Selection of Nanomaterials for Energy Harvesting and Storage Applications
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Lecture – 03
Perovskite Solar Cells

Hello my friends, we are going to discuss about the Perovskite Solar Cells as lecture 3. Basically if you remember in our my last lecture we have discussed about the different types of solar cells preparations, but in that particular lecture I have discussed about that what will be the future materials that it can give the maximum efficiency.

So, in this particular lecture we are going to discuss about the perovskite materials or maybe that perovskite solar cells, which basically now it is the scientist are working tremendously so, that we can get the maximum efficiency. I will show you some results that how we have achieved the maximum efficiency than the dye sensitized solar cells or may be some other kind of materials. So, basically now people are working on it.

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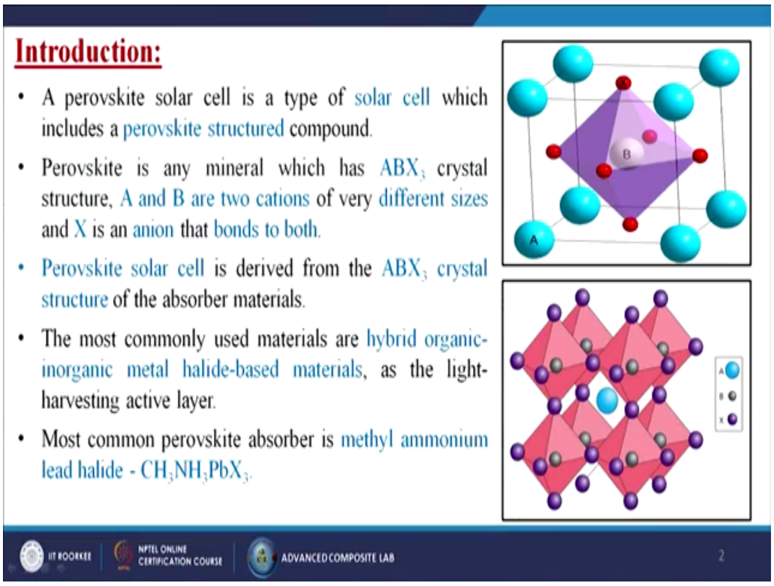

So, before going to know about the perovskite solar cell so, just let us know that what is the perovskite materials. So, basically a perovskite solar cells is a type of solar cell which includes a perovskite structure compound. So, basically the perovskite has come from the scientist name who has invented this particular materials or may be this particular formula. So, perovskite is any mineral which has ABX 3. So, that is a vital point ABX 3 crystal structure where A and B are the two cations of very different size and X is an anion that bonds to the both. So, basically both the sides I am having the A and B which is having the different size and in between I am having the X which is holding the hand of the A and B.

So, basically the perovskite solar cell is derived from the ABX 3 crystal structure of the absorber materials. The most commonly used materials are hybrid organic inorganic metal halide best materials as the light harvesting active layer. Most common perovskite absorber is methyl ammonium lead halide. So, you can see over CH 3 NH 3 and PbX 3. So, X can be anything. So, any kind of halogen group we can put it over there.

So, like this way the people are making the different types of the combinations of the perovskite materials and then that materials they are using for making the solar cells and just to test the efficiency of those materials and how the material is the giving the different types of efficiency we are going to see in our subsequent slides. So, basically if we talk about the history of this particular type of solar cell materials.

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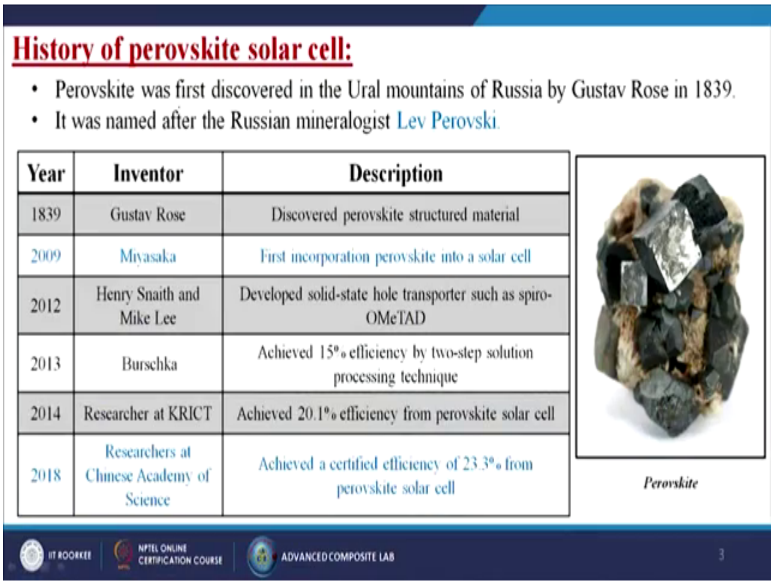

So, perovskite was first discovered in the Ural mountains of Russia by Gustavo Rose in 1839, it was named after the Russian mineralogist Lev Perovski. So, from this particular; so, just to give a respect to the inventor name so, the material has known as the perovskite material. So, if you see the total history we can find that in 1839 it has been invented by Gustavo Rose discovered perovskite structure material. In 2009 in Miyasaka who used this particular materials into the solar cell.

That means, the material is not new material has been invented more than 100 years ago, but now it is people are using that particular materials for the solar cell application. In 2012 Henry Snaith and Mike Lee they developed the solid state hole transport such as Spiro OMeTAD. In 2013 Burschka achieved 15 percent efficiency by two step solution processing technique. In 2014 researcher at K R I C T KRICT achieved 20.1 percent efficiency from the perovskite solar cell.

In 2018 researchers at the Chinese academy of science, they achieved a certify deficiency of 23.3 percent from perovskite solar cell. So, now, you can imagine what I am telling every time that only material is same just to change the halide group people are trying to increase the efficiency of this particular materials. And as per my knowledge till today we have achieved upto 223.7 percentage of the efficiency by using this perovskite solar material.

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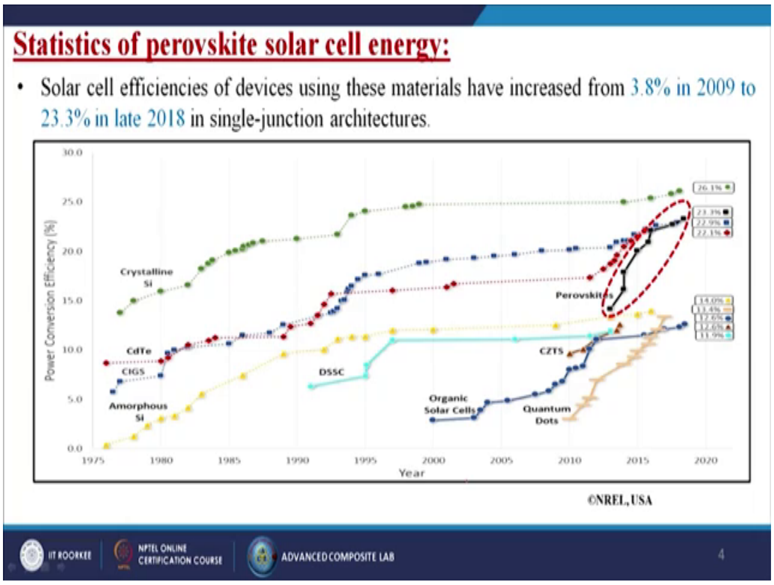

So, now if we talk about the statistics of the perovskite solar cell energy, so, solar cell efficiencies of devices using this materials have increase from 3.8 percent in 2009 to 23.3 percent in late 2018 in single junction architectures. So, now, you can see 1975 to 1980 we are using the amorphous silicon CIGSs CdTe crystalline silicon which already I have discussed in lecture 2. So, now, when we are going towards the 21st century so, you can see in 2015 we have reached here by using the perovskite materials where we are achieving the efficiency like 22.1 to may be 26.1 percent. So, now, maybe in few years the perovskite materials will cross that crystalline silicon also and it will take the number 1 position.

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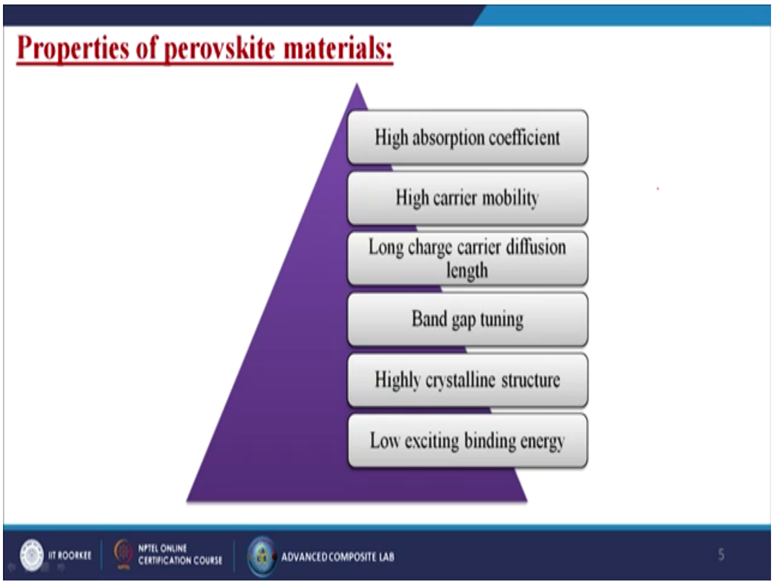

So, if we talk about the properties of perovskite materials. So, basically these materials is having high absorption coefficient, high carrier mobility, long charge carrier diffusion length, band gap tuning, highly crystalline structure and the low exciting binding energy. So, these all properties are very very useful for making any kind of solar cells.

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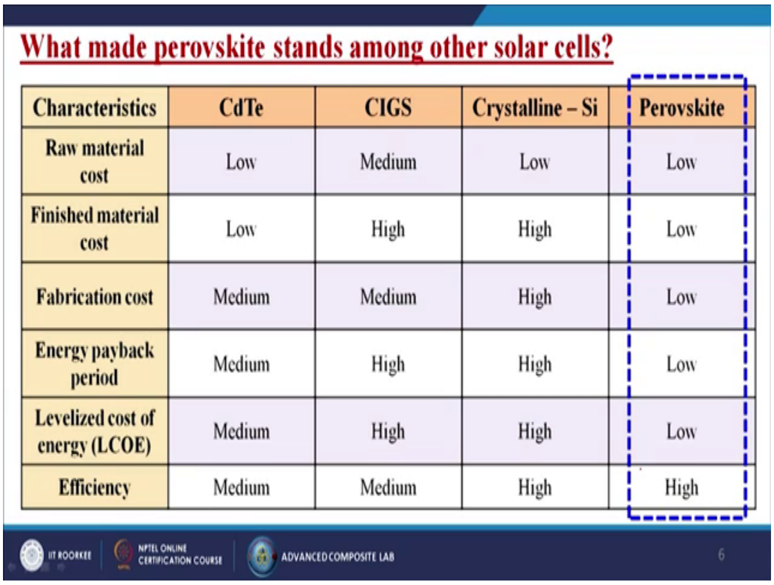
What made perovskite stands among other solar cells?

Characteristics	CdTe	CIGS	Crystalline – Si	Perovskite
Raw material cost	Low	Medium	Low	Low
Finished material cost	Low	High	High	Low
Fabrication cost	Medium	Medium	High	Low
Energy payback period	Medium	High	High	Low
Levelized cost of energy (LCOE)	Medium	High	High	Low
Efficiency	Medium	Medium	High	High

What made the perovskite stands among other solar cells? As I told already because why we are choosing the perovskite materials because they are lots of materials are available into the market, people have done so many research on already other materials. So, why basically we are tending to the perovskite materials? Basically if we talk about some properties which is very very crucial for choosing any kind of materials or maybe just to make our mind that no we can move to this particular materials because this properties are the essential input parameters for solar cells, whether that perovskite materials is satisfying those properties or not just to see or may be just to get the information from these particular table.

So, if we talk about the raw material cost of course, CdTe is having the low and same like perovskite material is also having the low cost. If we talk about the finished material cost. So, this is also low as like the others like CdTe, but if I talk about the CIGS and the crystalline silicon of course, the material finished material cost is little bit higher. So that means, if I use the perovskite material solar cells the operating cost or maybe the overall production cost will be reduced if I talk about the fabrication cost that is also the low.

If we talk about the energy payback period that is also the levelized cost of energy that is also low, if I talk about the efficiency it is quite high. So, that is why from the material point of view it is the cheapest materials, synthesis point of view fabrication point of view it is the low cost materials, but simultaneously I will get the higher efficiency than the others. Now come to the classifications of perovskite structure. So, basically as I told already the common perovskite structure is ABX 3 right.

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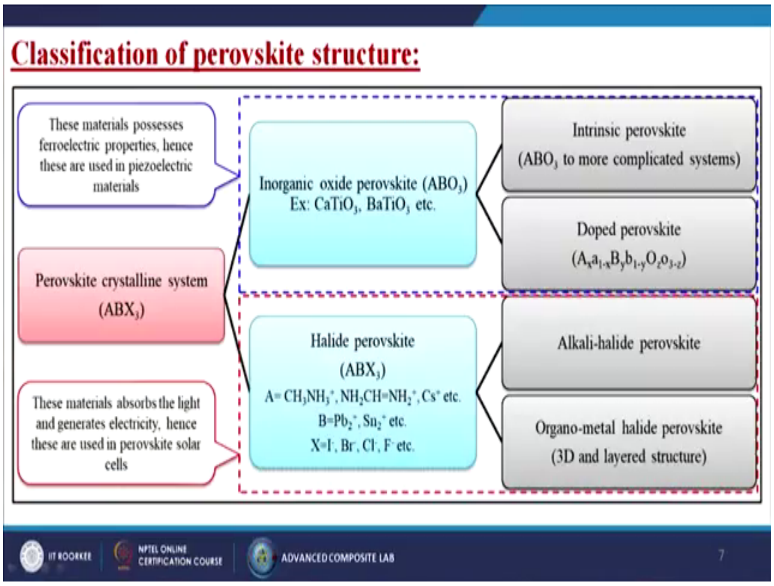

So, in this particular case when we talk about the perovskite crystal and systems basically it is divided into two parts; one is called the inorganic oxide perovskite where the basic formula is ABO 3, another one is called the halide perovskite as I told already. So, the X in place of X different halide groups will come like iodine bromine chlorine fluorine like this. So, basically it is divided into two parts; one is inorganic and other one is the halide.

Then inorganic oxide perovskite is also divided into two parts; one is called the intrinsic perovskite like ABO 3 to more complicated systems and other one is the doped perovskite; that means, I am introducing another third materials into the system. So, like this way Ax small a 1 minus x B y small b 1 minus y Oz and o small o 3 minus z. So, this is the complex structure basically and same simultaneously the halide perovskite is also divided into two parts; one is called the alkali halide perovskite another one is called the organo metal halide perovskite or maybe the 3D and the layer structure basically we are calling it.

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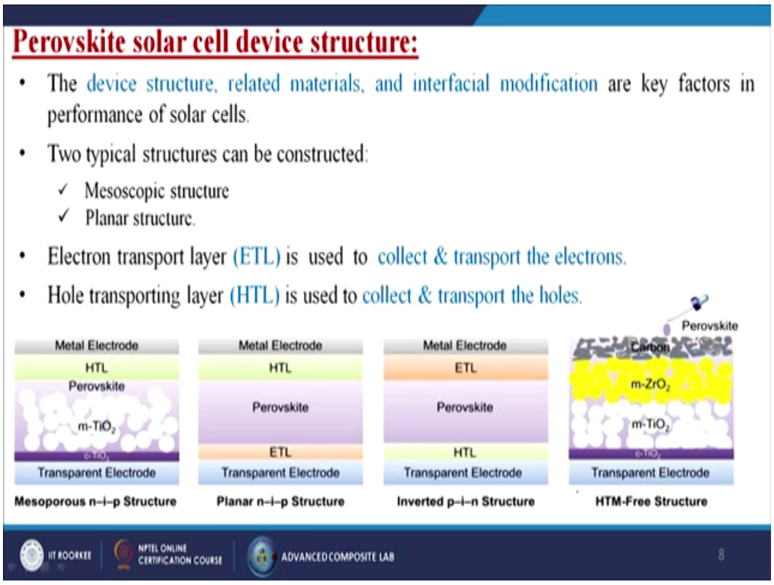

Next what is the perovskite solar cell device structure means how where basically we are using this particular materials into our solar cell fabrication system? So, basically the device structure related materials and interfacial modifications are key factors in performance of the solar cells. Yes because when we are talking from the material sign point of view. So, basically as a material scientist our demand is endless; that means, if I am achieving 20 percent efficiency today tomorrow my aim will be how to reach 20.1.

So, of course, when or wherever we are making any kind of new materials, every time after inventing that particular materials also we are doing so, many research, so many materials characterization, so many either in terms of may be doing some coating or maybe some kind of doping or maybe some kind of composite materials just to enhance their physical as well as the chemical properties. So, from this point of view there are two typical structures can be constructed; one is called the mesoscopic structure another one is called the planar structure.

So, in this particular case electron transport layer is used to collect and transport the electrons. When I am talking about the Electron Transport Layer or maybe the ETL; when I am talking about the HTL, the full form of the HTL is Hole Transporting Layer which is nothing, but to use for collecting and transport the holes. So, basically in this particular image we have shown so, many different structures like mesoporous n-i-p structure, in this particular case we are using the perovskite materials m TiO2 in this planar case we are using the perovskite materials here in between the HTL and the ETL in this inverted p i n structure it is inverted means just the opposite. So, automatically the up it is ETL and the bottom on is called the HTL. So, basically it is the opposite of planar n-i-p structure then if we talk about the HTM free structure.

So, in this particular case we are using the two layer materials one is the m-TiO 2 and the m-ZrO 2 and then top of that we are putting carbon and top of that we are using the perovskite materials. So, basically it is a sandwich like structure. So, in which positions basically you are using the perovskite materials and how you are using at the bottom or maybe the top and how it is working based on that we are giving the different nomenclature of this sandwich like structure.

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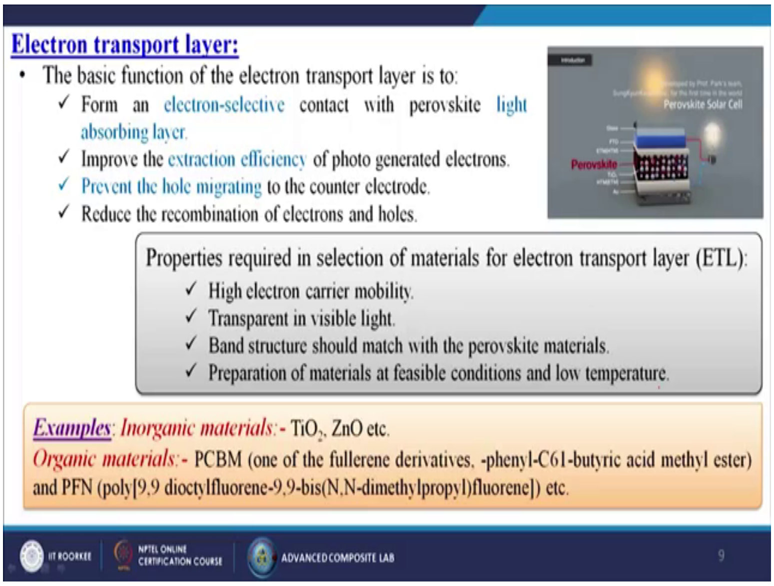

So, what is electron transport layer? So, the basic function of the electron transport layer is to form an electron selective contact with perovskite light absorbing layer; improve the extraction efficiency of auto generated electrons; prevent the whole migrating to the counter electrode; reduce the recombination of electrons and the holes.

So, from this particular image you can understand that this is the perovskite solar cell materials, we are having that fast is that gold AU on top of that we are having the HTM or maybe the ETM materials top of that we are putting the TiO 2 and then we are putting or perovskite materials and then I have if the below one will be the ETM of course, the upper one will be HTM or may be the vice versa then we are putting the FTO glass and top of that we are putting the glass substrate over there.

So, like this way you can see basically the parasite materials is in between our ETM and the HTM or maybe the opposite one. Properties required in selection of materials for electron transport layer systems high electron carrier mobility, transparent in visible light, band structure should match with the perovskite materials, preparation of materials at feasible conditions and low temperature.

So, basically in electron transport layer means is nothing from the name itself you can understand which will allow the electron to transfer from one place to another as simple as that. So, basically the examples are inorganic materials like titanium dioxide, zinc oxide etcetera organic materials like PCBM, one of the fullerene derivatives that is called the phenyl C 61 butyric acid methyl ester and PFN poly 9,9 dioctylfluorine 9,9 bis N, N in dimethyl propyl fluorine etcetera. So, its a complex kind of structure we can say.

Next come to the whole transport layer in the last lecture also I have discussed about that when the electron is moving from one place to another place simple it is leaving one hole over there. So, now, I am putting one layer basically in a just a imaginary case you think that when the electron is moving from this side to that side. So, automatically the whole will transfer from this side to that side. So, basically like this way just whole will leave or maybe whole will go just opposite to the electron.

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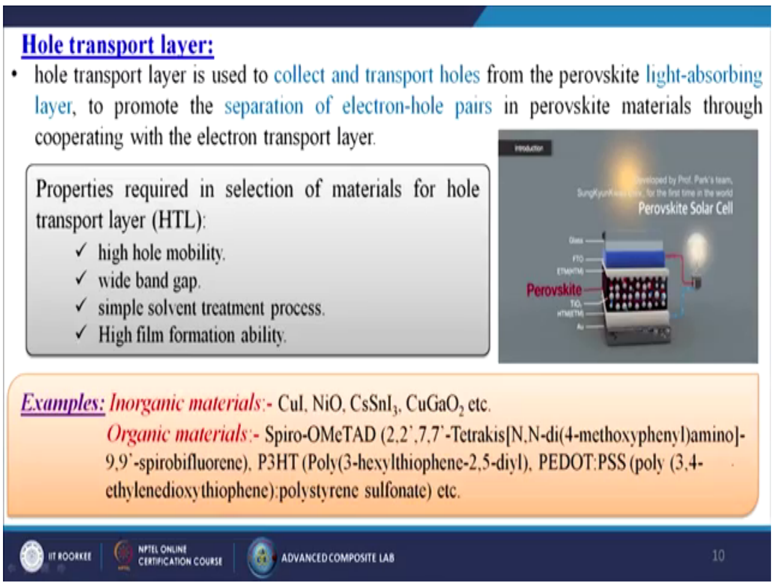

So, now, the hole transport layer is used to collect and transport holes as I told already from the perovskite light absorbing layer to promote the separation of electron hole pairs, in perovskite materials through cooperating with the electron transport layer. Properties required in selection of materials for Hole Transport Layer HTL basically the high hole mobility, wide band gap, simple solvent treatment process high film formation ability what are the examples? Inorganic materials like copper iodide, NiO CsSnI 3, copper gallium oxide organic materials like Spiro OMeTAD, P3HT, PEDOT PSS.

So, these all are may be the polystyrene sulfonate, this or these all are the examples of hole transport layer. So, now, basically if I talk about from the research point of view may be some people are working on the electron transport layer, some people are working on the whole transport layer or maybe some people are directly working on the perovskite materials just to increase the efficiency.

Basically because the solar cell efficiency does not only depend upon the perovskite materials, it depends upon that what type of electrode you are using, what is the properties of those electrode, what are the materials you are using as a electron transfer layer or maybe the whole transfer layer. So, basically its a combinations of different materials just to get the full efficiency of that particular solar cell.

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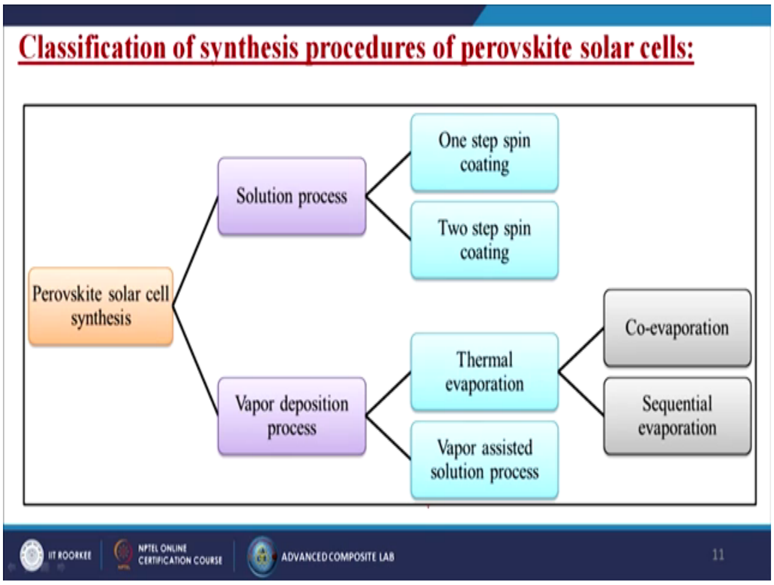

Now if we talk about the classification of synthesis procedures of the perovskite solar cells. So, basically the synthesis process is divided into two parts; one is called the solution process another one is called the vapor deposition process. Then solution process is also divided in to two parts; one is called the one step spin coating and another one is known as the two step spin coating.

If we talk about the vapor deposition process, it is also divided into two parts; one is called the thermal evaporation another one is called the vapor assisted solution process and thermal evaporations also divided into two parts; one is called the co evaporations another one is called the sequential evaporations. So, like this way we can divide the whole synthesis process of perovskite materials by this particular chat. Now basically what is solution process? So, in that particular process it is quite simple process basically.

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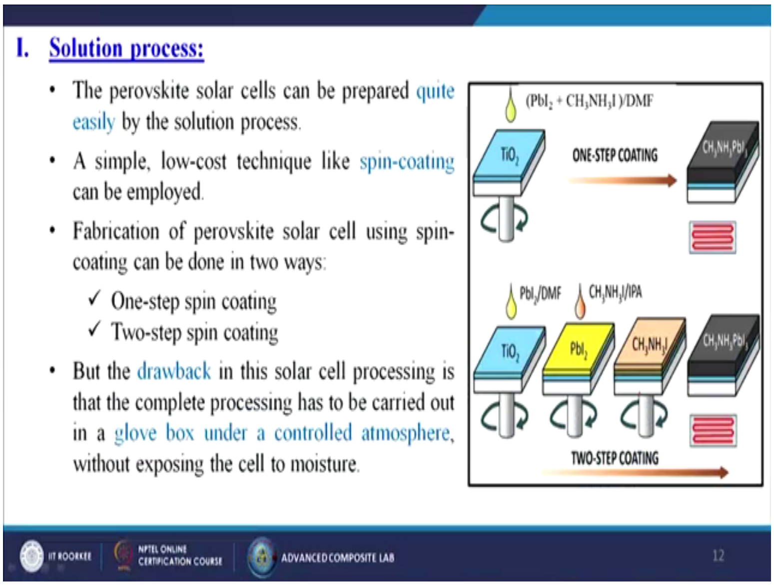

So, the perovskite solar cells can be prepared quite easily by the solution process a simple low cost technique like spin coating generally we are doing this particular process by using the spin coater. So, a simple low cost techniques like spin coating can be employed, fabrication of perovskite solar cell using spin coating can be done in two ways as I told already one is called the one step spin coating, another one is called that two step spin coating.

But the drawbacks in the solar cell processing is that the complete processing has to be carried out in a glove box under a controlled atmosphere without exposing the cell to moisture. Yes because the biggest problem of dealing the perovskite solar cells is that, if you do not do the synthesis into some specific environments, so, automatically the degradation of the material is very very fast.

So, you will lose the other properties of that particular materials. So, when we are synthesizing the perovskite materials in our lab. So, basically we are using the glove box; that means, a pre defined atmosphere we are creating with some inert gas and then in particular that environment we have to do the synthesis of that particular materials, we have to do the fabrications of the solar cells, then only we can test the full efficiency of that particular materials. Then after doing the whole fabrications of the solar cell, then after that we are able to take out that particular solar cell outside the glove box or maybe outside the chamber.

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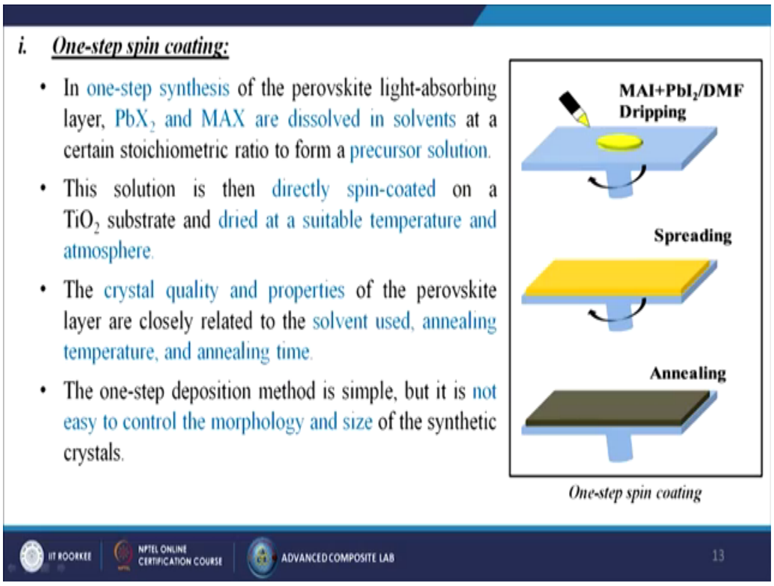

So, basically if you talk about the one step spin coating, in one step synthesis of the perovskite light absorbing layer PbX 2 and MAX are dissolved in solvents at a certain stoichiometric ratio to form a precursor solution.

This solution is then directly spin coated on a titanium dioxide substrate android at a suitable temperature and atmosphere as I told already. So, this suitable means it is the controlled one. So, basically in this particular case you can see we are putting the MAI, we are putting the PbI 2 in the DMF solutions, the whole mixings we are mixing properly and then we are putting or may be by using the dropper, we are putting that materials on to the titanium dioxide substrate.

And then after that we are using the spin coater; that means, what? That substrate we are rotating in a very high rpm so, that these material can be homogeneously dispersed onto my substrate material and then after that simple we are doing the annealing process means we are hitting that particular materials for drying the materials and my preparations has been completed.

So, the one step deposition method is simple, but it is not easy to control the morphology and size of the synthetic crystals. So, that is a small or maybe one kind of drawbacks by this one step sin a spin coating process.

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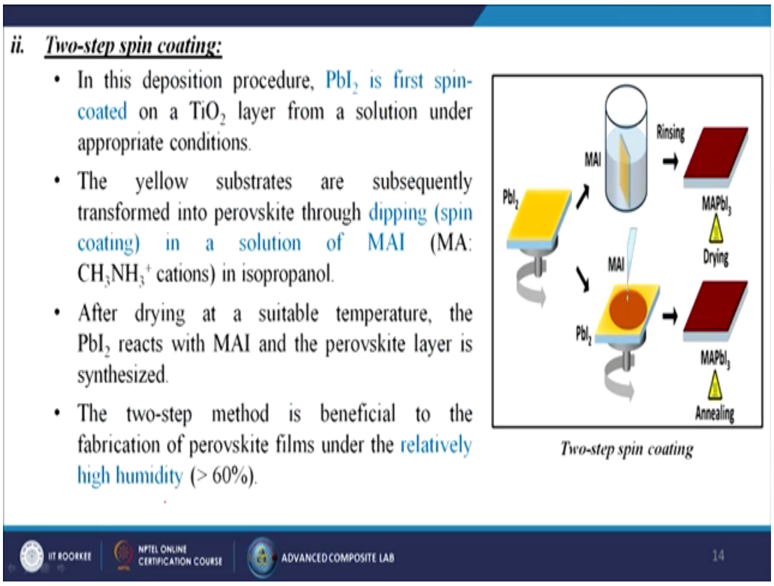

If we talk about the two step spin coating, in this deposition procedure basically PbI 2 is fast spin coated on a TiO 2 layer from a solution under appropriate conditions, the yellow substrates are subsequently transformed into perovskite through dipping or maybe the spin coating in a solutions of MAI in isopropanol. After drying at a suitable temperature of the PbI 2 reacts with MAI and perovskite layers is synthesized. So, in this particular case what is MAI? So, MAI is nothing, but the CH 3 NH 3 and I; that means, CH 3 NH 3 plus cations. The two step method is beneficial to the fabrication of perovskite films under the relatively high humidity.

So, I am having the A material B material before putting it onto the substrate we are mixing the both and then the mixer we are putting on to the substrate we are doing the sonications that is the one step process. In this particular case I am having the substrate initially I am putting the A materials, then I am drawing, then after certain time again I am putting the B materials and then I am trying and in between that they are reacting each other and they are making the whole materials on to the substrate itself and then the final stage is that annealing. So, we are drawing whole the materials and the perovskite materials will be formed on to the substrate itself.

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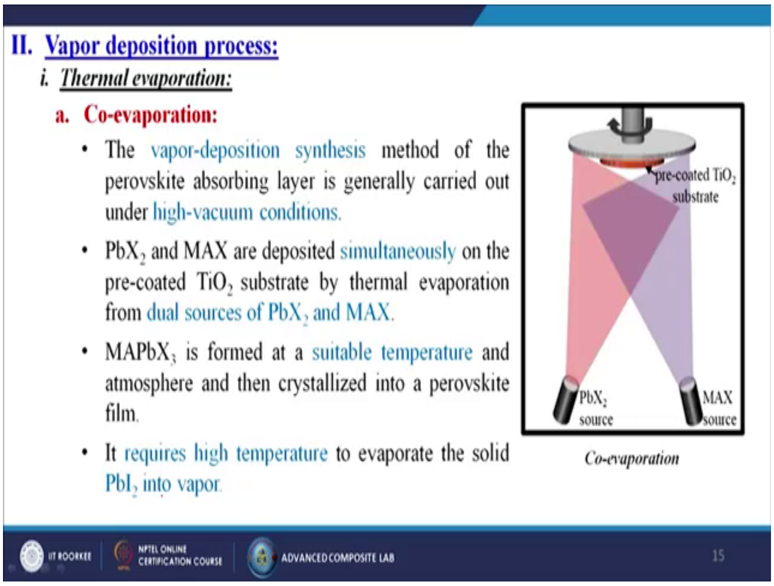

Next this vapor deposition process. So, basically from the name itself you can understand that it is a one kind of thermal evaporation process. So, basically that is also divided into several parts the first one is known as the co evaporation process. So, the vapor deposition synthesis method of the perovskite absorbing layer is generally carried out under high vacuum conditions. So, high vacuum means there is a less chance of the perovskite materials to degrade.

So, PbX 2 and MAX are deposited simultaneously on the pre coated titanium dioxide substrate by thermal evaporation from dual source of PbX 2 and the MAX. So, basically what happened? I am having that substrate. So, simple I am having one MAX source I am having the PbX 2 both the vapors are coming and it is depositing onto my substrate itself. So, MAPbX 3 is formed at a suitable temperature and atmosphere and then crystallized into a perovskite film, it requires the high temperature to evaporate the solid PbI 2 into vapor. So, this is one vapor source this is another vapor process.

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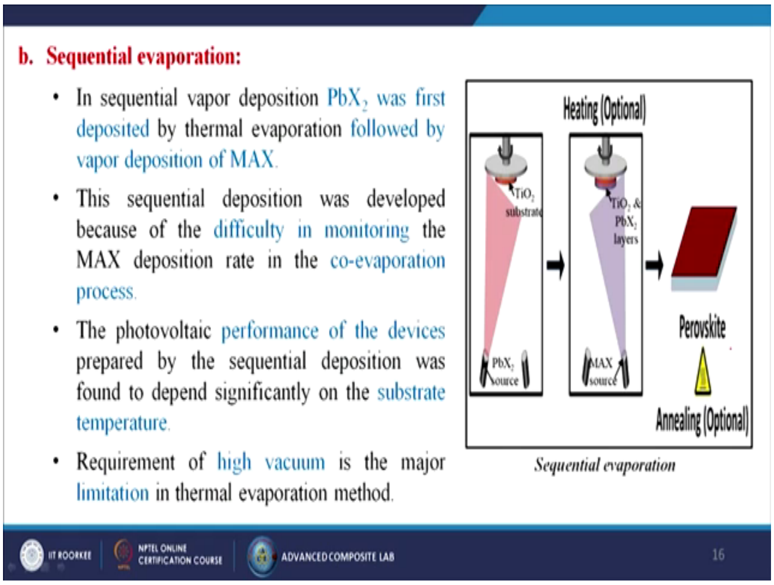

Next is called the sequential evaporations its like the same like that two step spinning process. So, one by one I am doing. So, basically in sequential vapor deposition PbX 2 was first deposited by thermal evaporation followed by vapor depositions of the MAX. In the earlier stage you can see that both the vapor is coming together and their depositing onto the substrate itself. In this particular case both the vapor source are coming separately and then they are depositing on top of another and then after that final stage we are doing the annealing process and we are drying and taking out the materials.

So, this sequential deposition was developed because of the difficulty in monitoring the MAX deposition rate in the co evaporation process. The photovoltaic performance of the devices prepared by the sequential deposition was found to depend significantly on the substrate temperature. Requirement of high vacuum is the major limitation in thermal evaporation method so, that is also a one of that drawback.

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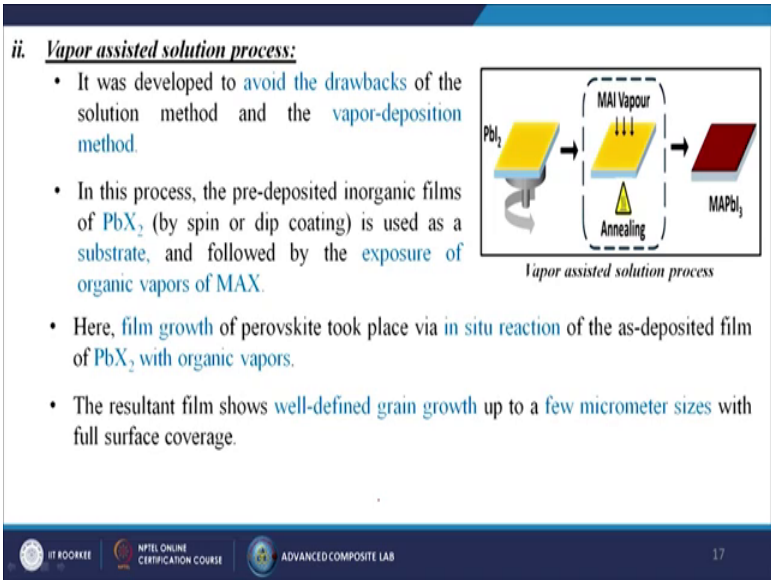

Then let us discuss about the vapor assisted solution process how we are doing. It was developed to avoid the drawbacks of the solution method and the vapor deposition method. In this process the pre deposited inorganic films or PbX 2 by spin or dip coating is used as a substrate and followed by the exposure of organic vapors of the MAX nothing its a mixing of both the thermal and the solution process. So, if you remember properly in the solution process, both the materials was into the solutions we are putting by drop casting or may be by mixing them.

In the vapor both the material into the vapor phase either we are doing together or maybe we are doing it one by one, but in this case the first step we are doing by the solution process like using the spin coating and the second one was just we are using the vapor on top of that materials. So, here film growth of perovskite took place in situ reaction of the as deposited film of PbX 2 with organic vapors.

The resultant film shows well defined grain growth up to a few micrometer sizes with full surface coverage. So, what are the advantages basically of the by use or maybe I can say that, what are the advantages if I am going to use this perovskite materials for making the solar cells? First of all it is having a very high efficiency.

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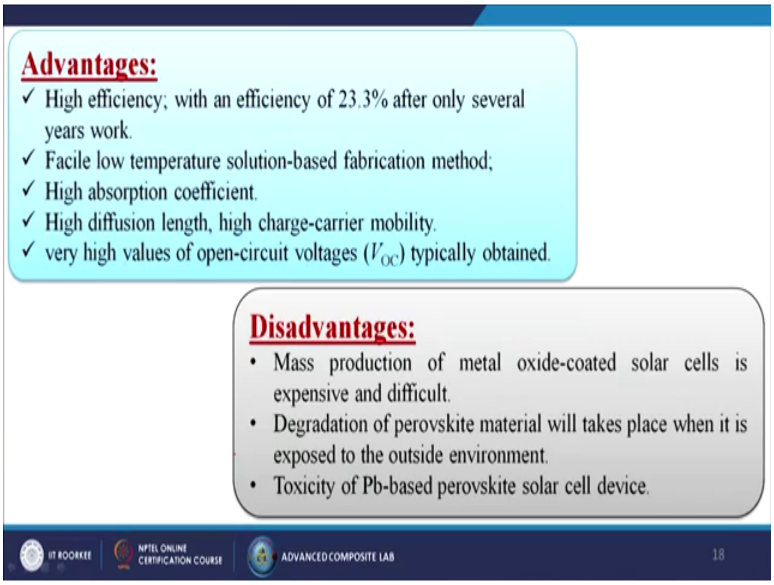

With an efficiency of 23.3 percent after only several years work, it has been achieved in the year of 2018, but till today we have achieved up to 23.7 percent of the efficiency. Facile low temperature solution best fabrication methods, high absorption coefficient, high diffusion length, high charge carrier mobility, very high values of open circuit voltages typically obtained. So, these all are the advantages of this particular materials. Of course, there is certain disadvantages, what are those? First is that mass production of metal oxide coated solar cells is expensive and the difficult one.

Degradation of peroxide materials will takes place when it is exposed to the outside environment as I told already, that is why we are synthesizing this particular materials into the controlled atmosphere or maybe into the vacuum chamber. And last one is the toxicity of lead base perovskite solar cell devices which is nothing, but generate the toxic gases to the environment. So, these all are the drawbacks that is why the scientist are rigorously working on it to solved this kind of disadvantages so, that in they can generate the maximum efficiency by using this particular materials. So, now, what are the applications?

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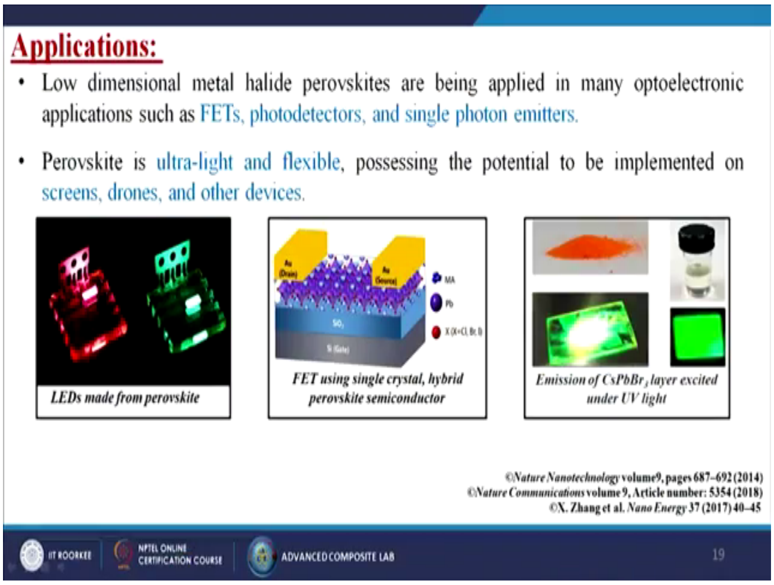

Low dimensional metal halide perovskites are being applied in many optoelectronic applications such as FETs, photo detectors and the single photon emitters. Perovskite is ultra light and flexible processing the potential to be implemented on screens drones and other devices. So, any kind of shapes simply you can stick that particular materials. So, it will be the flexible one.

These all are the examples we are using it for the LEDs made from the perovskite materials, if it using single crystals hybrid perovskite semiconductor emission of CsPbBr 3 layer excited under the UV light. So, these all are the examples and these all are the reference from where we received this particular informations.

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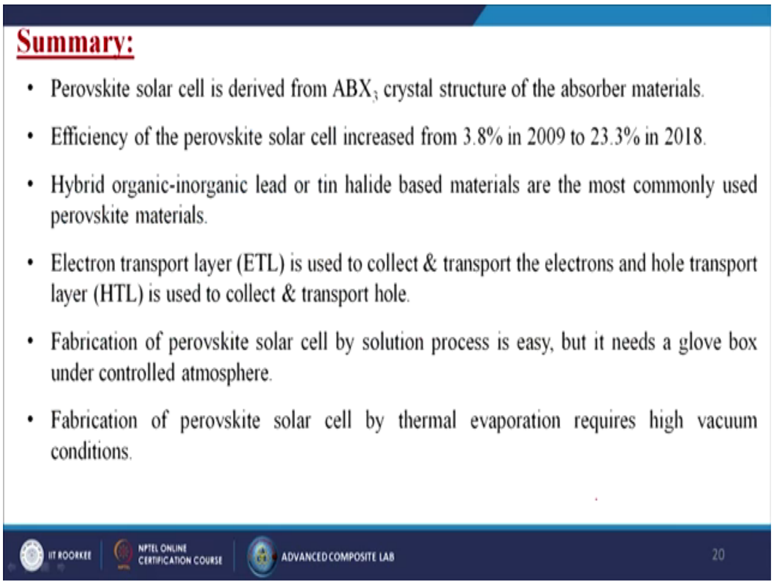

So, we have reached to the last slide of this particular lecture. So, in summary I can say that perovskite solar cells is derived from the ABX 3 crystal structure of the observer materials right. Efficiency of the perovskite solar cells increased from 3.8 percent in 2009 to 23.3 percent in the year of 2018 and till today it is 23.7 percent.

Hybrid organic inorganic lead or may be the tin halide best materials are the most commonly used perovskite materials. Electron transport layer is used to collect and transport the electron and hole transport layer is used to collect and transport the hole itself. Fabrication of perovskite solar cell by solution process is very very easy, but it needs a glove box or maybe the controlled atmosphere and particularly controlled temperature or maybe the controlled environment. Fabrication of perovskite cells by thermal evaporation requires the high vacuum conditions.

Thank you.