Selection of Nanomaterials for Energy Harvesting and Storage Applications
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Lecture – 13
Pyroeletric Nanogenerators

Hello my friends, today we are going to discuss about our new chapter based on Pyroelectric Nanogenerators. So, in this particular chapter we are going to discuss about that how the heat energy is converting into the electric energy. So, basically if I talk about the pyroelectric; that means, you are having certain kind of materials and you are giving certain kind of temperature or may be the heat to that particular materials due to the material characteristics will change and it will deliver you the electrical energy.

So, basically wasting heat is a reach source of energy that could be harvested, means that is the main tagline because why we are using; because when the sunlight is coming on to the earth or maybe somewhere else a large amount of sun light that we are wasting. So, now, if I am having certain systems where I can store that particular sunlight so, that wasted sunlight can be converted into the electric energy. So, that is a good idea so, based on that principal basically this technology has come.

So, in this particular case the harvesting of the wasted heat would provide a significant option for green and renewable energy yes of course, because simply I am having that materials the sunlight are coming or maybe any kind of heat sources are coming and then that is converting into the electrical energy. So, we are not going to do any kind of chemical reactions or may be any toxic gas can be generated.

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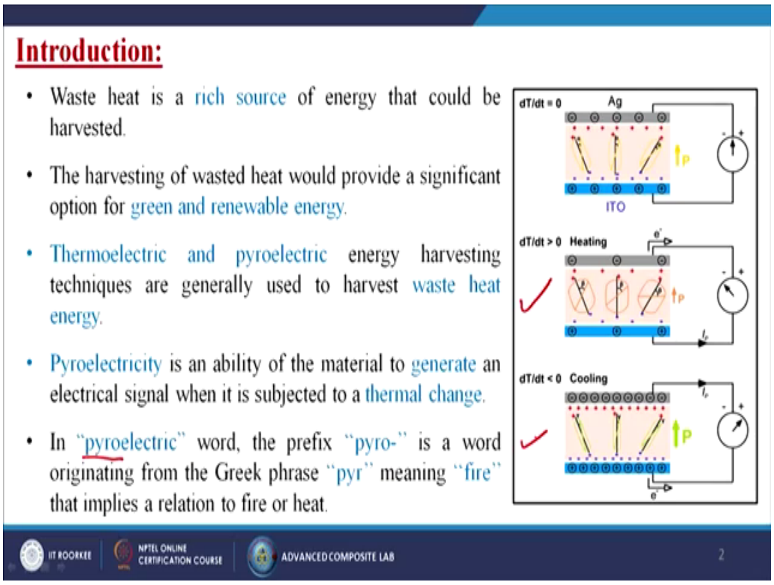

Thermoelectric and pyroelectric energy harvesting techniques are generally used to harvest waste heat energy. As I told already, because whatever the energy we need for our day to day life keeping that constant then rest of the energy we can utilize for generation the electricity, because in near future maybe our petroleum, maybe our coal products or maybe our fossil fuels can be finished. So, I have to think certain kind of renewable energy where we can use this kind of energy so, that we can sustain for a longer time.

So, pyroelectricity is an ability of the materials to generate an electrical signal when it is subjected to a thermal change, yes in the piezoelectric case also I told you that if I am having certain materials if I put the load due to that load or pressure or maybe that any kind of stress so, the material can generate the electricity. So, same thing in the pyroelectricity case also I am having that materials so, if I give little bit of temperature over there or maybe if I change the temperatures so automatically that energy will be converting into the electric energy.

So, basically in "pyroelectric" word, the prefix "pyro" so, basically this only this small terms "pyro" is a word originating from the Greek phase that is "pyr" means the "fire". So, fire means automatically the heat will come so, that implies a relation to fire or heat. So, basically in this particular case this is the whole mechanism. So, when I am changing the temperature or maybe when I am heating the materials or may be the cooling the materials automatically the thermal stress is generating inside the materials due to that the electricity is being produced.

So, now if you talk about the history you can see that this is not the newer technology, but newer in the sense of that scientists those who are working or may be those who are the pioneer in this particular field basically Professor Zhong Lin Wang. So, basically what they are doing the concept is same, but they are developing some new materials. So, due to a little bit change in the temperature they can produce the more energy; that means the efficiency of the materials people are trying to increase. So, that is the basic of this particular topic and they are working on it.

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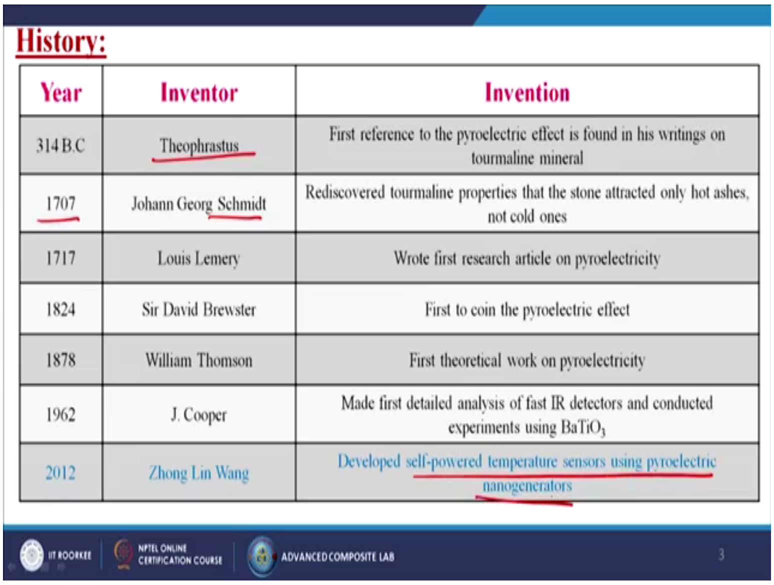

History:

Year	Inventor	Invention
314 B.C	Theophrastus	First reference to the pyroelectric effect is found in his writings on tourmaline mineral
1707	Johann Georg Schmidt	Rediscovered tourmaline properties that the stone attracted only hot ashes, not cold ones
1717	Louis Lemery	Wrote first research article on pyroelectricity
1824	Sir David Brewster	First to coin the pyroelectric effect
1878	William Thomson	First theoretical work on pyroelectricity
1962	J. Cooper	Made first detailed analysis of fast IR detectors and conducted experiments using $BaTiO_3$
2012	Zhong Lin Wang	Developed self-powered temperature sensors using pyroelectric nanogenerators

So, basically the concept it has been started in the year of 314 BC and of course, from the name itself we can understand that that is the Greek name. So, the technology has invented from the Greek side itself. So, Theophrastus so, first reference to the pyrolytic effect is found in his writings on tourmaline mineral.

Then we have come to 1707 by Professor Schmidt who did discovered the tourmaline properties that the stone attracted only hot ashes not the cold ones. So, the concept is slowly-slowly it is became modernized and now we have reached in the year of 2012 where Professor Zhong Lin Wang develop the self powered temperature sensors using the pyroelectric nanogenerators. Till they are working they are developing so many new materials just to increase the efficiency.

Now what are the some basic points or may be the basic parameters which we need to be considered?

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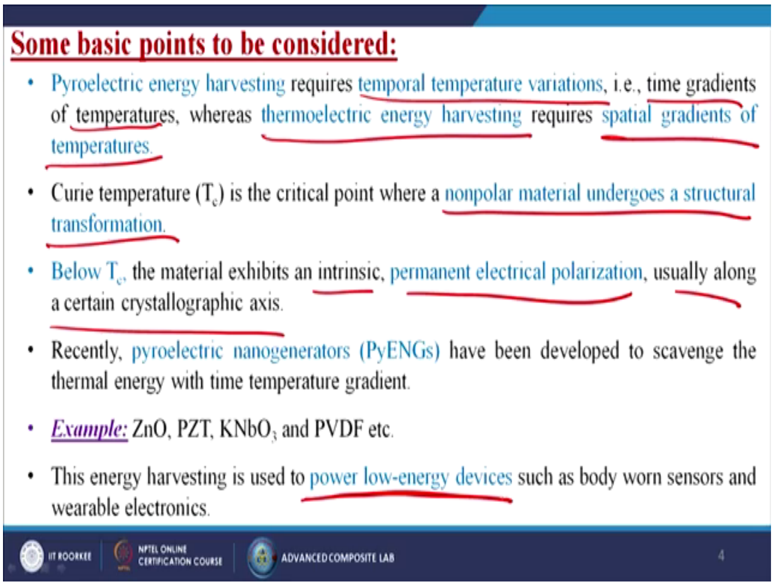

So, first is that pyroelectric energy harvesting requires temporal temperature variations, as I told already when the material is I am having. So, the material is having some temperature, that temperature is nothing, but the room temperature or maybe the environmental temperature.

Now, I have to give certain kind of heat over there or maybe I have to take certain kind of heat from there so, automatically there will be a some temperature change or may be the variation inside the materials. Now time gradient of temperature where as the thermoelectric energy harvesting requires the spatial gradients of the temperature it should be or maybe rather I can say there should be some kind of fluctuations of temperature inside the material.

Curie temperature is the critical point where a nonpolar material undergoes a structural transformation. So now, if I give certain kind of temperature for a particular material or may be the any kind of temperature so, that the material can generate the electricity. Below T c; that means, curied temperature the material exhibits an intrinsic permanent electrical polarization, usually along a certain crystallographic axis. Recently pyroelectric nanogenerators have been developed to scavenge the thermal energy with time temperature gradient.

So, there are lots of applications where we are using these pyroelectric nanogenerators by just to use the waste heat over there so that we can get the electricity. What are the examples of this pyroelectric nnaogenerator materials? Like Zinc oxide, PZT, then KNbO 3 and the PVDF. So, these energy harvesting is used to power low energy devices such as body worn sensors and the wearable electronics.

Now, you can see in our body temperature it is 98.4 degree Fahrenheit that is the normal one. So, if I am able because and that is a waste. So, now, if I put any kind of wearable sensor and that can be take our 98.4 degree Fahrenheit and then if that device is able to convert that heat energy into the electricity, that is a wonderful one.

So, in future we can think like that we are putting a particular wearable or flexible heat sensor on to our body and then we can be able to charge our gadgets like iPod, like mobile phones or maybe some other means so, that is a wonderful idea. So, basically this is the concept so simple we are gathering the heat energy and we are converting that heat energy into the electricity. What is the mechanism of this?

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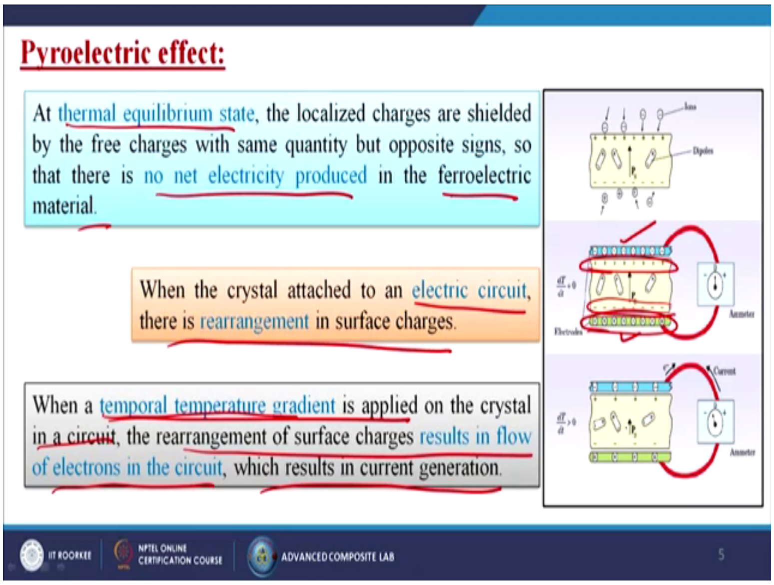

So, basically at thermal equilibrium state the localized charges are shielded by the free charges with the same quantity, but opposite signs so that there is no net electricity produced in the ferroelectric materials.

So, in this particular case simply I am having the materials though the charge is there at the surface itself. So, one side will be the positive, another side will be the negative, now what we are doing, simple we are putting 2 electrodes over there. So, one is in to the top positions, another one is into the bottom positions. So, when the crystal attached to an electric circuit there is an rearrangement in the surface charge yes of course, because when I am putting the minus over here automatically it will became the positive and when I will put the positive over here automatically this surface will became the negative.

Now, when a temporal temperature gradient is applied on the crystal in a circuit; the rearrangement of surface charges results in flow of electrons in the circuit, which results in current generation. So now, that means what, when we are giving the temperature change in that particular materials so automatically the current will flow, because due to that the charge transfer taking place in between the material surface and your electrode.

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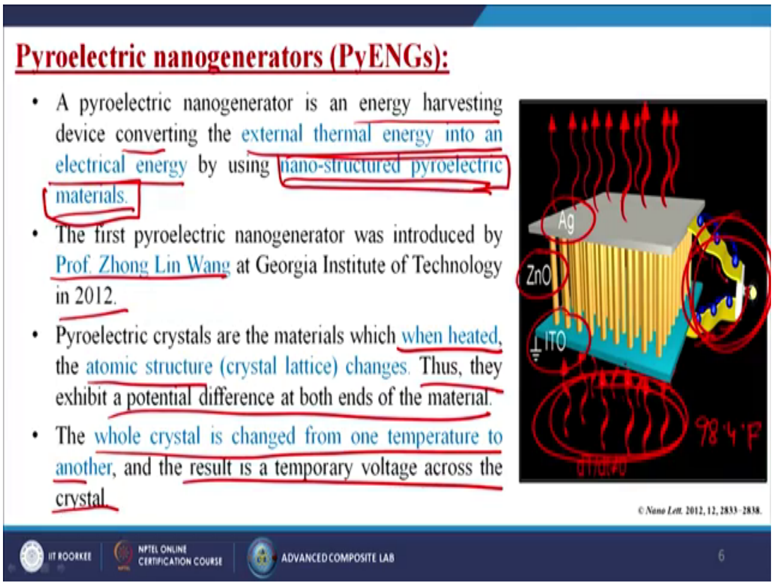

Now, come to the pyroelectric nanogenerators or in short we are calling it as a PyENGs. So, a pyroelectric nanogenerator is an energy harvesting device converting the external thermal energy into an electrical energy, as I told already by using nanostructured pyroelectric materials. That means, these materials is having that capability that when I am giving the temperature to the particular materials it is generated the current or may be the floor of the electrons. So now, the first pyrolytic nanogenerator was introduced by

Professor Zhong Lin Wang at Georgia Institute of Technology in the year of 2012. So, pyrolytic crystals are the material which when heated, the atomic structure or maybe the crystal lattice or may be the crystal lattice structure basically changes.

Thus they exhibit a potential difference at both ends of the materials. So, that is the beauty of this particular material. In this examples we have given the examples of the zinc oxide and we are having 2 electrodes, one is made by the silver A g, another one is the ITO: Indium Tin Oxide. So, basically in this particular case you can see we are giving the temperature to the particular materials and automatically the electron is flowing and then we are getting the current over in this particular region.

So, the whole crystal is changed from one temperature to another and the result is a temporary voltage across the crystal. So, now, if this heat basically the waste heat we are applying. Now, if you think that if we these material we put on to our body so, automatically from the body 98.4 degree Fahrenheit automatically it will get and constantly it will generate the electricity. Now I am putting certain kind of energy storage device over there which can store that electricity and later on when we need we can utilize it. Now what is the mechanisms? Basically there are two types of mechanisms based on that the pyroelectric nanogenerator works.

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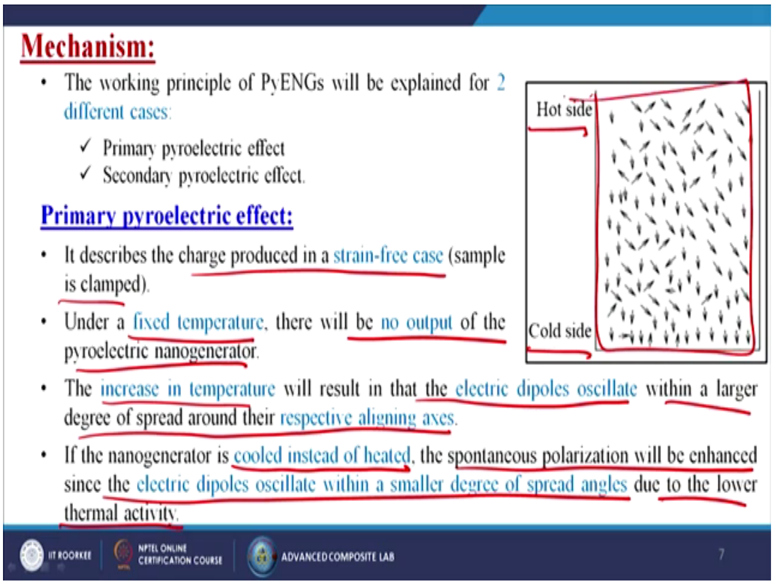

So, first working principle is known as the primary pyroelectric effect and the second one is known as the secondary pyroelectric effect. So, what is primary pyroelectric effect? In this particular case you can see that I am having that materials so, I am giving the heat. So, one side became the hot one and another side became the cold one of course, so, now, it describes the charge produced in a stream free case sample is clamped. So, I am having that sample from the both side I am clamping it, I am giving the temperature so, one side will became the more hotter than the another one.

Under a fixed temperature there will be no output of the pyroelectric nanogenerator that is due to the material thermal conductivity, because the heat is distributing along the material itself. The increase in temperature will result in that the electric dipoles oscillate within a larger degree of spread around their respective aligning access. Now if we little bit increase the temperature. So, automatically now the dipole moment acts over there, now the atoms is try to move into the different directions.

If the nano generator is cooled instead of heated the spontaneous polarization will be announced since the electric dipoles oscillate within a smaller degree of spread angles due to the lower thermal activity.

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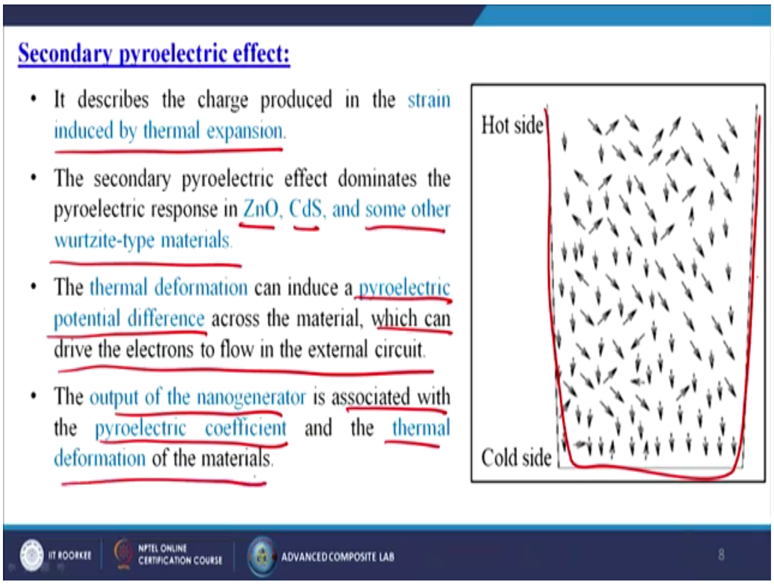

Now, if we talk about the secondary pyroelectric effect. So, it describes the charge produced in the strain induced by thermal expansion. So, in this particular case you can see in the last case when you are giving the heat the shape is not going to be changed, but in this particular case when I am going to give the heat you see the shape is going to be changed; that means, what the elongations or may be the contractions is taking place inside the material.

So, the secondary pyroelectric effect dominates the pyroelectric response in zinc oxide, cadmium sulphide and some other wurtzite type material. The thermal deformation can induce a pyro electric potential difference across the material which can drive the electrons to flow in the external circuit, so that means, in this particular case the material shape is changing so, the electric energy is getting produced. The output of the nanogenerator is associated with the pyroelectric coefficient and the thermal deformation of the materials, as I told already either the material will elongate or maybe it will be compressed. So, in other way the material will generate the electricity.

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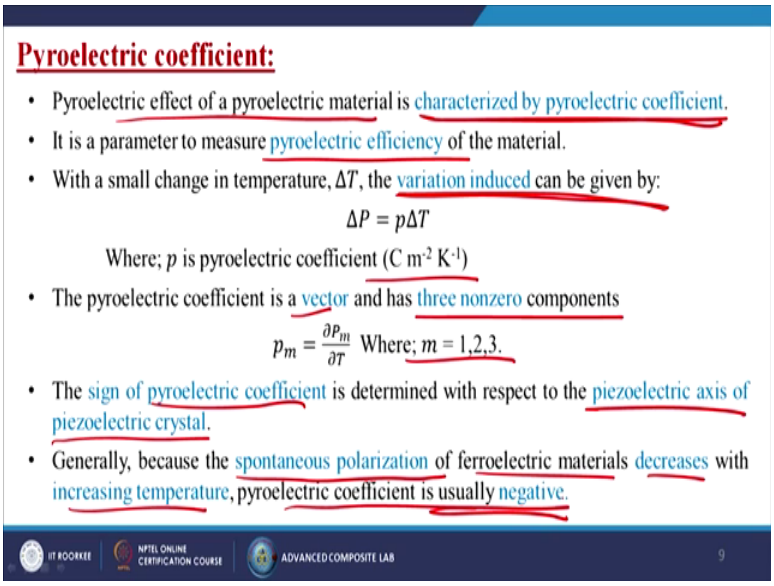

Now, we are going to talk about the pyroelectric coefficient what is that, basically the pyroelectric effect of a pyroelectric material is characterized by pyroelectric coefficient which I told. So, main aim of the scientist in today's world to increase that pyroelectric coefficient so, that they can get the maximum efficiency from that particular materials. From the material scientist point of view people are working to enhance the material properties or maybe some bear materials they are taking if it is not possible then they are doing some kind of coating some kind of doping so, that the material can enhance their physical properties so, that they can get the maximum efficiency from that particular material.

So, it is a parameter to measure the pyroelectric efficiency of that particular materials. So, with a small change in temperature that is del capital T the variation induced can be given by del capital P is equal to small p into del capital T, where small p is the pyroelectric coefficient whose unit is coulomb per metre square per Kelvin. So, the pyroelectric coefficient is a vector and has 3 non-zero components. So, p m is equal to del p m by del capital T, where m is nothing, but the 1, 2, 3.

The sign of pyroelectric coefficient is determined with respect to the piezoeletric axis of the piezoeletric crystal. Generally because of spontaneous polarization of ferroelectric materials decrease with increasing temperature pyroelectric coefficient is usually the negative one yes. So, when I am increasing one another one is decreasing or may be another one I am increasing so this one is decreasing. So, automatically it is coming to the negative sides. Now what are the factors that to be considered in selecting the materials for PyENG.

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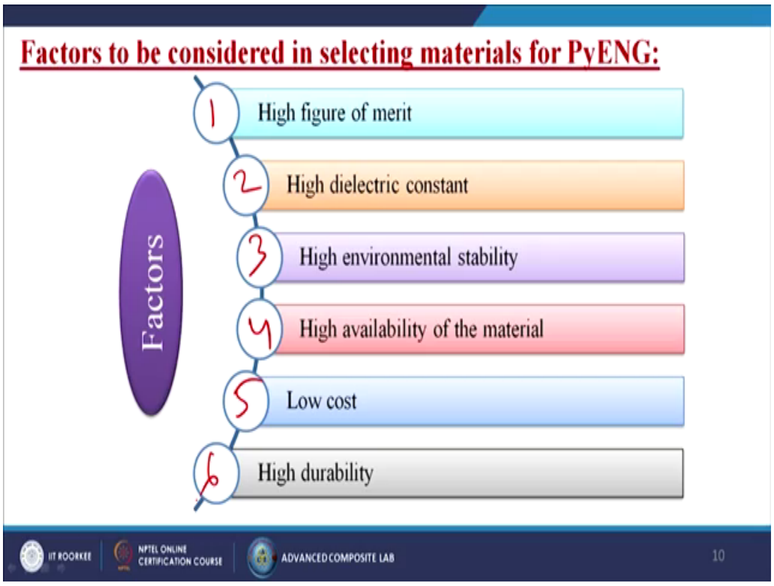

So, basically there are several factors like high figure of merit, high dielectric constant, high environmental stability, high ability of the material, low cost and it should have high durability. So, these all are my prime considerations for choosing any kind of pyroelectric material.

So now, if I talk about the overall pyroelectric material characteristics so, in this particular case in the left hand side image you can understand that when you are talking about the ferroelectric materials so, that basically that comes under the pyroelectric materials.

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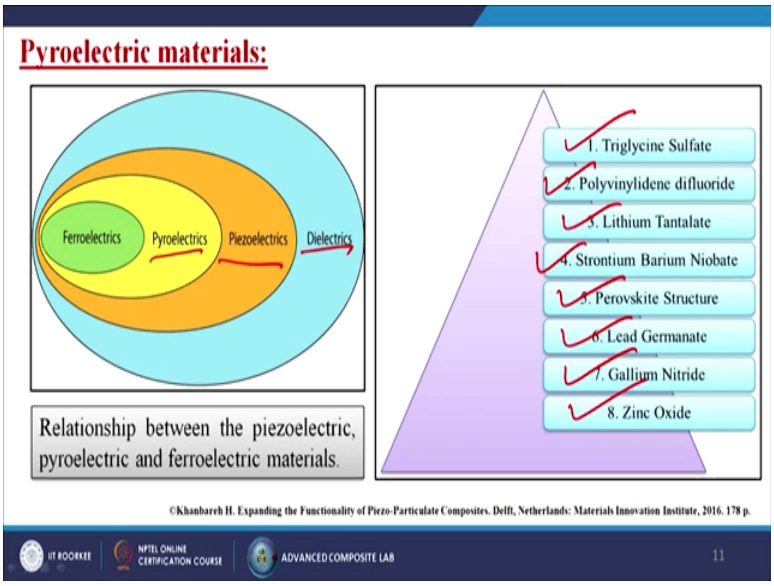

When we are talking about the pyroelectric materials basically that comes under the piezoeletrics materials and when you are talking about the piezoeletric materials it is coming under the dielectrics, that means, the dielectric is the whole universe. In dielectrics some parts are piezoelectrics, in piezoelectrics some parts are pyroelectrics, in pyroelectrics some parts are the ferroelectrics material. So, this is the basically the relationship between the piezoelectric, pyroelectric and the ferroelectric materials.

Now if we talk about the examples there are lots of examples are available because scientist are everyday they are preparing some kind of new materials, for getting the more efficiency, but if I want to tell you some few examples looks like tryglycine sulphate, polyvinylidene difluoride PVDF, then lithium tantalite, strontium barium niobate, perovskite structure, lead germinate, gallium nitride and last one is the zinc oxide.

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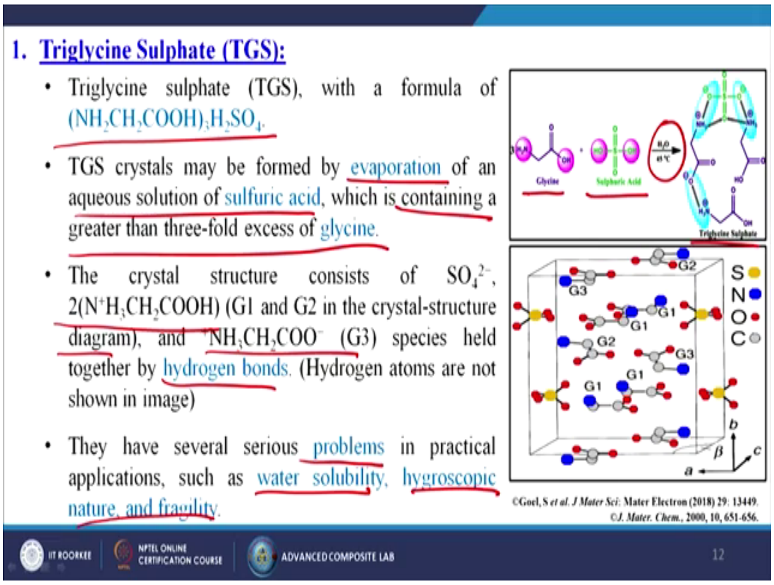

Now, if we talk about the triglycine sulphate. So, basically it is having the formula is this one. So, it is having the sulphuric acid basically H 2 SO 4 groupers attached with that materials. So, we are having that glycine, we are adding with the sulphuric acids and in the presence of water at 45 degree centigrade if we heat it then we can find this particular triglycine sulphate material. So, in short basically you are calling is a TGS.

So, now, TGS crystal maybe form by evaporation of an aqueous solution of sulfuric acid so, as I told already. So, we are basically doing the evaporations at 45 degree centigrade, which is containing a greater than 3 fold excess of glycine. The crystal structure consists of sulphate ion then this particular ion which is nothing, but the G 1 and G 2 in the crystal structure diagram and G 3 species held together by the hydrogen bonds. So, basically this is the whole structure of that TGS system.

They have several series problems in practical applications such as water solubility, hygroscopic nature and fragility. So, if I keep that materials for a longer time into the environment maybe it can absorb the moisture from the environment itself or maybe the material can break very easily so, it can be very fragile. This is the most interesting materials from the electronics point of view, because PVDF is a very nice materials which is showing different properties we can use it as a dielectric materials, we can use it some kind of nanogenerators and maybe any kind of electricity generations, we can use the PVDF materials. So, basically the full form of PVDF is known as polyvinylidene difluoride.

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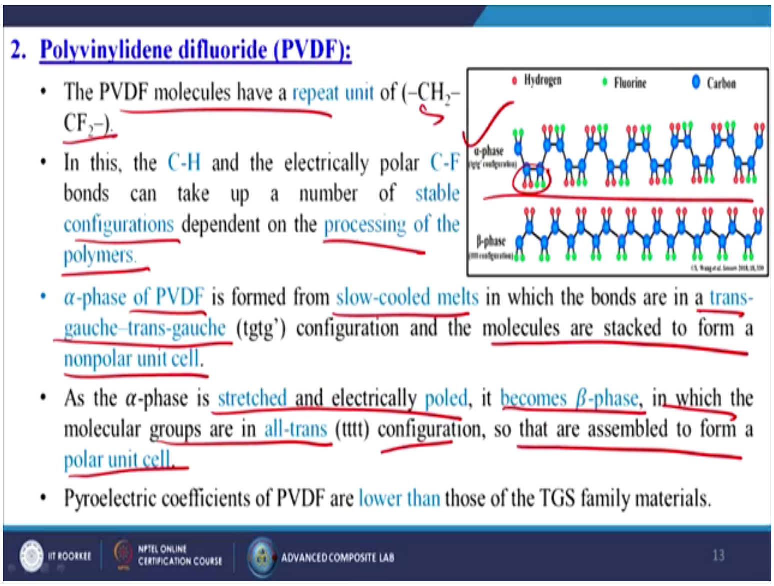

So, basically the PVDF molecules have a repeat unit of CH 2 and CF 2. So, in this particular case you can see so that is having a repeating unit. In this the C-H and the electrically polar CF bonds can take up a number of stable configurations dependent on the processing of the polymers. So, basically PVDF is one kind of polymer so, sometimes we are using this PVDF with some other materials also to make it more conductive or maybe sometimes PVDF we are using to generate the electricity or maybe to pass the electricity through the non conducting material.

So, basically the alpha phase of PVDF is formed from slow cooled melts. So, this one in which the bonds are in a trans - gauche - trans - gauche configurations. So, basically the tgtg' configurations we are telling and the molecules are stacked to form a non polar unit cells so, this one is the structure. As the alpha phase is stretched and electrically poled it becomes the beta phase, in which the molecular groups are in all - trans tttt configurations so that are assemble to form a polar unit cell.

So, in this particular case what happened you see, in this particular case it is 1, then it is having the 2 over there. So, in this particular case it is 1 1 1 1 1 1 into the consecutive manner. So, it becomes the more polar over there. So, it is having the more power to generate the maximum efficiency. So, pyroelectric coefficients of PVDF are lower than those of the TGS family materials that is also a one kind of drawback of this particular material. So, next is called the lithium tantalite.

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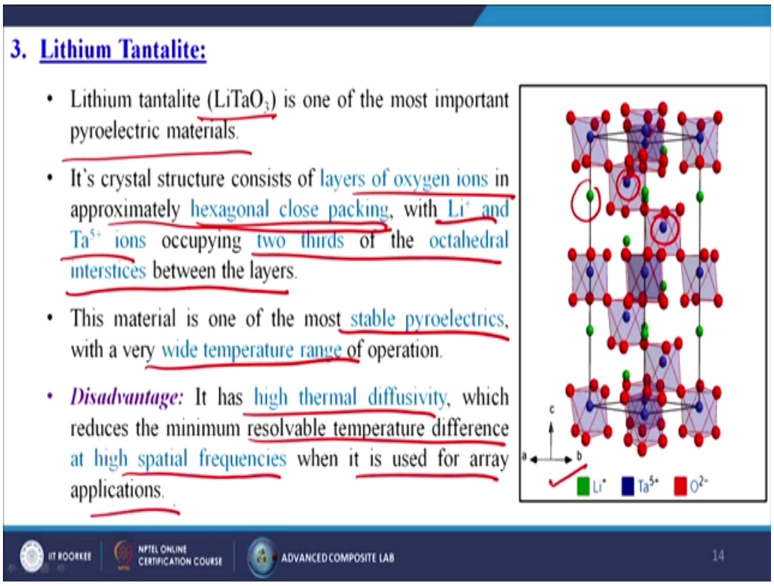

So, basically the lithium tantalite the formula is this one LiTAaO 3 is one of the most important pyroelectric materials. It is crystal structure consists of layers of oxygen ions in approximately hexagonal close packing, with lithium ion and tentalium ions occupying two thirds of the octahedral interstices between the layers.

So, this is the basically the structure if we talk about that green colour that is the lithium ion, if you talk about the blue colour that is the tantalum over there so, these all are the tantalum ion and red one is the oxygen so, that is also the repeating unit basically it is forming. This material is one of the most stable pyroelectrics, with a very wide temperature range of operations.

Of course, there are certain kind of disadvantages what is that, it has high thermal diffusivity which reduces the minimum resolvable temperature difference at high spatial frequencies when it is used for array applications. That means, I cannot use that particular materials at higher temperature the material will diffuse. But in the lower temperature this material is fantastic and it is giving some good efficiency.

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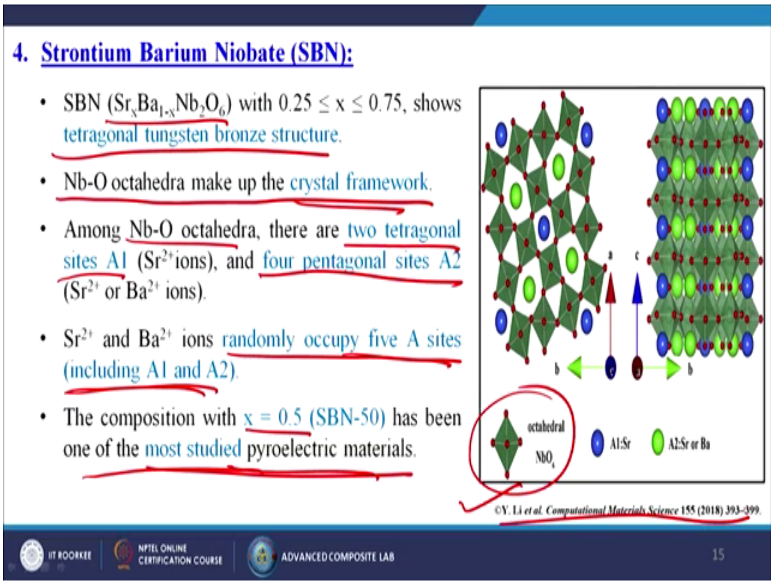

Next one is called the Strontium Barium Niobate so, in short basically we are calling it has a SBN. So, SBN the formula is this one with 0.25 less than is equal to x which is less than is equal to 0.75 that means, x varies from 0.25 to 0.75, shows the tetragonal tungsten bronze structure. Then niobium oxygen octahedra make up the crystal framework over there so, now, we can see what a nice crystal structure over there it is the octahedral crystal structure like this.

And then among Nb-O octahedral, there are 2 tetragonal sites A 1 and 4 pentagonal sites A 2. So, basically A 1 by the strontium 2 plus ions and A 2 is basically the strontium or maybe the beryllium 2 plus ions. So, strontium 2 plus and the beryllium 2 plus ions randomly occupy 5 A sites including A 1 and A 2 the composition with x is equal to 0.5. That means, we are given the like nomenclature like SBN - 50 has been one of the most studied pyroelectric materials and also the people have use that materials in these particular journal also. So, basically this is the crystal structure of that SBN. Next is the perovskite structure.

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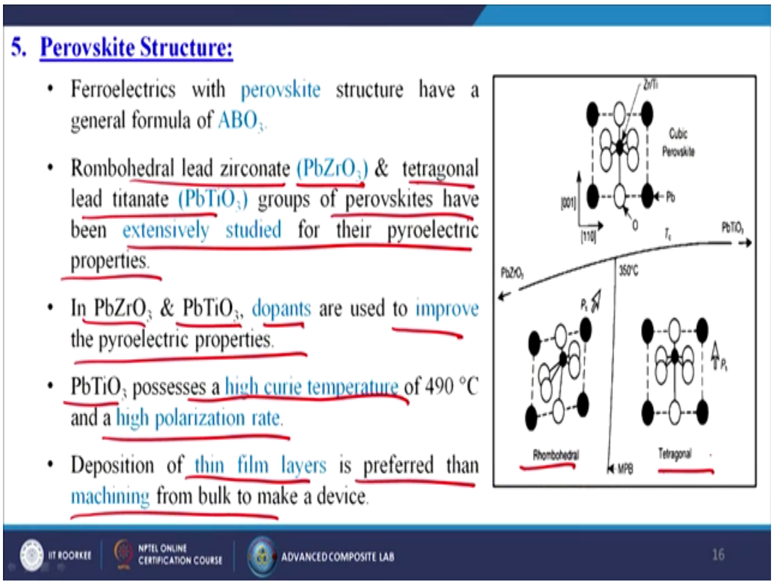

So, ferroelectrics with perovskite structure have a general formula is basically ABO 3. So, in these particular case rombohedral lead zirconate PbZrO 3, tetragonal lead titanate PbTiO 3 groups of perovskite have been extensively studied for their pyroelectric properties. In PbZrO 3 and PbTiO 3 dopants are used to improve the pyroeletric properties. That means, we are introducing certain kind of third party materials inside the systems to increase the efficiency. PbTiO 3 possesses a high curie temperature of 490 degree centigrade and the high polarization rate.

Deposition of thin film layers is preferred than machining from bulk to make a device. So, basically perovskite materials is also having different crystal structure like rhombohedral, like tetragonal. So, based on that material configurations and the dopants we can change the crystal structure of that perovskite materials so, that it can give you the maximum efficiency.

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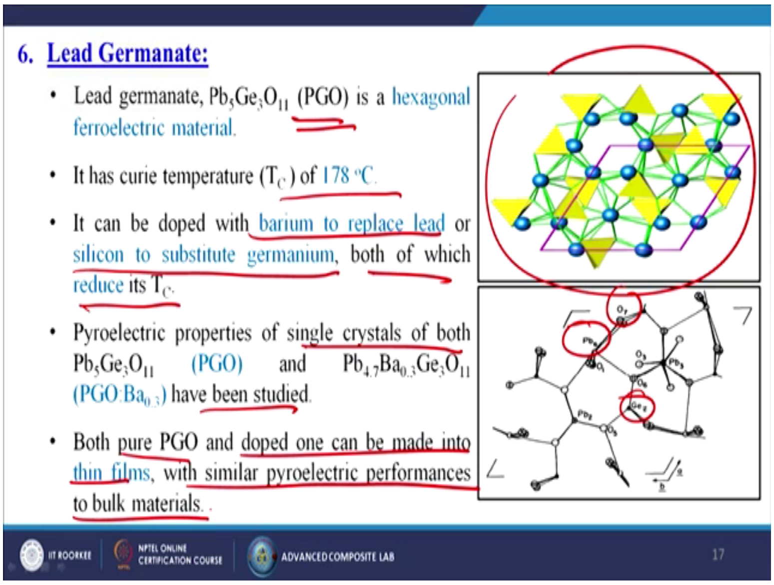

Next one is called the lead germanate. So, basically the lead germanate, Pb 5 Ge 3 O 11 in short basically we are calling it as a PGO is a hexagonal ferroelectric material. It has Curie temperature of 178 degree centigrade, it can be doped to barium to replace lead or maybe silicon to substitute germanium both of which reduces it is curie temperature. So, this is the crystal structure basically. So, in this particular case this is the lead, this is the oxygen and here we are putting the germanium so, this is the crystal structure.

Basically the pyroeletric properties of single crystals of both PGO and PGO attached with the barium have been studied. So; that means, we are having the PGO now the people are trying to incorporate the barium inside, it is crystal structure like a dopant or maybe some other means. Both pure PGO and doped one can be made into thin films, with similar pyroeletric performance to bulk materials.

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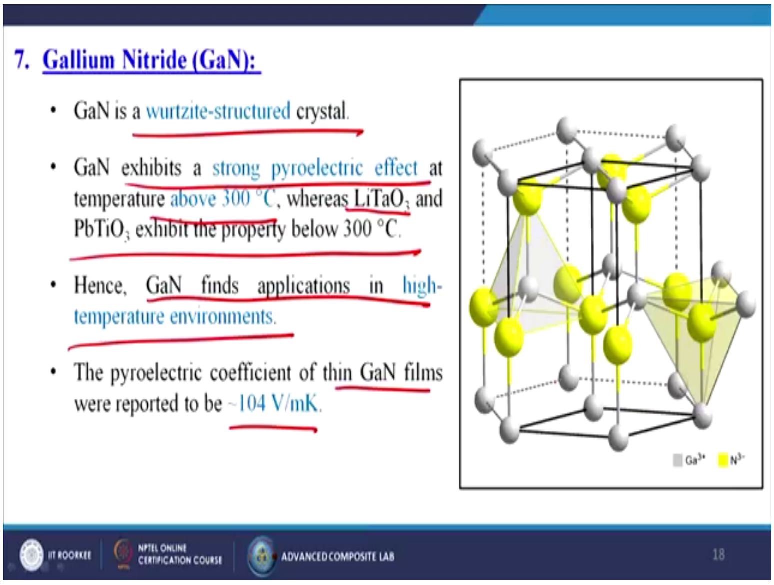

Next one is call the gallium nitride GaN. So, GaN is a wurtzite - structured crystals. Gallium nitride exhibits a strong pyroelectric effect at temperature above 300 degree centigrade, where as a LiTaO 3 and PbTiO 3 exhibit the property below 300 degree centigrade, so that means, for these particular materials you need the higher temperature. Hence, gallium nitride finds applications in high temperature environments. The pyroelectric coefficient of thin gallium nitride films were reported to be 104 volt per metre kelvin. So, basically this is the standard structure of the gallium nitride which can work into the higher temperature.

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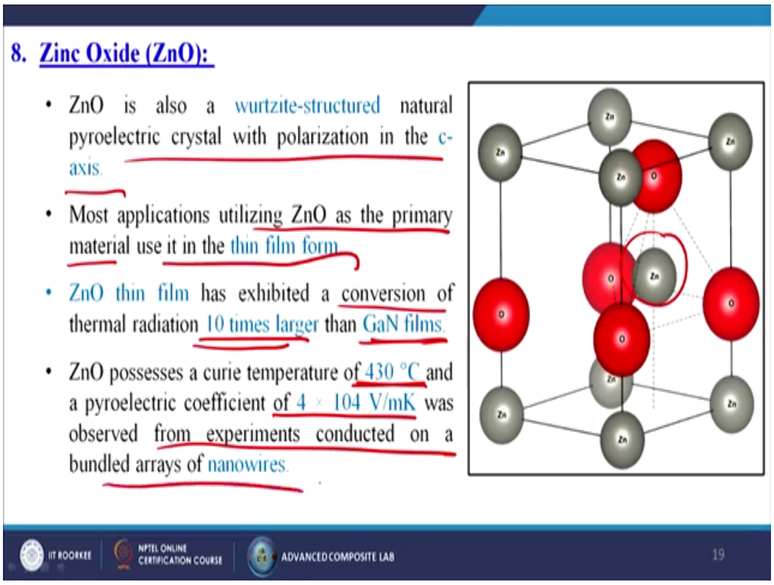

Next one is the zinc oxide. So, basically the zinc oxide is also a wurtzite - structured natural pyroelectric crystal with polarization in the c axis. So, in this particular case this is the structure the uppermost surface is taking by the zinc atom and then the below most and I am having that oxygen and in between that also I am having the one zinc atom. So, you can see it is a very close packed kind of structure formation over there. Most applications utilizing zinc oxide as the primary material use it in the thin film form. Zinc oxide thin film has exhibited a conversion of thermal radiation 10 times larger than the gallium nitride films.

Zinc oxide possesses a curie temperature of 430 degrees centigrade and a pyroelectric coefficient of 4 into 104 volt per meter Kelvin was observed from experiments conducted on bundled arrays of nanowires. So, people have done lots of work on the zinc oxide and it is a wonderful material for giving the electricity. Now if we talk about the applications of this pyroelectric nanogenerators.

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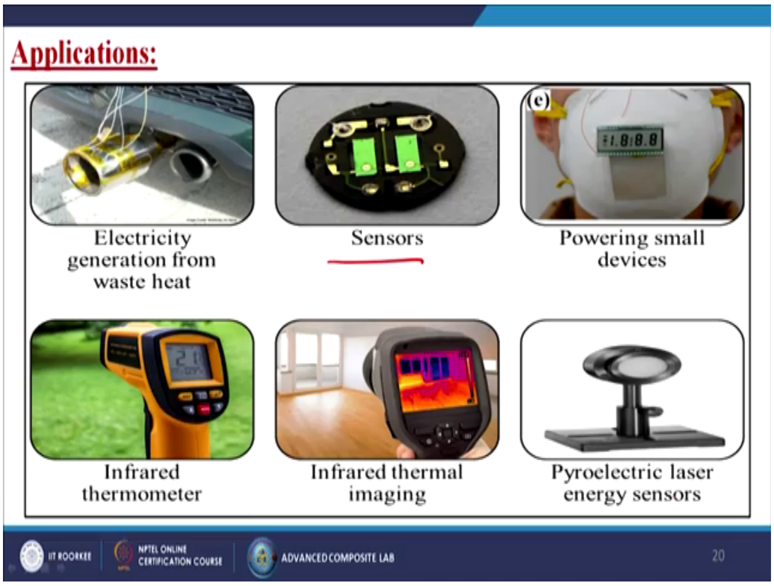

So, we can put it at the exhaust of our car or maybe the automobiles. So, that when the hot gases means carbon dioxide or carbon monoxide or may be the pollutions or maybe the smokes are coming. So, it is heated because it is coming directly from the engine itself.

Now, if I put certain kind of sensors over there and the sensor can above to convert that particular temperature into the electricity that will be a great idea because that is the full wastage one. Next we are putting certain kind of sensors, we are using the power in small devices simply we are putting on our body or maybe we can directly put on our skin and then from the body temperature we can be able to convert it into the electricity.

We are having that infrared thermometer, infrared thermal imaging systems or maybe the pyroeletric laser energy sensors so, these all are basically the sensing device. Nowadays the thermometer is also come the for measuring the body temperature, no need to put directly contact with your body. Simply you are having one gun you are having small ir over there, you put the ir anywhere in your body and directly the what is the temperature it will come to your screen.

So, like this way say suppose I am working into some high temperature material say suppose 2000 degree 3000 degree. So, that time for measuring that particular temperature it is really-really difficult, because I cannot use any kind of materials direct contact because the material will be melted or maybe the distorted. So, if I am having this infrared thermometer simple from a particular cell distance I can put that inferred on to that particular material and easily I can measure.

So, there are n number of applications not only that here I have given only 7 types of materials, but if you try to find it. So, you can get n number of materials basically people are working for this pyroelectric effect, which can sense heat can be converted into the electricity. Now we are come to the last part of this particular lecture or maybe other I can say last slide.

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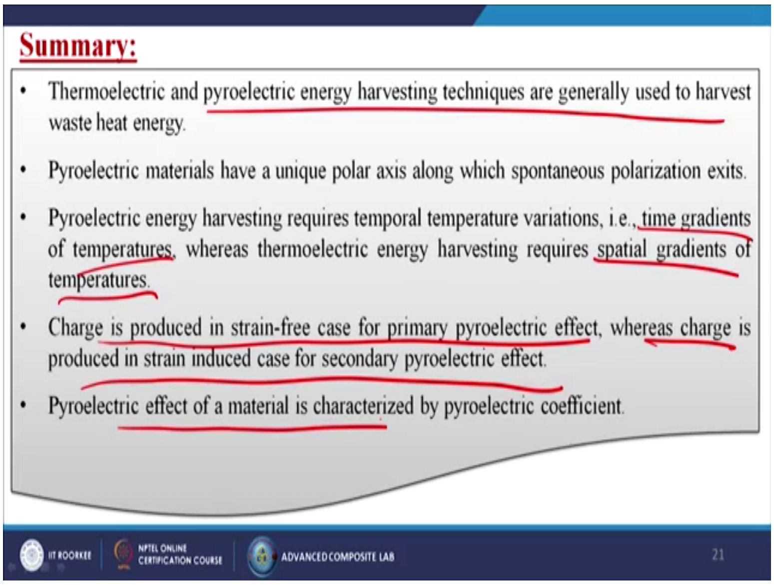

So, basically in summary we can say that thermoelectric and pyroelectric energy harvesting techniques are generally used to harvest the waste heat energy as I told already. Pyroelectric materials have a unique polar axis along which spontaneous polarization exist. Pyroeletric energy harvesting requires temporal temperature variations that is time gradients of temperatures, whereas, thermoelectric energy harvesting requires a spatial gardens of temperatures so, that is the basically the difference between these two.

Charge is produced in strain free case for primary pyroeletric effect whereas, charge is produced in strain induced case for secondary pyroelectric effect. Pyroelectric effect of a material is characterized by the pyroelectric coefficient. So, whenever we are making any kind of materials our main aim to increase the pyroelectric coefficient of that particular material. So, that in a little bit changing in the heat also if the material be able to convert that very low fluctuation of heat into the electricity. So, that is the basic motto of this pyroelectric nanogenerator.

Thank you.