

Selection of Nanomaterials for Energy Harvesting and Storage Application
Prof. Kaushik pal
Department of Mechanical and Industrial Engineering
Indian Institute of Technology, Roorkee

Lecture - 11
Nanogenerators: Introduction & Piezoelectric Nanogenerators

Hello my friends, in this particular lecture, we are going to discuss about the Nanogenerators, their Introductions and the Piezoelectric Nanogenerators, because why I am talking because in my subsequent slide you can find out that there are several types of nanogenerators by using the different types of materials. So, in this particular lecture, basically we are going to discuss about the materials which is having the piezoelectric effect, and only using that materials we are generating the electricity, so that is why basically this particular topic is about the piezoelectric nanogenerator.

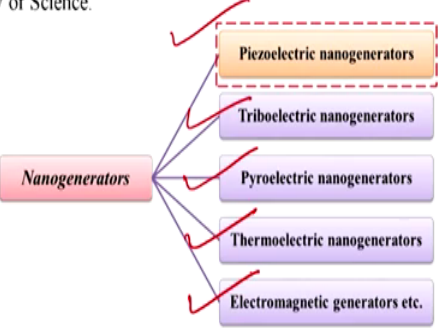
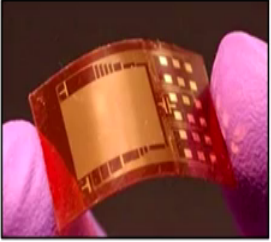
So, before going to discuss let us know that what is nanogenerators. So, nanogenerator is nothing but a device say suppose it is a one kind of device which converts the energy from one form to another. So, either maybe you can do a hammering or maybe give some pressures, the material can generate the electricity or maybe you are rubbing the two materials, it is generating certain kind of electricity. Sometimes we are giving the heat to a particular materials, then due to that also the material can generate the electricity. Sometimes we are having some kind of electromagnetic force in between two materials and that electromagnetic force is converting into some electrical energy.

So, there are different types of materials behaves differently. In some cases, we need to give certain kind of pressure; certain cases, we need to give certain kind of frictions; in some cases, we need to give some kind of electromagnetic force over there, so that the material can convert those forces into the electricity. So, based on this, we are dividing this whole nano chapter's topic into different parts. So, how it has come?

(Refer Slide Time: 02:17)

Nanogenerators:

- A nanogenerator is a type of device that converts **mechanical/thermal energy** as produced by small scale physical change into **electricity**.
- The discovery of nanogenerators is the top 10 world discoveries in science according to academicians of Chinese Academy of Science.



Nanogenerators

- ✓ Piezoelectric nanogenerators
- ✓ Triboelectric nanogenerators
- ✓ Pyroelectric nanogenerators
- ✓ Thermoelectric nanogenerators
- ✓ Electromagnetic generators etc.

IT ROORKEE | NPTEL ONLINE CERTIFICATION COURSE | ADVANCED COMPOSITE LAB | 2

So, the discovery of nanogenerators is the top 10 world discoveries in science according to the academicians of the Chinese Academy of Science. They believe that this nanogenerator concept is one of the versatile things or maybe one of the latest discovery that which can be ranked within the top 10 innovations in the world till today. So, as I told already nanogenerators basically we are dividing into several parts. Based on that which type of materials we are going to use and what type of energy basically we are using on those particular materials to get the electricity. But output for all the cases are remain same that is the electricity, and input are variable like heat, pressure, magnetic force, friction, so these all are the cases.

So, now, if you see that nanogenerators has been divided into several parts, one is called the piezoelectric, triboelectric, pyroelectric, thermoelectric and electromagnetic. So, basically we are going to discuss about piezoelectric nanogenerators in this particular lecture. So, what is piezoelectric materials? So, in our childhood, or maybe in our class 10, 12 or maybe in some other classes, we have seen that when we are having certain materials. So, if we give a certain particular pressure on that particular materials, at some particular positions, or maybe at some particular angle, then that materials can generate the electricity, so that is the beauty of that particular materials. And the materials those shows basically these type of properties are known as piezoelectric materials.

(Refer Slide Time: 04:05)

What is Piezoelectric Materials?

- Piezoelectric materials are those, which have ability to generate electrical charges when subjected to a mechanical pressure through piezoelectric effect.
- The prefix word "piezo" derives from the Greek word "piezin" which means "to press", so, literally, piezoelectricity means "pressure electricity".
- A more sophisticated definition of piezoelectricity was given by Cady as being an electric polarization produced by mechanical strain in some crystals belonging to certain classes of materials.
- The phenomenon of piezoelectricity, was discovered by the Curie brothers Jacques and Pierre in 1880, during their investigation on the effect of pressure on the generation of electrical charge by some natural crystals such as quartz or tourmaline.

IIIT ROORKEE | NPTEL ONLINE CERTIFICATION COURSE | ADVANCED COMPOSITE LAB | 3

So, basically the piezoelectric materials are those which have ability to generate electrical charges when subject to a mechanical pressure as I told already. So, suppose you are having one materials, and if you give a pressure on that, then that materials can generate the electricity through the piezoelectric effect, so that phenomena is known as the piezoelectric effect. The prefix word piezo, so in this particular case, the piezo derives from the Greek word piezein which means to press, so, literally, piezoelectricity means the pressure electricity that means you are giving the pressure onto those materials.

A more sophisticated definition of piezoelectricity was given by Cady as being an electrical polarizations produced by mechanical strain, of course, because when you are giving certain kind of load or pressure onto some materials, so automatically the mechanical strength will be generated inside the material, so due to that the material is giving certain kind of electricity. In some crystals belonging to certain class of materials as I told already, it is not that every material if we press it, it will give the electricity. That material should have that capability or maybe certain kind of properties it is having that is why only after getting the pressure or maybe the load, it is giving us the electricity.

The phenomenon of piezoelectricity was discovered by the Curie brothers Jacques and Pierre Curie in 1880, during their investigations on the effect of pressure on the generation of electrical charge by some natural crystals such as quartz or maybe the

tourmaline. So, basically these all are the materials. So, they have developed, they have seen these phenomena first time in the year of 1880. And then after that, the piezoelectric materials has come into the market. Now, scientist has done so many research on that, they have try to make some new materials, so that the electrical efficiency will be increased. So, now, basically let us know that what is piezoelectric effect how or maybe why this material is working or maybe behaving like this.

(Refer Slide Time: 06:21)

Piezoelectric effect:

- The piezoelectric effect in piezoelectric crystals manifests itself in two ways:
 - The direct piezoelectric effect: When electrical charge is generated as a result of a mechanical stress applied to the crystal.
 - The converse piezoelectric effect: When a strain is generated as a result of an electrical field applied to the crystal.
- Theoretically these two effects are described by two basic equations which relate the elastic variables, stress (T) and strain (S), to the electric variables, field (E) and displacement (D).
- The two equations of state are written as follows:

$$D = dT + \epsilon^T E D \text{ ----- Direct effect}$$

$$S = s^E T + dE \text{ ----- Converse effect}$$

Here, d : Piezoelectric coefficient or charge constant
 s : Elastic compliance and
 ϵ : Dielectric constant (permittivity).

IT ROORKEE | NPTEL ONLINE CERTIFICATION COURSE | ADVANCED COMPOSITE LAB | 4

So, the piezoelectric effect in piezoelectric crystals manifests itself in two ways. What are those? First one is called that the direct piezoelectric effect. When electrical charge is generated as a result of a mechanical stress applied to the crystal; and the second one the converse piezoelectric effect when a strain is generated as a result of an electrical field applied to the crystal.

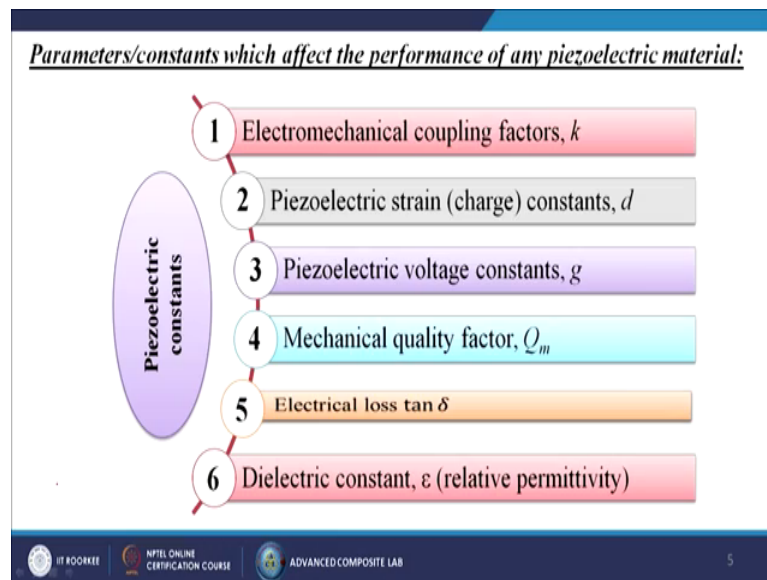
Actually, if you see this material is having a very good beauty, so suppose you give the pressure or maybe the load, it will generate the electricity. And simultaneously if you give the electricity to those materials, then the materials will be under stress or maybe strain. So, it will change its shape and size means some kind of deformation will be happened inside the materials, so that is basically the vice versa case over there.

So, in this case you see, so, when I am giving the strain input and output over there, it is giving me the voltage and simultaneously when I am giving the voltage input and output, so automatically it is under deformations or maybe the under the strain. So, theoretically

these two effects are described by two basic equations which relate the elastic variables, stress which is nothing but the capital T and the strain capital S, to the electric variables that is field E and displacement capital D. So, basically the two equations of states are written as follows say capital D is equal to dT plus epsilon to the power T ED which is nothing but known as the direct effect. And capital S is equal to smallest to the power E capital T plus small dE, so that is known as the converse effect.

So, here small d is the piezoelectric coefficient or may be the charge constant, and small s is the elastic compliance, and epsilon is the dielectric constant which is nothing but known as the permittivity of that particular material. So, by these equations, we can calculate.

(Refer Slide Time: 08:28)



Now, what are the parameters or may be the constants which affect the performance of any piezoelectric materials. As I told already it is not that every material can show this kind of property. So, basically some properties should be there inside the material, then only it can show the piezoelectric effect. What are those, first is that electro mechanical coupling factors which is nothing but known as the small k, piezoelectric strain charge constants which is denoting by the small d, piezoelectric voltage constants which is denoting by small g, then mechanical quality factor Q m, electrical loss tan delta, and the dielectric constant that is epsilon which is nothing but the relative permittivity. So, basically these all are known as the piezoelectric constants. So, now I will discuss one by

one. So, first what is known by the electromechanical coupling factor or maybe the small k.

(Refer Slide Time: 09:25)

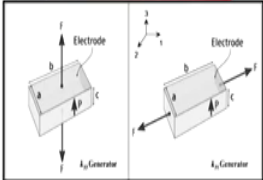
1) Electromechanical coupling factors, k:




- It is an indicator of the effectiveness with which a piezoelectric material converts electrical energy into mechanical energy, or converts mechanical energy into electrical energy.

$$k^2 = \frac{\text{Mechanical energy converted to electrical energy}}{\text{Input mechanical energy}} \text{ ----- Direct piezoelectric effect}$$

$$k^2 = \frac{\text{Electrical energy converted to mechanical energy}}{\text{Input electrical energy}} \text{ ----- Converse piezoelectric effect}$$

- Generally denoted by k_{ij} , i (electric field direction), j (longitudinal vibration direction).
- A typical piezoelectric ceramic can convert 25 - 50% of the energy delivered to it in one form into the other form depending on structure.
- A high k usually is desirable for efficient energy conversion.



It is an indicator of the effectiveness with which a piezoelectric material converts electrical energy into mechanical energy, or converts mechanical energy into electrical energy means the vice versa thing. So, in this particular case, small k square is equal to mechanical energy converted to electrical energy by input mechanical energy, of course, because basically that is giving the efficiency kind of things. So, how much input parameters you are putting inside the materials, and as a result of that particular input parameters how much efficiency basically or maybe output you are getting, so that is the direct piezoelectric effect or may be the ratio. Or maybe the vice versa things electrical energy converted to mechanical energy and input of the electrical energy that is known as the converse piezoelectric effect.

Generally denoted by k_{ij} , i is the electric field directions, j is the longitudinal vibration direction. A typical piezoelectric ceramic can convert 25 to 50 percent of the energy delivered to it in one form into the other form depending on the structure. So, now, you can see 25 to 50 percent, so that means, if you give the pressure, and if you think that is the 100 percent, then the 50 percent of the pressure will be converting into the electrical energy. Or maybe the vice versa thing, if we give the 100 percent whatever the electrical input to that particular material, if you think that is as a 100 percent, so you can get the

mechanical strain maybe 25 to 50 percent. So, that depends upon the material properties and the crystal structure of that particular material. So, a high k usually is desirable for efficient energy conversion, yes, of course, because that is the well-known fact.

(Refer Slide Time: 11:14)

2) Piezoelectric strain (charge) constants, d:

- The piezoelectric charge constant is the ratio between the electric charge generated per unit area and an applied force and is expressed in Coulomb/Newton (C/N).

$$d = \frac{\text{Charge density (Open circuit)}}{\text{Applied stress}} \text{ ----- Direct piezoelectric effect}$$

$$d = \frac{\text{Strain developed}}{\text{Applied field}} \text{ ----- Converse piezoelectric effect}$$

$$d = k \times \sqrt{\epsilon_0 \epsilon_s E^E} \text{ (C/N)}$$

where; k : Electro-mechanical coupling factor
 ϵ_0 : Relative permittivity of free space
 ϵ_s : Dielectric constant (relative permittivity)
 E^E : Compliance ($10^{-12} \text{ m}^2/\text{N}$)

➤ Generally denoted by d_{ij} , i (Induced polarization direction), j (Stress applied direction).
 ➤ d is an important indicator of a material's suitability for strain-dependent (actuator) applications.

Now, next one is called the piezoelectric strain constant or which basically we are denoting by the small d. So, the piezoelectric charged constant is the ratio between the electric charge generated per unit area and an applied force and is expressed in Coulomb per Newton. So that means when you are giving the pressure and maybe the load, of course, it is acting onto some area, so basically in this particular case that load per area that this A right. So, this A basically depends upon how much area you are going to cover. So, now, d is the charge density - open circuit by the applied stress which is nothing but the direct piezoelectric effect. Small d is equal to strain developed by the applied field that is converse piezoelectric effect. So, small d is equal to k and multiplied by root over epsilon 0 epsilon s to the power E Coulomb per Newton.

So, where k is nothing but the electromechanical coupling factor; epsilon 0 is the relative permittivity of the free space; epsilon is the dielectric constant which is nothing but the relative permittivity; and s to the power E is nothing but the compliance which value is basically 10 to the power minus 12 meter square per Newton. So, generally denoted by d i j, i – induced polarization directions, and j is the stress applied directions. So, d is an

important indicator of a material suitability for the strain-dependent or maybe the actuator applications.

Basically what is happening suppose you are choosing certain area over there, now you are giving the pressure in these area or maybe you are giving the pressure in this area, or maybe whatever the pressure you are giving, or maybe the load you are giving which is acting on the whole area, depending upon that your material efficiency will be changing.

(Refer Slide Time: 13:13)

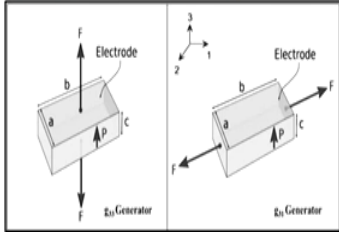
3) Piezoelectric voltage constants, g:

- The piezoelectric voltage constant is the ratio of the electric field produced to the mechanical stress applied and is expressed as Volt. meter/Newton (Vm/N).

$$g = \frac{\text{Field developed}}{\text{Applied mechanical stress}} \quad \text{----- Direct piezoelectric effect}$$

$$g = \frac{\text{Strain developed}}{\text{Applied charge density}} \quad \text{----- Converse piezoelectric effect}$$

- It is generally denoted by g_{ij} , i (Induced electrical field direction), j (Stress applied direction).
- g is important for assessing a material's suitability for sensing (sensor) applications.



IT ROORKEE NPTEL ONLINE CERTIFICATION COURSE ADVANCED COMPOSITE LAB 8

Next, third one is called the piezoelectric voltage constants. So, the piezoelectric voltage constant is the ratio of the electric field produced to the mechanical stress applied and is expressed as Volt meter per Newton. So, it is basically denoted by small g which is nothing but the field developed by the applied mechanical stress for the direct piezoelectric effect; and for the converse piezoelectric effect, it is nothing but the strain developed by applied charge density. It is generally denoted by g_{ij} , where i is the induced electrical field directions, and j is the stress applied directions. So, in this particular case, what happened small g is important for assessing a material suitability for sensor or maybe the sensing applications.

(Refer Slide Time: 14:13)

4) Mechanical quality factor, Q_m :

➤ the mechanical quality factor is defined as

$$Q_m = 2\pi f \frac{U_e}{P_d}$$

Where; U_e : Stored mechanical energy of the system ✓
 P_d : Power dissipated (watts)
 $2\pi f$: Angular frequency

➤ Piezoelectric material with high Q_m is desirable for piezoelectric nanogenerators.

5) Electrical loss $\tan \delta$:

➤ The dielectric loss factor, is defined as the tangent of the loss angle ($\tan \delta$). $\tan \delta = \frac{1}{Q_m}$

➤ The loss factor is inverse of mechanical quality factor Q_m .

9

Next come to the mechanical quality factor which is nothing but the Q_m . So, the mechanical quality factor is defined as Q_m is equal to $2\pi f U_e$ by P_d . So, where U_e is the stored mechanical energy of the system, that means, whatever the mechanical energy before any giving load or pressure has been consumed by that particular material. P_d power dissipated that is of course in watts, and $2\pi f$ is the angular frequency. So, piezoelectric materials with high Q_m is desirable for piezoelectric nanogenerators; otherwise, what will happen if we give little bit load or pressure the material there is a chance of the breakage. So, the material should have high mechanical strength, so that we can give the continuous load onto that particular materials and it can generate the electricity.

Next electrical loss and delta, so the dielectric loss factor is defined as the tangent of the loss angle which is nothing but known as tan delta. The loss factor is inverse of mechanical quality factor Q_m . So, basically the tan delta is nothing but 1 by Q_m .

(Refer Slide Time: 15:21)

6) Dielectric constant ϵ (relative permittivity):

➤ The dielectric constant is defined as the ratio of the permittivity of the material to the permittivity of free space.

$$\epsilon = \frac{C_0 h}{\epsilon_0 A}$$

where; ϵ : relative permittivity of the material ✓
 ϵ_0 : relative permittivity of free space (8.854×10^{-12} F/m) ✓
 h : distance between electrodes (m) ✓
 A : area of the electrodes (m^2) ✓
 C_0 : measured capacitance at 1kHz (F) ✓




Logo of IIT ROORKEE, NPTEL ONLINE CERTIFICATION COURSE, and ADVANCED COMPOSITE LAB. Page number 10.

Next dielectric constants or may be the epsilon which is nothing but known as relative permittivity. So, the dielectric constant is defined as the ratio of the permittivity of the material to the permittivity of free space. So, basically that is the ratio. So, this is the equations where epsilon is nothing but $C_0 h$ by $\epsilon_0 A$, where epsilon is the relative permittivity of the material, ϵ_0 is the relative permittivity of free space which is nothing but 8.854×10^{-12} Farad per meter, h is the distance between electrodes which is in meter, A is the area of the electrodes that is in meter square, and C_0 is the measured capacitance at 1 kilo hertz which is nothing but in Farad value.

(Refer Slide Time: 16:11)

Piezoelectric constants of different materials:

| Type of material | PZT-4 | PbNbO ₃ | PVDF | LiNbO ₃ | AlN thin film | PMN-PT |
|---|-------|--------------------|------|--------------------|---------------|--------|
| Electromechanical coupling coefficient (k) | 0.47 | 0.33 | 0.19 | 0.16 | 0.24 | 0.57 |
| Piezoelectric strain constant (d) | 290 | 85 | 25 | 5.9 | 5.5 | 1400 |
| Piezoelectric voltage constant (g) | 26 | 32 | 230 | 22 | 52 | 30 |
| Mechanical quality factor (Q _m) | High | Low | Low | Very high | Very high | Low |
| Electrical loss tangent (tan δ) | 0.004 | 0.01 | 0.3 | 0.001 | 0.0005 | 0.01 |
| Relative permittivity at constant stress (ε') | 1270 | 300 | 8.4 | 29.8 | 12.0 | 3950 |




11

So, now come to the piezoelectric constants of the different materials. So, now, we are going to discuss. Till now we are discussing about the different input parameters. Now, I am going to discuss about the materials which can satisfy these all kind of input parameters over there. Say suppose if I took PZT-4, or maybe the PbNbO₃, or maybe PVDF or maybe Li NbO₃ or maybe that Al N thin film or maybe the PMN-PT. So, now, I am having different materials. Now, these all are the gathered information from the literature basically. So, if I talk about the electronic mechanical coupling coefficient for PZT, it is 0.47. And for PMN-PT, it is 0.57.

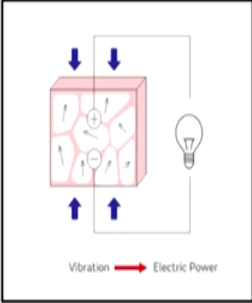
Now, if I talk about the piezoelectric strain constant, for PZT, it is 290, but PMN-PT is the 1400. Now, from this particular case, you can see, in this particular case, mechanical quality factor for PZT is high, but whereas the PMN-PT is very, very low. So, now based on this you can choose your materials that which can give you the maximum efficiency or maybe how much surface area you have to cover to get that maximum efficiency, or maybe the what is the piezoelectric voltage constant, so that means, you can get lots of information from these particular materials. And based on these, you choose your own materials or maybe the combinations of materials to get the maximum efficiency.

Now, piezoelectric nanogenerators, what does it mean? So, in short basically we are calling it as a PENG; for triboelectric nanogenerator basically we are calling it as a TENG – TENG; for piezoelectric nanogenerators, we are calling it as a PENG.

(Refer Slide Time: 18:07)

Piezoelectric nanogenerators (PENG):

- A piezoelectric nanogenerator is an energy harvesting device capable of converting external mechanical energy into electrical energy via action by a nanostructured piezoelectric material. (Discussed in Lecture 1)
- Based on mode of operation, PENG can be divided into:
 - I. Force exerted perpendicular to the axis of the nanowire.
 - II. Force exerted parallel to the axis of the nanowire.
- Based on structural configuration, PENG can be divided into:
 1. Vertical nanowire Integrated Nanogenerator (VING).
 2. Lateral nanowire Integrated Nanogenerator (LING).
 3. Nanocomposite Electrical Generators (NEG).



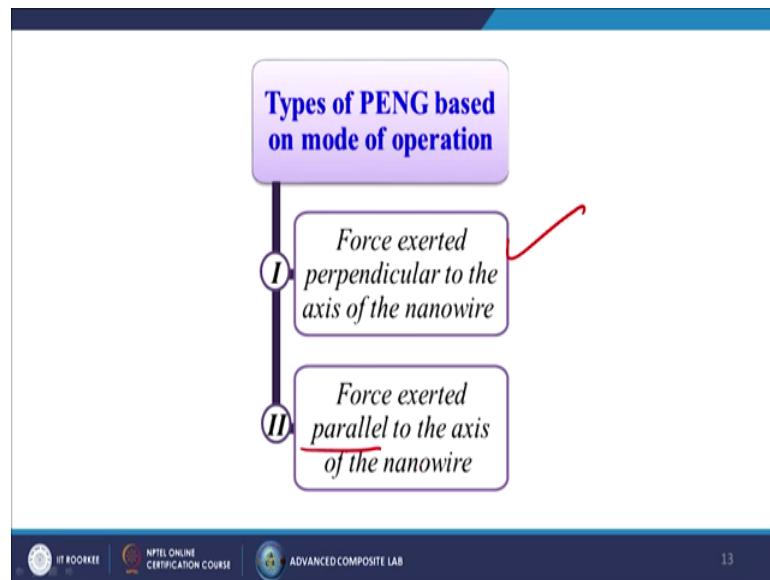
Vibration → Electric Power

IIIT ROORKEE NPTEL ONLINE CERTIFICATION COURSE ADVANCED COMPOSITE LAB 12

So, a piezoelectric nanogenerator is an energy harvesting device capable of converting external mechanical energy into electrical energy by action by a nanostructure piezoelectric materials, which we have already discussed in our introductory lecture. So, based on mode of operations, PENG can be divided into force exerted perpendicular to the axis of the nano wire, force exerted parallel to the axis of the nanowire. So, basically now in this particular case, you can see that we are giving the vibrations or maybe the pressure onto that materials. Due to that, it is generating the electricity.

Now, in this particular case, how you are keeping your materials, whether you are keeping your materials into the horizontal manner or maybe the vertical manner. So, based on these, there are two types if it is vertical types whether you are giving the strain or maybe the stress in these directions or maybe the in these directions. So, depending upon that, there are two different phenomena. So, based on structural configuration, PENG can be divided into three parts; one is called the vertical nanowire integrated nanogenerator that is VING, lateral nanowire integrated nanogenerator that is the LING, and the nanocomposite electrical generators that is the NEG.

(Refer Slide Time: 19:28)



So, here types of PENG based on the mode of operations as I told already there are two types, one is called the force exerted perpendicular to the axis of the nanowires, another is the parallel to the axis of the nanowire.

(Refer Slide Time: 19:42)

1. Force exerted perpendicular to the axis of the nanowire:

- When a piezoelectric structure is subjected to the external force by the moving tip perpendicularly, the deformation occurs throughout the structure.
- The stretched part with the positive strain will exhibit the positive electrical potential, whereas the compressed part with the negative strain will show the negative electrical potential.
- The ohmic contact that is formed between the bottom metal electrode and the nanostructure (NS) causes neutralization of the electric field generated at the tip of the NS.
- The schottky contact that is formed between the top metal electrode and the tip of the NS is responsible for the generation of an electric current.

IIT ROORKEE NPTEL ONLINE CERTIFICATION COURSE ADVANCED COMPOSITE LAB 14

So, now we are going to discuss about the first one which is nothing but force exerted perpendicular to the axis of the nanowire. So, when a piezoelectric structure is subjected to the external force by the moving tip perpendicularly, the deformation occurs

throughout the structure. So, in this case particular what you are seeing, the material is like this, they are standing like this.

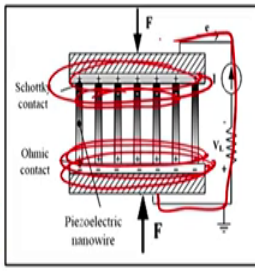
Now, when you are giving the perpendicular force over here, so all the structure will try to lying down like this. So, in this particular case, when you are giving the perpendicular force, so automatically the deformation occurs throughout the whole structure. So, simply we are having you are giving the load like this. So, deformation is taking place throughout the whole structure. So, the stretch part with the positive strain will exhibit the positive electrical potentials, whereas the compressed part with the negative strain will show the negative electrical potentials, yes of course, because when you are tilting that particular materials, so tension is acting in these sides and the compression is acting in these sides. So, one will be along it, and one will be compressed the same thing is here.

The Ohmic contact that is formed between the bottom metal electrode and the nanostructures causes the neutralization of the electric field generated at the tip of the NS means nanostructure. So, this is known as the Ohmic effect. So, it is actually working over here. The Schottky contact that is formed between the top metal electrode and the tip of the nano structure is responsible for the generation of an electric current that is basically known as the Schottky behavior.

(Refer Slide Time: 21:27)

II. Force exerted parallel to the axis of the nanowire:

- In this working principle, when the force is applied toward the tip of the nanowire, uniaxial compressive is generated in the nanowire.
- Due to the piezoelectric effect, tip of the nanowire will have a negative piezoelectric potential.
- A positive electric potential is created at the other tip owing to the flow of electrons from the top tip to the bottom.
- When the external force is removed, the induced piezoelectric effect instantly vanishes.
- The positive potential at the bottom tip of the NS is neutralized because of the migration of accumulated electrons from the bottom to the top electrode of the NS via the external circuit.



The diagram shows a piezoelectric nanowire with a Schottky contact at the top and an Ohmic contact at the bottom. A downward force F is applied to the top tip, causing compression. This generates a negative piezoelectric potential at the top and a positive potential at the bottom. Electrons flow from the top tip to the bottom tip through an external circuit containing a voltmeter (V_p) and a ground symbol.

Next force exerted parallel to the axis of the nanowire. So, in this particular case, when the force is applied toward the tip of the nanowires, uniaxial compressive is generated in the nanowires, because in this particular case you are pressing the materials in this manner. So, in this particular case, this is known as the Ohmic contact, and this is known as the Schottky barrier or maybe the Schottky contact. So, particularly you are applying the force. So, the material is getting compressed in between two electrodes. So, due to the piezoelectric effect, the tip of the nanowire will have a negative piezoelectric potential.

A positive electric potential is created at the other tip owing to the flow of electrons from the top tip to the bottom. So, in this particular case, so the here it is the minus one, so automatically this will get the positive ion; and in this particular case, this is the positive and this is the negative. So, automatically the current will flow from this way to the this way.

So, when the external force is removed the induced piezoelectric effect instantly vanishes. So, of course, when you are releasing the pressure, so automatically there will not be any kind of generations of the electricity. The positive potentials at the bottom tip of the nanostructure is neutralized because of the migration of accumulated electrons from the bottom to the top electrode of the nanostructure via the external circuit, so through basically this circuit. So, they are balancing each other. Now, basically there are different type of PENG based on the structural configurations.

(Refer Slide Time: 23:11)

Type of PENG based on structural configuration

1. Vertical nanowire Integrated Nanogenerator (VING)
2. Lateral nanowire Integrated Nanogenerator (LING)
3. Nanocomposite Electrical Generators (NEG)

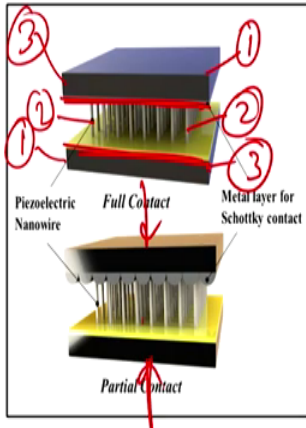
16

As I told already so what are those Vertical nanowire Integrated Nanogenerator – VING, Lateral nanowire Integrated Nanogenerator that is the LING, and the last one is the Nanocomposite Electrical Generators that is nothing but the NEG. So, we are going to discuss one by one.

(Refer Slide Time: 23:33)

1. Vertical nanowire Integrated Nanogenerator (VING):

- VING is a 3-D configuration consisting of a stack of 3 layers:
 - ✓ Base electrode
 - ✓ Vertically grown piezoelectric nanostructure and
 - ✓ Counter electrode.
- The piezoelectric nanostructure is usually grown from the base electrode by various synthesizing techniques.
- Then they are integrated with the counter electrode in full or partial mechanical contact with its tip.



The diagram illustrates the VING structure. The top part shows a 3D view of a stack of three layers: a base electrode (1), a vertically grown piezoelectric nanowire (2), and a counter electrode (3). The nanowire is shown in full contact with the counter electrode. The bottom part shows a 2D cross-section of the same structure, highlighting the 'Full Contact' and 'Partial Contact' configurations. The 'Full Contact' configuration shows the nanowire tip touching the counter electrode, while the 'Partial Contact' configuration shows the nanowire tip touching the counter electrode at a point. Labels include 'Piezoelectric Nanowire', 'Full Contact', 'Metal layer for Schottky contact', and 'Partial Contact'.

17

So, first is that vertical nanowire integrated nanogenerator or which is known as VING. So, VING is a 3-D configuration consisting of a stack of three layers. First one is the base electrodes, then vertically grown piezoelectric nanostructure and the counter

electrode. So, this is number 1, this is number 2 and this is number 3; or maybe in the opposite way also you can do this is number 1, this is number 2 and this is number 3.

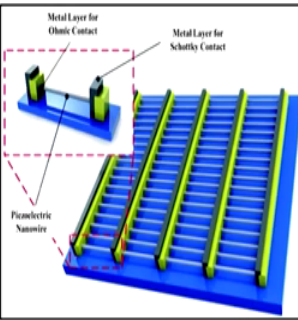
So, one is the electrode - base electrode, top of that you are having that materials which is having the vertically grown piezoelectric nanostructure. On top of that you just you are doing the vertically grown piezoelectric crystals, and then you are having that counter electrode. And both the electrode is having certain kind of back plate kind of things. So, basically in this particular case, this is the electrode that grey one and the yellow one.

The piezoelectric nanostructure is usually grown from the base electrode by various synthesizing techniques. Now, you can see from this image that all the piezoelectric crystals are into the vertical positions. Then they are integrated with the counter electrode in full or partial mechanical contact with its tip. Now, you are going to give the pressure like this.

(Refer Slide Time: 24:44)

2. Lateral nanowire Integrated Nanogenerator (LING):

- LING is a 2-dimensional configuration, consisting of three sections,
 - ✓ Base electrode.
 - ✓ Laterally grown piezoelectric NSs and
 - ✓ Top metal electrode.
- The first metal electrode is used for establishing the Schottky contact, whereas the second metal electrode is responsible for the creation of the Ohmic contact.
- The voltage generated by an LING can be increased by arranging a large number of LINGs in series.



IT ROORKEE NPTEL ONLINE CERTIFICATION COURSE ADVANCED COMPOSITE LAB 18

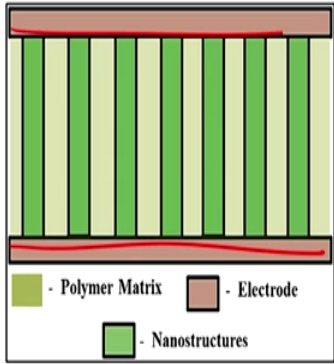
Next called the lateral nanowire integrated nano generator or maybe the LING. So, LING is a two-dimensional configuration consisting of three sections, base electrode, laterally grown piezoelectric nanostructures, and the top metal electrode. So, the first metal electrode is used for establishing the Schottky contact, whereas the second metal electrode is responsible for the creation of the Ohmic contact. The voltage generated by a LING can be increased by arranging a large number LING in series.

So, basically in this particular case, you can see that how we are putting our piezoelectric materials over there. So, now, in this particular case, this is one electrode and this is the second electrode over there, so that is why basically it is known as the lateral nanowire integrated nano generator or maybe the LING.

(Refer Slide Time: 25:40)

3. Nanocomposite Electrical Generators (NEG):

- NEG is a 3-dimensional configuration consisting three main parts:
 - ✓ Metal plate electrodes
 - ✓ Vertically grown piezoelectric nanostructure
 - ✓ Polymer matrix.
- Polymer matrix fills the space between the piezoelectric nanostructure.
- It was shown that NEG has a higher efficiency compared to original nanogenerator configuration which a ZnO nanowire will be bended by an AFM tip.
- It is also shown that it provides an energy source with higher sustainability.



Legend:
- Polymer Matrix
- Electrode
- Nanostructures

IT ROORKEE | NPTEL ONLINE CERTIFICATION COURSE | ADVANCED COMPOSITE LAB | 19

Then third one is the Nanocomposite Electrical Generators, which is nothing but the N E G or maybe the NEG. So, NEG is a three-dimensional configuration consisting of three main parts. Metal plate electrodes, here we are having two electrode over there right, so that is metal plate. Now, in between these it is like composites. In the composites, you are having that polymer matrix as well as the nano structure materials. Next particle grown piezoelectric nanostructure and the polymer matrix.

Polymer matrix fills the space between the piezoelectric nanostructure. As I told already, so this is like a pillar and in between the pillar the gap is filled by the polymeric matrix. It was shown that NEG has a higher efficiency compared to original nanogenerator configurations which a zinc oxide nanowire will be bended by an AFM tip. It is also shown that it provides an energy source with higher sustainability.

(Refer Slide Time: 26:42)

Materials used in piezoelectric nanogenerators:

- The mechanism of power generation mainly relies on
 - ✓ Electromechanical properties of the material.
 - ✓ Formation of a Schottky contact between the tip of the NS and the metal electrode.
- Piezoelectric semiconductor materials with the wurtzite structure, such as ZnO, GaN, and CdS because they exhibit both semiconducting and piezoelectric properties simultaneously.
- Inorganic materials have a limited number of applications, because of their low formability and brittle nature.
- Polymers (mostly PVDF) are used as alternative materials in applications in which a lightweight generator design is required.
- Based on the unit cell structure there are three main groups of piezoelectric materials:
 - 1) Perovskite group (ABO_3)
 - 2) Bismuth layer-structure group ($Bi_2A_{x-1}B_xO_{3x+3}$)
 - 3) Pyrochlore group ($A_2B_2O_7$)

iiit ROORKEE NPTEL ONLINE CERTIFICATION COURSE ADVANCED COMPOSITE LAB 20

Now, basically what kind of materials we are using for these piezoelectric nanogenerators. So, the mechanism of power generation mainly relies on electromechanical properties of the material and the formations of the Schottky contact between the tip of the nanostructure and the metal electrode that is the second one. So, these all are two are the prime considerations. Now, piezoelectric semiconductor materials with a wurtzite structure, such as zinc oxide, gallium nitride and cadmium sulfide because they exhibit both semiconducting and piezoelectric properties simultaneously.

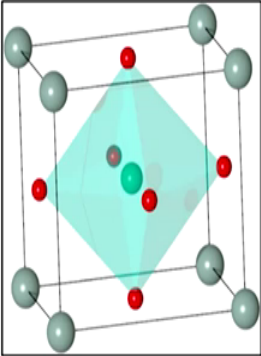
Inorganic materials have a limited number of applications because of their low formability and brittle nature. So, suppose I am having that materials, and if it is brittle in nature, when I will give the compress over there, so material will break, so that is why I need the material which is having the ductility. So, polymers mostly PVDF are used as alternative materials in applications in which a lightweight generator design is required. Based on the unit cell structure there are three main groups of piezoelectric materials like perovskite group, the configuration is nothing like ABO_3 , bismuth layer-structure group that is $Bi_2A_{x-1}B_xO_{3x+3}$ and the pyrochlore group that is the $A_2B_2O_7$. So, basically the peroxide group which is nothing but the ABO_3 structure.

(Refer Slide Time: 28:21)

1) Perovskite group (ABO₃):

- Perovskite group is by far the most important class of piezoelectric materials, having the highest piezoelectric constants and an immense number of applications.
- In the perovskite families the PZT-type ceramics play the leading role.
- The structure may be described as a simple cubic unit cell with a large cation on the corners (A site), a smaller cation in the body center (B site), and oxygen in the centers of the faces.

Examples: BaTiO₃, PbTiO₃, PbZr_{0.52}Ti_{0.48}O₃, (Na_{0.5}K_{0.5})NbO₃ etc.)



IT ROORKEE NPTEL ONLINE CERTIFICATION COURSE ADVANCED COMPOSITE LAB 21

So, perovskite group is by far the most important class of piezoelectric materials, having the highest piezoelectric constants and an immense number of applications. In the perovskite families the PZT-type ceramics play the leading role. The structure may be described as a simple cubic unit cell with a large cation on the corners A site, and a smaller cation in the body center - so in this particular case B site, and oxygen in the centers of the faces. So, basically it is forming the ABO₃ structure.

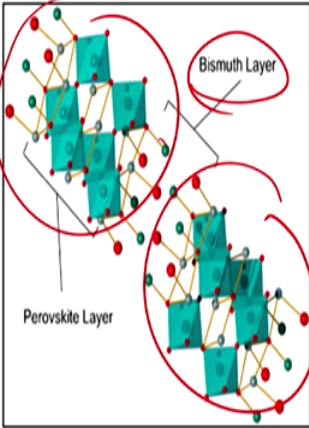
What are the examples like BaTiO₃, PbTiO₃, and then some kind of complex structure because as I told already always the scientist are trying to make the newer kind of materials to get the more efficiency over there. So, here I have given four, but till today people have already developed more than 15 to 20 different types of perovskite structure.

(Refer Slide Time: 29:19)

2) **Bismuth layered structures ($\text{Bi}_2\text{A}_x\text{B}_x\text{O}_{3x+3}$) (BLS):**

- This structure can be considered as a layer of perovskite unit cells, infinite in two dimensions, separated by $(\text{Bi}_2\text{O}_2)^{2+}$ layers.
- The perovskite layer can have a thickness of one or more unit cells, denoted by the parameter x in the chemical formula.
- Materials with BLS have a tetragonal symmetry in the high-temperature phase.

Examples: $\text{SrBi}_2\text{Ta}_2\text{O}_9$, Bi_2WO_6 , $\text{PbBi}_2\text{Nb}_2\text{O}_9$ etc.



The diagram illustrates the Bismuth Layered Structure (BLS). It shows a repeating unit consisting of a perovskite layer and a bismuth layer. The perovskite layer is represented by a 3D lattice of atoms (blue, red, and green spheres) forming a cube-like structure. The bismuth layer is shown as a layer of bismuth atoms (red spheres) coordinated to oxygen atoms (green spheres). The layers are stacked in an alternating fashion, with the perovskite layer on top and the bismuth layer on the bottom. Labels 'Perovskite Layer' and 'Bismuth Layer' are present in the diagram.

iiit ROORKEE NPTEL ONLINE CERTIFICATION COURSE ADVANCED COMPOSITE LAB 22

Now, the second one is known as the bismuth layered structures which is nothing but the $\text{Bi}_2\text{A}_x\text{B}_x\text{O}_{3x+3}$ or in short we are calling it as a BLS. This structure can be considered as a layer of perovskite unit cells infinite in two dimensions separated by Bi_2O_2 ions layers. So, in this particular case, what happened, I am having this one unit, and this one is the another unit, and in between I am having the bismuth layer over there. So, in between two perovskite, just I am putting one bismuth layer and that is then acting as a repeating unit.

So, the perovskite layer can have a thickness of one or more unit cells denoted by the parameter x in the chemical formula. Materials with BLS have a tetragonal symmetry in the high temperature phase. What are the examples like strontium $\text{Bi}_2\text{Ta}_2\text{O}_9$. So, we are having the bismuth, we are having the tantalum, we are having the strontium. So, these all are the basically examples.

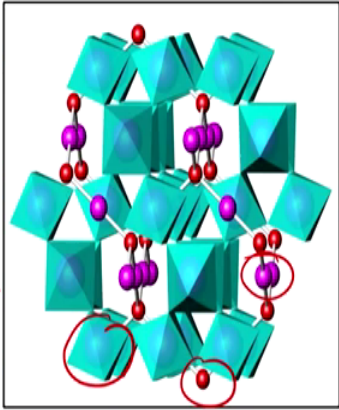
So, in between two peroxide materials, so we are having one bismuth layer over there, so in this particular case, so in this particular case. So, basically in between the repeating units we are having one bismuth layer. Then third one is called the pyrochlore group which is nothing but the $\text{A}_2\text{B}_2\text{O}_7$. So, the pyrochlore structure displays the cubic symmetry with a journal stoichiometry of $\text{A}_2\text{B}_2\text{O}_7$.

(Refer Slide Time: 30:47)

3) Pyrochlore group ($A_2B_2O_7$):

- The pyrochlore structure displays cubic symmetry with a general stoichiometry of $A_2B_2O_7$.
- In this generally A is a large low valence cation and B is a small more highly charged cation capable of octahedral coordination.
- The typical structural makeup of a $A_2B_2O_7$ pyrochlore showing the two interlinked structures of blue BO_6 octahedral and A_2O' frameworks (oxygen shown as red and A site cations in purple).

Examples: $La_2Ti_2O_7$, $Sr_2Nb_2O_7$, $Gd_2Ti_2O_7$, $Sm_2Mo_2O_7$ etc.



iiit ROORKEE NITEL ONLINE CERTIFICATION COURSE ADVANCED COMPOSITE LAB 23

In this generally A is the large low valence cation and B is a small more highly charged cation capable of octahedral configurations or maybe the coordinations. The typical structure makeup of $A_2B_2O_7$ pyrochlore showing the two interlinked structure of blue BO_6 , octahedral and A_2O' framework oxygen shows us red in this particular color and A site cations is in to the purple, so like this structure. So, basically this blue color is BO_6 basically.

So, example is that $La_2Ti_2O_7$, $Sr_2Nb_2O_7$, $Gd_2Ti_2O_7$, $Sm_2Mo_2O_7$. So, these are not the examples of the pyrochlore group basically $A_2B_2O_7$. Now, basically what are the challenges we are facing for making this kind of materials or maybe working on these particular materials.

(Refer Slide Time: 31:57)

Challenges:

- The following listed several crucial issues required to be improved:
 - ✓ Increase of output power density.
 - ✓ The integration packaging of energy storage unit with the nanogenerators.
 - ✓ Optimization on harvesting efficiency of mechanical energy from various working conditions.
 - ✓ Optimization of electromechanical conversion efficiency through structural design.
 - ✓ Long-term stability, mechanical strength, and chemical stability of the nanogenerators.
 - ✓ Temperature drift during the sensing process for active/self-powered sensors.
 - ✓ The integration of active or self-powered system with data processing and transmitting systems.

IT ROORKEE | NPTEL ONLINE CERTIFICATION COURSE | ADVANCED COMPOSITE LAB | 24

So, first is that increase of output power density that is the number one challenge basically we are facing for our research purpose. So, every day, we are trying to increase the efficiency of our materials. Second the integration packaging of energy storage unit with the nanogenerators. Third optimization on harvesting efficiency of mechanical energy from various working conditions, because if I change the environmental conditions. So, certainly if the temperature will change or maybe certainly if the humidity will change, then what will be the effect on those particular efficiency. Optimization of electromechanical conversion efficiency through structural design. So, if I change the structure of those particular materials or what will happen, long-term stability, now it is giving the results, but if I use that particular materials for a several times, so whether that materials will give the same results after certain time or not.

Mechanical strength and the chemical stability with the time whether the material will degrade or maybe the material properties will remain same, so that is the chemical stability. Temperature drift during the sensing process for active and the self-powered sensors. The integration of active or self-powered system with data processing and the transmitting systems. So, these all are the challenges basically we are facing. And based on these we are trying to make the new materials to solve these kinds of problems.

(Refer Slide Time: 33:28)

Advantages:

- ✓ Piezoelectric Nanogenerator (PENG) is portable and wearable.
- ✓ PENG can interface with biological systems.
- ✓ PENG has Compact configuration.
- ✓ It is compatible with Micro-Electro Mechanical Systems (MEMS).
- ✓ PENG don't release any harmful gases.

Disadvantages:

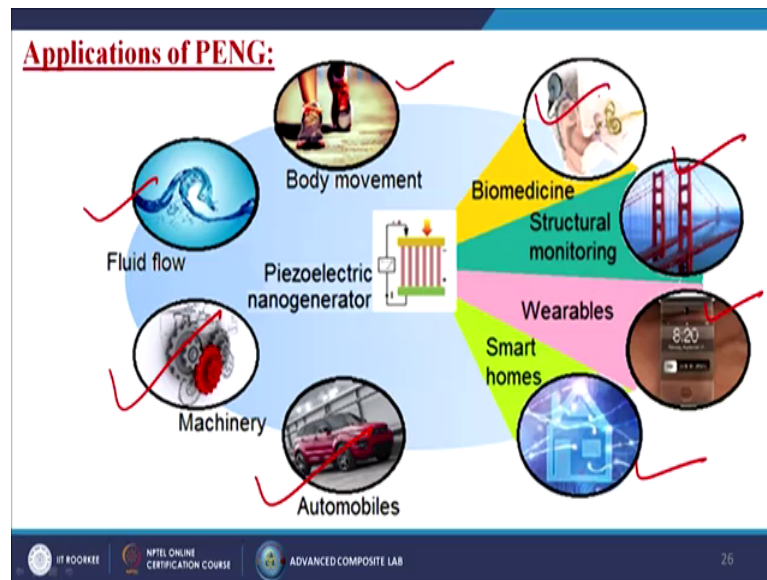
- ✓ Brittleness in PZT.
- ✓ Uniformity in alignment of nanowires.
- ✓ Need to be protected from water.
- ✓ Durability of the structures is less.

IIT ROORKEE NPTEL ONLINE CERTIFICATION COURSE ADVANCED COMPOSITE LAB 25

Now, what are the advantage? So, basically the piezoelectric nano generator is portable and the wearable, as I shown already you are having only the piezoelectric crystals. So, if you make it a small miniature device, you can take it from one place to the another very easily and it is the handy one. PENG an interface with the biological systems. PENG has compact configurations; that means, very compactness having in these particular materials. So, only you are having the piezoelectric crystals and the two electrode, so very compact structure it is having. It is compatible with micro electromechanical systems or maybe the MEMS. PENG, do not release any harmful gases in there is no any kind of chemical reactions.

So, automatically it will not generate any kind of toxic gases to the environment. Of course, the material is having certain disadvantages as I told already first these advantages is the brittleness. The material should have ductile properties, otherwise when we are giving load the material may break. Then uniformity in alignment of the nanowires, because when I am trying to do the vertical alignment maybe some crystals may lay down or maybe can horizontal positions. So, all the crystals if it is it will be through the vertical positions, then only we can get the maximum efficiency over there. Need to be protected from the water and the durability of the structure is less.

(Refer Slide Time: 34:48)



So, in this particular case, basically we are showing the different applications of the PENG. From the various image you can understand that basically where we can put this particular PENG device and we can generate the electricity. So, in this particular case, when we are doing the body movement, if in our shoes we can put these kind of materials. So, while working so each and every step when we are pressing our shoes onto the surface, so automatically it can generate the electricity. In the fluid flow, say suppose you are putting this kind of PENG materials into some pipes or maybe on the sea or maybe on the pond, so when the water wave is coming due to that the material can be compressed and it can generate the electricity.

For any kind of machinery applications automobile basically for the cars or maybe the car tires or maybe the brake, so we can put these kind of materials in the smart homes, wearable gadgets, structural monitoring and the biomedicine case also we can use this kind of particular technology. Basically in any cases where any kind of force or maybe the motions or maybe the movement is generating we can put this particular device, so that it can absorb that pressure or maybe the movement or maybe the strain and it can give you the electricity. So, that is the basic concept of for using this kind of materials.

(Refer Slide Time: 36:13)

Summary:

- ❖ Piezoelectricity or “Pressure energy”, was discovered by the Curie brothers Jacques & Pierre in 1880.
- ❖ Electromechanical coupling factor (k), is the major parameter which affect the performance of piezoelectric material.
- ❖ VING & NEG are in 3-dimensional where as LING is in 2-dimensional configuration.
- ❖ ZnO, GaN, CdS exhibit both semiconductor and piezoelectric properties simultaneously.
- ❖ PZT is the most used ceramic piezoelectric material for generating electricity.
- ❖ In polymers, PVDF is used as material to produce electricity from piezoelectric nanogenerators.

IIT ROORKEE NPTEL ONLINE CERTIFICATION COURSE ADVANCED COMPOSITE LAB 27

So, now we have come to the last slide of this particular lecture. So, in summary, we can say that piezoelectricity or maybe the pressure energy as I told already was discovered by the Curie brothers Jacques and Pierre Curie in 1880. Electromechanical coupling factor is the major parameter which affects the performance of piezoelectric materials. So, when we are going to choose the materials, we have to check that material should have the higher electromechanical coupling factor.

VING and NEG are in three dimensional, whereas LING is in 2-dimensional configurations. Zinc oxide, gallium nitride, cadmium sulphide exhibit both semiconductor and the piezoelectric properties simultaneously. PZT is the most used ceramic piezoelectric materials for generating the electricity. In polymers, PVDF is versatile used as material to produce the electricity from piezoelectric nanogenerators. So, basically the materials we are choosing which can give the maximum efficiency after absorbing any kind of load pressure or maybe the strain.

Thank you.