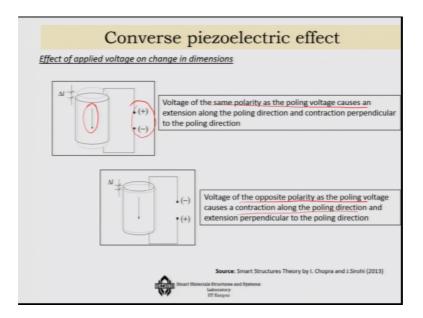
Now, direct piezoelectric effect how would it look like well, if you consider a block like this and if you are applying voltage you are getting this, you know expansion and contraction of the block. If you try to stop that you are going to get actually compressive stress and at the polarization direction so, that is one way that the this plus minus consideration is giving you a compressive stress and, if you reverse this plus minus to minus plus then; that means, you are applying these opposite to the polarization direction, then you will be getting tensile stress in the system this is very important that you have to follow the polarization direction ok, that will be always you know given you with that point as I told you in the last case.

And if I give reverse polarization to a large extent in some ceramic materials it may actually crack. So, you know we have to know that which way we have to apply the voltage for certain class of materials. Now, in this particular case here you know you are applying the compressive stress, which is perpendicular to the polarization direction so, in this case I have applying the mechanical stress and as a result you know we are getting so, if you are applying this it is going to expand and we are going to get this kind of a voltage generation out of the system.

And the opposite thing will happen if I actually apply the tensile force and, then the material will get thickened here right it will be shortening. So, you know you will be getting positive and negative voltage similar to this particular condition. So, there is a

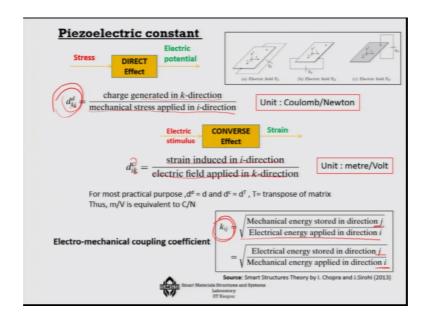
compression and, there is a tension and the corresponding you know sign that we have to keep in our mind in terms of the constitutive relationship.

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If you look at the converse piezoelectric effect, in this case you are applying voltage and how that is so, in this case you can clearly see that, as you are applying positive and negative and this your direction of polarization it is going to expand ok.

So, voltage of the same polarity as the polling voltage will cause an extension in the system. And if I apply voltage of the opposite polarity as the polling voltage, then it will create a compression in the system so, that sign convention for converse direct we have to keep in our mind.



Now, what is the single most important constant that is important for us well that is known as piezoelectric constant which is d k i d, if you look at it. Then in this particular case let us look at it that what exactly it is going to tell us well this is a ratio of charge generated along the kth direction, when the mechanical stress is applied in the i direction.

So, you know you are getting the charge. Now, the d also can be actually expressed in terms of d C where it is the strain induced in i direction and electric field is applied in the k direction. So, as I told you that you are getting the coupling either, because you are applying the mechanical stress or because you are apply; you know applying the electric field either of the thing can generate d. So, you can have a d d or a d C and the k i and the i k, if input is the mechanical stress, then the i is appearing here and if input is the electric field applied, then it is appearing here ok. So, that we have to keep in our mind.

So, this is a single most important constant which will tell us, that how much of this coupling is happening the more the coupling the better is that material as a smart material the other important thing is that, what is the coupling coefficient because this is a electro mechanical coupling constant the coefficient is actually the ratio of the mechanical energy stored in the direction j to the electrical energy applied in direction i the square root of it or the electrical energy stored in direction j and mechanical energy applied in direction i.

So, in either of the ways because you can either convert electrical energy to mechanical energy, or you can convert mechanical energy to electrical energy either way the k i j tells us that what is the coupling coefficient that is involved it. Once again the higher is this coupling coefficient the better will be the material in terms of transduction.

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Prop.	Unit	BaTiO ₃	PZT-A	PZT-B	PbNb ₂ O ₆	LiNbO ₃	PbTiO
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	μm²/N	8.6	12.2	14.5	29	5.8	11

Let us compare some of the materials towards this direction. So, if you consider barium titanate look at its k 1 1 that is 0.21 and if you consider piezoelectric highest is 0.39. So, about you know if the entire energy could have been converted it could have been close to 1, but here it is about close to 39 percent conversion whereas, some materials which will have very low conversion like lithium niobium or lead titanate, but they have other suitability's in comparison to this.

Another interesting thing to look at it is that almost everywhere the 3 3 properties are actually higher. If you look at it in comparison to the 3 1 properties which means that most of this crystals are such a manner the crystal you know structure is that. If I apply the voltage along the three direction I get maximum deformation along the same direction and the same thing is true for voltage generation also. So, the 3 3 effect is that is very useful you know in terms of the design of the system we have to keep this particular property in our mind.

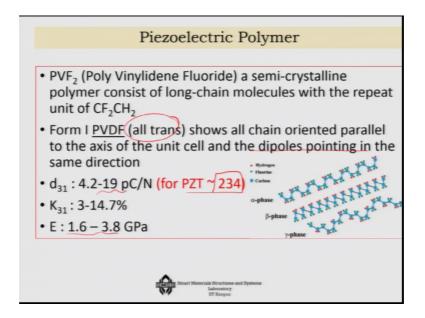
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A few observations • PZT family has highest piezoelectric coupling. • Curie Point: PZT family 220-315°C, Li family 600-1200°C • Instead of polycrystalline Piezoceramics, a single cut PMN could give k₃₃ = 0.92 and d₃₃ = 2070 pC/N

Another two observation is that piezoelectric family has the highest elect[ric]-piezoelectric coupling and curie point wise the PZT family temperature, that curie point is important that the temperature beyond which you will not get the piezoelectric effect ok. So, the you know orientation of the polarization that will be lost. So, that is about 220 to 315 per PZT family where as for lithium family it is 600 to 1200 degree centigrade. So, as a result even if the lithium family shows lower piezoelectric coupling coefficients etcetera, but they are much better in the high temperature piezoelectric effect.

So, that is a point and another important point is that if you can generate some very specific single crystal like PMNs, then you would get a k 3 3 which can be as I as 0.92 and a d 3 3 which is about 2070 phenomenal, but the single crystals are generally very brittle in nature and they are only developed in laboratory based situations, where they are still not commercial. So, far can piezoelectricity be only observe A B O 3 ceramics, they are also observed in polymers this is something that was discovered in Japan.

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That there is some PVDFs Poly Vinylidene Fluoride in a in its particularly in all trans state, where all the you know poles are dipoles are actually in one direction, they have observed that this particular case you get a good amount of piezoelectricity in the system in the polymeric chain. Although it is only about 19 picocoulomb per newton, but in comparison to PZT which is 234 picocoulomb per Newton, but the good part is that this materials are more flexible so, the other materials are actually ceramics are not flexible.

So, you cannot give any arbitrary shape to them, but this materials you can give arbitrary shapes. So, they are more useful wherever you know you are applying there was a layer on a say for example, on a curved surface etcetera. So, there the polymers are very very useful.

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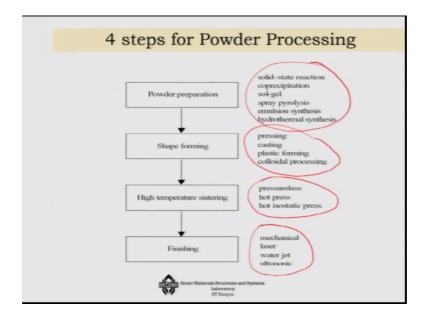
How to prepare a Piezoceramic Actuator?

- Start with <u>fine powders of component</u> metal oxides (PZT or Barium Titanate family) e.g., for PZT you need PbO, ZrO₂ and TiO₂ powders.
- · Mix them in fixed proportions.
- · Use an organic binder.
- · Form into specific shapes.
- Heat for a specific time and specified temperature 650-800°C
- · Cool apply electrode (sputtering).
- Polarize the sensor/actuator using a DC electric field.



How do you prepare a Piezoceramic actuator, well you have to first start with fine powders of any of these families of piezoelectric material and this fine powder you have to mix then say for example, lead oxide and zarconia and titanium oxide you have to mix them in a fixed proportion and you use an organic binder to actually bind the ceramic powders form, them in a specific shape heat it for a specific time and temperature at a high temperature apply pressure along with, then you know this organic binders will be evaporated. And it will retain that form you cool it you apply the electrode by sputtering and you polarize it with a high voltage high dc voltage. You have the sensor at the actuator ready with you that is the way we generally produce such a system.

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So, this there are many steps like the powder preparations you can take so, many different types of steps this is just for your information shape forming you can take. So, many different types of steps or high temperature you can take you know pressureless hot press, or hot isostatic press condition and finishing you know you can give different types of finishing mechanical finishing, laser finishing, water jet fishing, using ultrasonic etcetera. So, each one of these blocks can be achieved in various ways or a combination of this ways ok. So, it is a field which is a very very well developed you know technology.

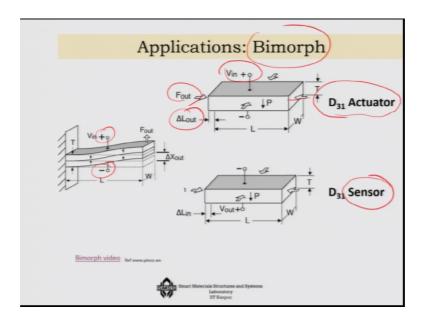
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Piezoelectric Composite Composite made of a polymer and PZT Polymer phase – lower density, permittivity and increased elastic compliance. Smaller PZT particles (5-10 μm) in Polyurethane (PU) matrix. Larger 120μm particles in a silicone rubber matrix. Skinner et.al: Smaller particles generate series connectivity, while larger generate parallel connectivity.

Now, the can we make a composite out of this piezoelectric system well, if you mix a polymer and piezoelectric you can get a composite out of it ok, why should we make a composite, because I told you that piezoelectric are ceramics are generally brittle in nature. So, if you mix them in a polymer you actually get some compliance to it so, that you can shape it for various applications.

So, you first take small PZT particles and you put them in matrix like PU matrix ok, sometimes you also put larger particles in silicon rubbers and, then you can actually make a composite out of it. This is a particular paper that you can see where you know they have shown various techniques of different techniques of making piezoelectric composites.

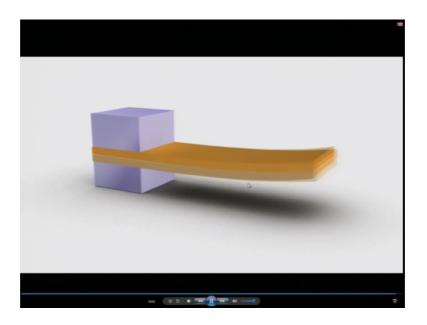
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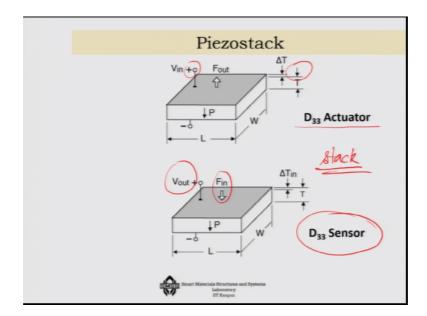
We can apply this piezoelectric composite in one good way if you remember in the last lecture, we have shown that in the printer how it was used for bending control. So, that is what we call as a bimorph; that means there will be two layers in it ok. So, if you look at it each one of them say if it is a D 3 1 actuator I already told, you that for a d three one you are applying forces, or voltage along the horizontal you know plane direction and you are getting the voltage in the vertical direction. So, if it is an actuator you are doing the other way around; that means, your applying voltage across it and your getting deformation or force out of the system.

So, if I reverse the voltage I am getting the other way you know force and the deflection in the system. And if you imagine that I actually add this two layers together and, I give the common voltage and the this point then; that means, when one will be expanding the other will be contracting. So, you can see it in a particular video that how this particular thing is going to behave.

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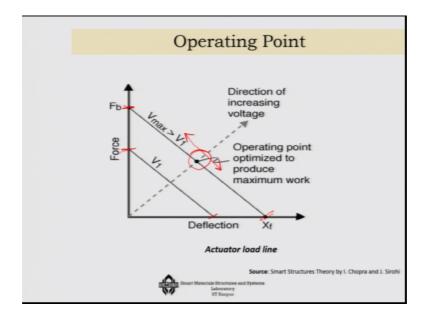
So, you can see that there are two of them and you are getting a bending in the whole system. So, that is what you know a bimorph would actually behave like ok. So, this is you know when we are making a D 3 1 actuators. And similarly you know when you are deforming, it you can get a D 3 1 sensors out of it. So, D 3 1s basically tell us is that you are doing something in one plane and you are getting the effect in the other plane.



So, that is D 3 1 system if I do it everything in one direction only for example, I am applying the voltage in the z direction and, I am getting the deformation in the z direction itself then it is a D 3 3 actuator. And similarly I am applying force in the z direction and I am getting voltage in the z direction, then it is a D 3 3 sensors these are also known as stack actuators that is the common name stack actuator or stack sensors.

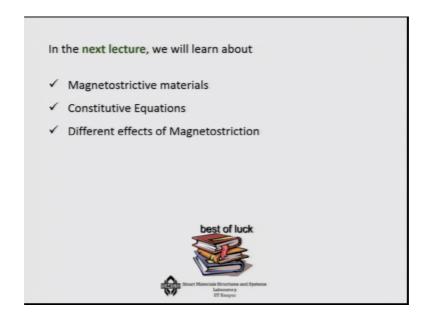
So, that is what are the different types of systems that you can build up by using the simple you know system of piezoelectricity. And one important thing here is that there is operating point involves.

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Suppose you do not apply any force on a piezoelectric material then you are only going to get deflections out of it. Suppose you stop it to deform totally, then you are going to get only force out of it, but in reality we actually we will be always somewhere in the middle; that means, we will get some force out of the system and some deflection will be happening to it. So, that is what from application to application you have to decide, where this operating point will be how much of force and how much of deflection you are you know getting from the system.

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So, this is brief about the piezoelectric materials in the next lecture, we will talk about the Magnetostrictive material its constitutive equations and different effects of Magnetostriction.

Thank you.