Solar Photovoltaics:
Fundamental Technology and Applications
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Lecture-28
Stability in Perovskite Solar cells

Welcome everyone to our solar photovoltaic course, today we have 6th week and 4th module. So far we are discussing about Perovskite solar cell and very important category of third generation solar cell. We have discussed that the charge carrier dynamics and morphology plays an very important role in determining the efficiency of this kind of solar cell. Now we have also seen that the perovskite solar cell with a very short span of research has increase is efficiencies starting from 3.8% to almost above 22%.

But still we do not see lot of perovskite solar module in the market, so what can be the reason behind is that. Now for any technology to become commercially successful there are lot of aspect has to be optimize simultaneously. For example like for photovoltex or solar cell technology also, the efficiency is not the only parameter as for as the commercial license is concerned. Of course we need a highly efficient solar cell.

But the solar cell also has to work in an environmental condition, we usually install the solar module in the rooftop. So that means and especially for a country like India where you have so much temperature variation in a single place, if you take up for example Delhi, so in hot summer it goes upto 40 to 45 degree Celsius and in winter it can go even to 0 degree Celsius. So the solar cell module has to undergo this huge temperature difference.

Now we have seen that the temperature affects the current density especially the short circuit current density. So because of that the efficiency of the solar cells will also vary and also there are some material since these are also the organic based materials. Some materials also undergo thermal degradation, so now because of this huge temperature variations so there is a probability that this materials can undergo a thermal degradation.

On top of that for same example in our country we have a huge humidity variation we can go to your place where we have 80 to 90% humidity or there are places where the humidity level is very very low 20 to 30% or 40% even. So, the installed solar module has to undergo this huge humidity variations and in principle it should preserve the efficiency intact over this humidity scale.

So what the means of all of these is that when you design a solar panel or a solar module in addition to the efficiency thermal degradation, humidity induced degradations and intrenstic degradations these are all the parameters needs to be simultaneously optimized before bringing the solar panels for any commercial or practical applications. Now the silicon is a time tested technology over and over we have seen that, the silicon solar panels are there for quite a long time.

And it is successfully gives it is efficiency I means performance is quite stable, for organic solar cell the efficiency is not as high as silicon solar cell like in a module we get 4 to 6% efficiency in an organic PCH to BCDM solar cell usually you can say 4% efficiency. So the efficiency wise it cannot compute to the silicon solar cell. But when you talk about the perovskite solar cell efficiency is not an issue you can still get an efficiency which is comparable to the silicon solar cell and sometimes it is higher than that.

But the question is one of the major problem with the perovskite as you mentioned in the last class also one of them is the toxicity due to the lead. We have seen that most of this organic inorganic perovskite material they use lead as one of the ingredient and lead is a very known neurotoxic and nephrotoxic material. So, we wanted to replace the lead with non lead compound but when you replace the lead with non lead compound the stability of the compound increase but we get compromised in the efficiency parameter.

So the second parameter which is extremely important in terms of the perovskite is a stability, now of course we have the environmental degradation like degradation due to the thermal variations or humidity variations. But moreover the most important thing is that the instability of this devices, perovskite materials at intrinsic instable by the photoimp exposure. If fact commonly known as the ion migration, so unless until we address all this issues we come across with a solution to protect the material against the thermal degradation.

The humidity induced degradations or even if we can slow down the ion migration we cannot make a good stable perovskite devices. So, today's lecture we will discuss about all the stability issue and at the end we will see that what are the solutions for the stability issues ok let us take a look on that.

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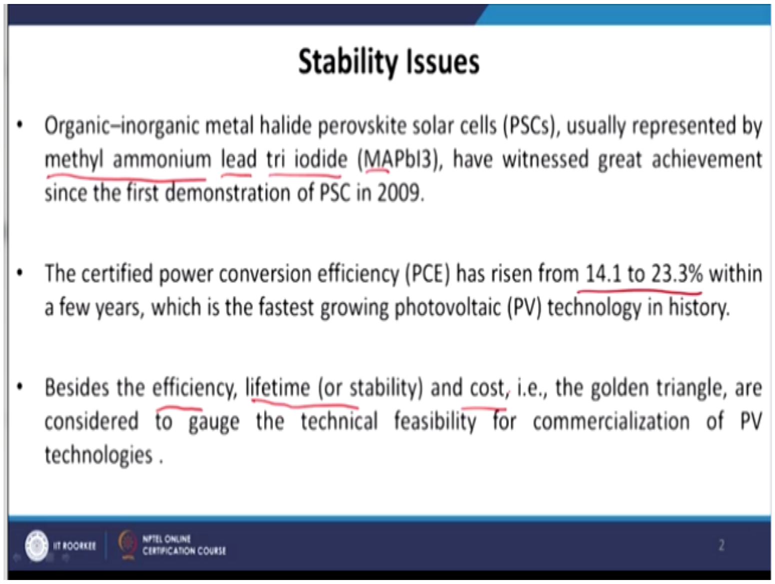

Stability Issues

- Organic–inorganic metal halide perovskite solar cells (PSCs), usually represented by methyl ammonium lead tri iodide (MAPbI3), have witnessed great achievement since the first demonstration of PSC in 2009.
- The certified power conversion efficiency (PCE) has risen from 14.1 to 23.3% within a few years, which is the fastest growing photovoltaic (PV) technology in history.
- Besides the efficiency, lifetime (or stability) and cost, i.e., the golden triangle, are considered to gauge the technical feasibility for commercialization of PV technologies .

So stability issues organic-inorganic metal halide perovskite solar cells usually represented by methyl ammonium lead tri iodide. Now I have talked in the class that this methyl ammonium this is an organic cation which is sometimes written as MA and then the iodide this is the halogen compound and lead is the metal cation. Now this organic-inorganic MAPbi3 that has witnessed great achievement since the past demonstration of perovskite solar cell in 2009.

The certified power conversion efficiency has raised from 14.1% to 23.3% within a few years which is the fastest growing photovoltaic technology in history. So from 14.1% to 23.3% in a very short amount of research activities or in a very small span of time. So that is the huge growth potential and also one important thing one should know that when I say that it is a certified efficiency.

Now who gives the certification, so basically there is an association called national renewable energy laboratory NREL in USA which aggregate or which certify the power conversion efficiency of the solar cell. So whenever we make a new kind of solar cell or high efficient solar cell we usually send to them and then they independently test that things and then they put a stamp or like you know aggregate or certify the efficiency number.

Besides the efficiency lifetime of stability and cost that is the golden triangle are considered to gauge the technical feasibility for commercialization of PV technologies. So whenever as I said that whenever you want to bring a technology in the market, so they are 3 things has to be considered. Now for photovoltaic industry these 3 things are one is the efficiency another is the lifetime or stability and another is the cost.

And these 3 parameters they form a triangle it is called a golden triangle and each of these parameter is dependent on others. So we have to optimize each of the parameter individually to get the maximum output from this photovoltaic solar cell.

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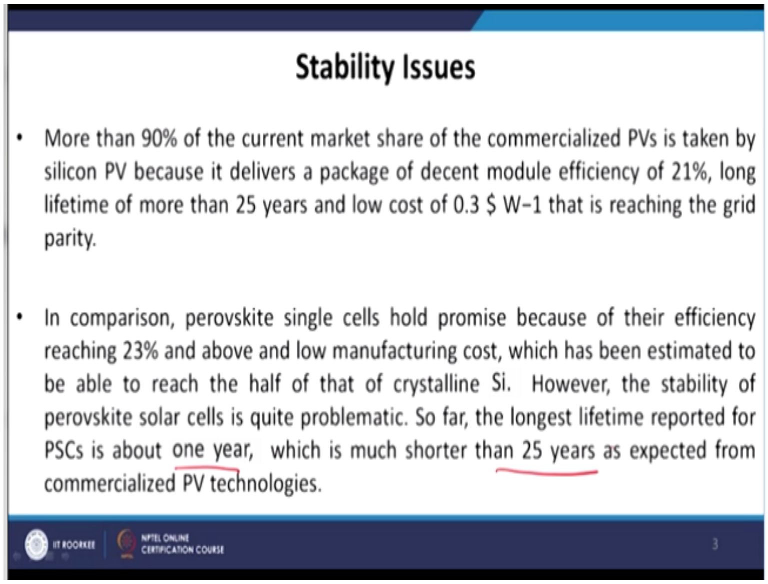

Stability Issues

- More than 90% of the current market share of the commercialized PVs is taken by silicon PV because it delivers a package of decent module efficiency of 21%, long lifetime of more than 25 years and low cost of 0.3 \$ W−1 that is reaching the grid parity.
- In comparison, perovskite single cells hold promise because of their efficiency reaching 23% and above and low manufacturing cost, which has been estimated to be able to reach the half of that of crystalline Si. However, the stability of perovskite solar cells is quite problematic. So far, the longest lifetime reported for PSCs is about one year, which is much shorter than 25 years as expected from commercialized PV technologies.

So more than 90% of the current market share of the commercialized PVs is taken by silicon PV. Because it delivers a package of decent module efficiency of 21% long lifetime of more than 25 years and low cost of 0.3 dollar/watt that is reaching the grid parity. So when you use a silicon solar panel, so it not only gives a high efficiency but it lifetimes is also very high 25 years once you install it in your rooftop, so we do not have to be consent about for the 25 years.

And also because of the continuous research this is a very matured technology the cost is somewhat around 0.3 dollar/watts. In comparison perovskite's single cells hold promise because of their efficiency reaching 23% and above and low manufacturing cost which has been estimated to be able to reach the half of the crystalline silicon. However the stability of the perovskite solar cell is quite problematic.

So for the longest lifetime reported for the PSC is about 1 year which is much shorter than the 25 years as expected from the commercialized PV technology ok. Now again like if you talk about this golden triangle efficiency, cost and stability, so perovskite has efficiency which is comparable to the silicon solar cell 23%. It cost is much lower than the silicon solar cell but you think about the lifetime or the stability whereas silicon solar cell can run up to 25 years, a perovskite solar cell can run for only one years.

So it cannot beat in terms of the stability or lifetime to the silicon but as I said that one has to modify these 3 parameters simultaneously to get a good technology so you look at this golden triangle in this figure.

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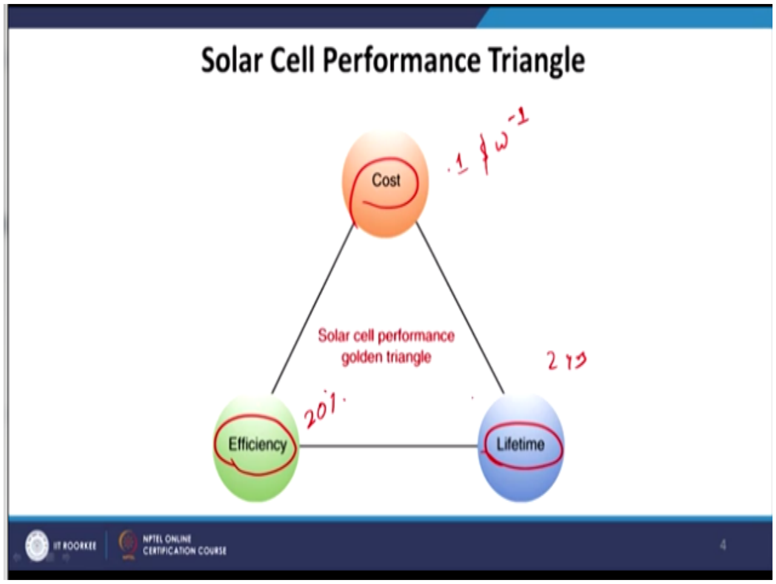

Solar Cell Performance Triangle

So there of this efficiency parameters and then there of this lifetime or the stability and then there is this cost. So this is one of the parameters is dependent on others and this triangle is called a golden triangle solar performance golden triangle. So the importance of this triangle is that each of the parameter determines the other. For example like a solar cell an unknown solar cell let us we have designed which has an efficiency of very high efficiency something like let us say 20%.

But it lifetime is only 2 years while the cost is also very low but still this is not a very successful technology because at least the installed solar panel has to run for another 20 to 25 years. People do not want to invest the money every time, so the lifetime or the stability of the device should be also be very high in addition to the efficiency and as well as the low cost. So this triangle is very very important when designing a solar module.

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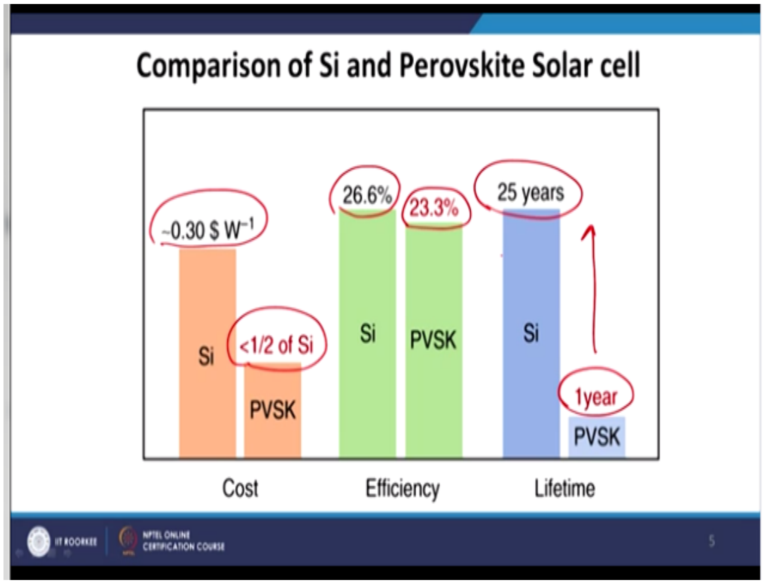

Comparison of Si and Perovskite Solar cell

Now if you take look up the different varieties of the silicon solar cell and perovskite solar cell and if you compare this the 3 parameters of the golden triangle for the silicon and perovskite we can see this histogram. So in terms of the cost you see that the silicon solar cell the cost is 0.3 dollar/watt. Now this dollar rate is changing everyday let us say today it is like you know 1 dollar is 71 rupees, so 0.30 dollar you can calculate, so it is almost about 2 to 2.5 rupees.

And this number is I mean we got up the market fluctuation that changes but PVSK or the perovskite solar cell the cost is half of the silicon solar cell. So if I have to buy 1 watt power at 2 rupees in silicon I can buy at 1 rupees/perovskite solar cell. So this is very very good news, you look at the efficiency silicon solar cell the histogram it is showing that the efficiency can go up to 26.6%.

Although when you make a module the efficiency decreases somewhat around like 20 21%, amorphous silicon solar cell routinely gives 15 to 16%. But a perovskite solar cell efficiency number is almost comparable 23.3%, so it is not bad. So efficiency wise perovskite solar cell and silicon solar cell are comparable, cost wise perovskite solar cell can beat silicon solar cell but what about the lifetime the third parameter.

You see the comparison between the 2 histogram silicon solar cell can last for 25 years once installed where the perovskite solar cell the lifetime is only one year. So this is way less than the silicon solar cell. So although we gain in terms of cost and comparable efficiency but you lose significantly in terms of the stability. So that is why major his research is our focused so that this histogram can be increased, so that we can get a higher lifetime or higher stability as comparable to the silicon.

Then this technology is almost comparable to the silicon solar cell technology. Now this is a very important features when I talk about the lifetime or stability. So lifetime of the stability of a device comes into 2 different areas one is that once I make a solar panel or let us say I make a solar module to prevent the environmental degradation like thermal degradation or humidity degradation, I can put a layer of encapsulant or barrier layer.

And that very well can take care for that environmental degradation but what about the material intrinsic robotics. If I have a material which undergoes spontaneous degradations under sunlight then how can we erase that or how can I inhibit that. So that is the intrinsic photo instability of the materials, so the major problem with the perovskite is that perovskite shown an intrinsic photo instability an effect called ion migration.

So we will look into all thus parameters which contribute to the ion migration and the thermal instability as well as the humidity instability. Now to understand this thing we have to understand the material properties so as he mentioned again and again that the efficiency in a solar cell is a product function. It depends upon 4, 5 different parameters simultaneously, it depends upon the excite on generation it depends upon excite on diffusion, excite on dissociation as well as charge carrier collection.

Now these 2 parameters excite on diffusion and excite on dissociation that is very much related to the morphology of the solar cell. If I have an optimum morphology then we will get a very good excite on dissociation. Now this term morphology is very different in terms of the organic solar cell and perovskite solar cell. In organic solar cell we have seen that by an optimized morphology we mean a bicontinous space separated network.

In a perovskite solar cell we need a uniform, phenol free or crack free continuous thin film because here we do not have the excited by we have the free charge carriers here. If we have a very good morphology then we can control the charge carrier dynamics somehow. So basically all the things comes about the controlling the morphology or the morphology optimize and to get a better stable perovskite solar cell.

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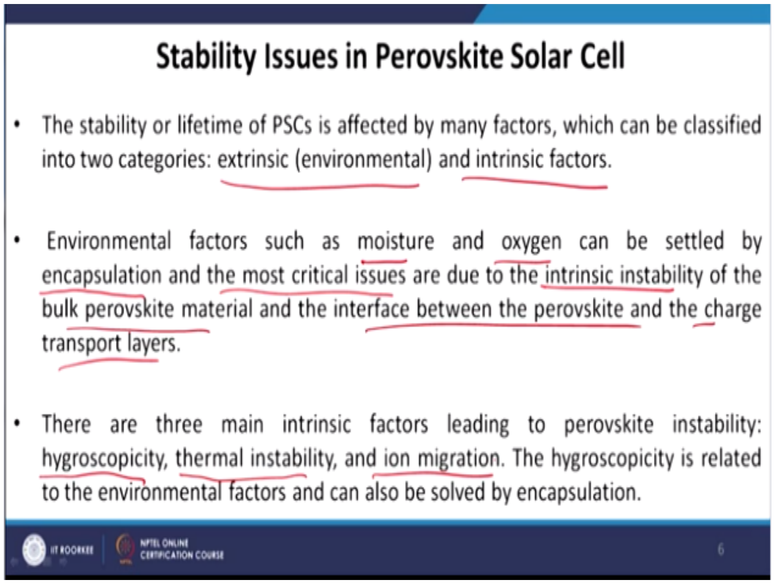

Stability Issues in Perovskite Solar Cell

- The stability or lifetime of PSCs is affected by many factors, which can be classified into two categories: extrinsic (environmental) and intrinsic factors.
- Environmental factors such as moisture and oxygen can be settled by encapsulation and the most critical issues are due to the intrinsic instability of the bulk perovskite material and the interface between the perovskite and the charge transport layers.
- There are three main intrinsic factors leading to perovskite instability: hygroscopicity, thermal instability, and ion migration. The hygroscopicity is related to the environmental factors and can also be solved by encapsulation.

The stability or lifetime of perovskite solar cell is affected by many factors as you mention which can be classified into 2 categories one is extrinsic or environmental like temperature humidity or moisture and another is the intrinsic factors. If the material is such that it undergoes spontaneous disintegration under the sunlight then that is the intrinsic factor. Environmental factors such as moisture and oxygen can be settled by encapsulation that is what we mention that.

Most of the cost in the solar cell technology goes for the encapsulation or the making barrier layers. So the effect of the moisture and the oxygen can be taken care by encapsulation and the most critical issues are due to the intrinsic instability of the bulk perovskite material and the interface between the perovskite and the charge transport layer. So there are 2 aspects in this thing one is the bulk perovskite material another is the interface.

So whenever you make a in the perovskite solar cell, so we usually put an electron transport layer or hole transport layer before the metal electrode or the ITO substrate. Now the interface between perovskite and the charge transport layer that plays an very important role also determine it is intrinsic stability. There are 3 main intrinsic factors leading to the perovskite instability hygroscopicity, thermal instability and ion migration. The hygroscopicity is related to the environmental factors and can also be solved by encapsulation.

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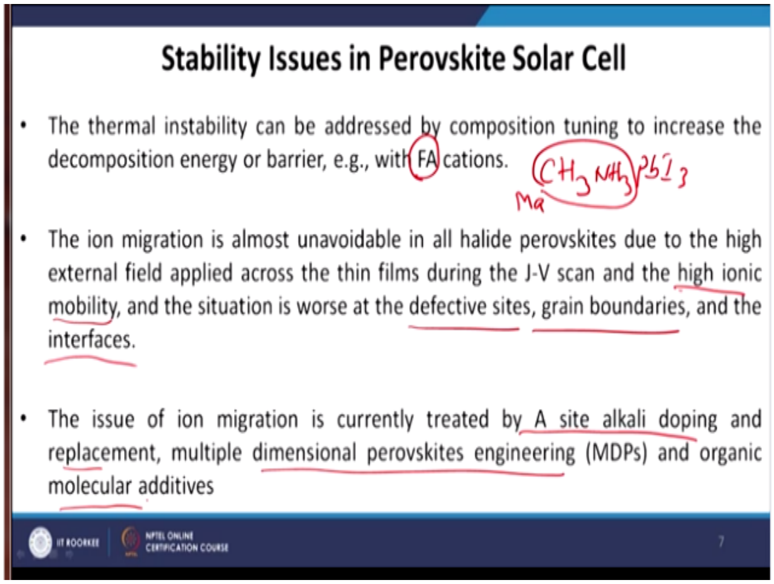

Stability Issues in Perovskite Solar Cell

- The thermal instability can be addressed by composition tuning to increase the decomposition energy or barrier, e.g., with FA cations.

$(CH_3NH_3)PbI_3$
Ma

- The ion migration is almost unavoidable in all halide perovskites due to the high external field applied across the thin films during the J-V scan and the high ionic mobility, and the situation is worse at the defective sites, grain boundaries, and the interfaces.
- The issue of ion migration is currently treated by A site alkali doping and replacement, multiple dimensional perovskites engineering (MDPs) and organic molecular additives

The thermal instability can be addressed by compositional tuning to increase the decomposition energy or barrier as per example with a FA cation. So what does it means like we have seen that when we fabricate the perovskite solar cell what materials we use there we said that every commonly used perovskite material for fabricating solar cell is CH3 NH3 lead iodide. And we say that this organic cation that is also called MA.

Now this MA cation as a particular cationic radius instead of this CH3NH3 if we use CH3CH2NH2 or if I increase if I use a large cation if I increase that cationic diameter or of the MA. For example if we use the thermo radiant cation which is also abbreviated as FA then due to the steric hindrance the decomposition energy or the thermal stability will be changed. So for example let us say I have a very viscous liquid in a jar or in a glass.

Now I dipped a small metal ball and in the other case I dipped a very large metal ball, so obviously the motion of the large metal ball and the small metal ball will be completely different. The large metal ball will experience more drag. So similarly if we increase the diameter of the organic cations so it fills because of it is mass more steric (()) (19:55) hindrance and because of that it cannot move or migrate spontaneously like a smaller cations.

So but then I mean one might ask the question if we keep on increasing the diameter of the organic cation then this problem is solved, no we cannot do it. Because we know that to get a perovskite which tells structure we need to satisfy certain stoichiometric ratio is called tolerance factor. Tolerance factor is a ratio of the cation and anionic radius and it gives a particular kind of crystal structures, a crystal structure necessary for the charge transport.

See if we keep on increasing the cationic radius we will destroy that tolerance factor we will not get the desired perovskite crystal structure. So keeping the tolerance factor in the mind we can increase the cation, the ion migration is almost unavoidable. In all halide perovskites due to the high external field applied across the thin films during the J-V scan and the high ionic mobility and the situation is worse at the defective sides, grain boundaries and the interface.

Now the ion migration that is a very intrinsic properties and when we measure the solar cell efficiency like when you do the I-V scan usually you apply bias. So whenever you apply a bias see if they were ions are there so those ions haves some mobility. So this ion start moving alongside the crystal. Similarly if there are some trap state or defective sites if there are lot of grain boundaries the boundary between the 2 grains.

If they are lot grain boundaries like that and if there are some lot interface inside the crystals, so those all actually is a potential energy minima and they acts like a trap states. So whenever the ion can goes and then go and trap there so that can inhibit the (()) (21:48). The issue of ion migration is currently treated by A site alkali doping and replacement multiple dimensional perovskite engineering and organic molecular additives.

So either by adding and organic molecules or by alkali doping or multiple dimension perovskite engineering one can address this stability issue.

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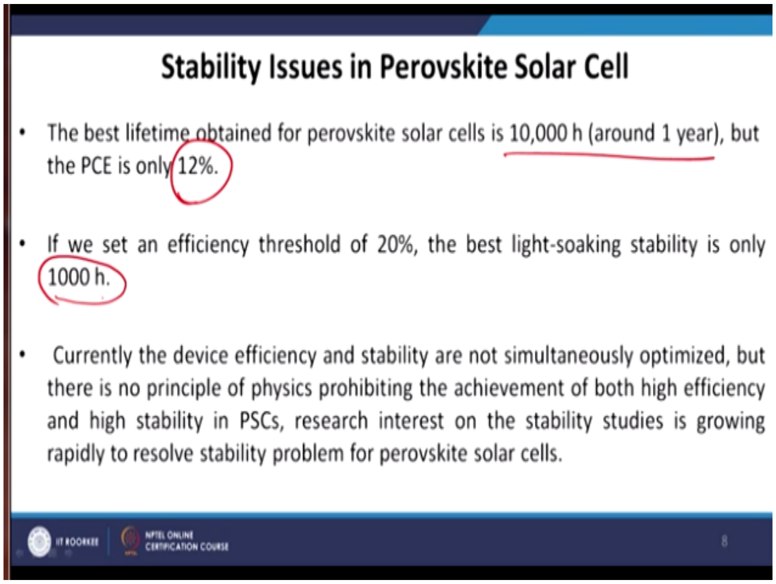

Stability Issues in Perovskite Solar Cell

- The best lifetime obtained for perovskite solar cells is 10,000 h (around 1 year), but the PCE is only 12%.
- If we set an efficiency threshold of 20%, the best light-soaking stability is only 1000 h.
- Currently the device efficiency and stability are not simultaneously optimized, but there is no principle of physics prohibiting the achievement of both high efficiency and high stability in PSCs, research interest on the stability studies is growing rapidly to resolve stability problem for perovskite solar cells.

The best lifetime obtained for perovskite solar cell is 10,000 hour around 1 year but the PCE is only about 12%. If we set an efficiency threshold of 20% the best light soaking stability is only 1000 hour. So with a 12% efficiency they can keep 1 year but if we put the target as 20% the lifetime is only 1000 hour. So again that golden triangle cost efficiency and lifetime or stability.

Currently the device efficiency and stability are not simultaneously optimized but there is no principle of physics prohibiting the achievement of both high efficiency and high stability in PSC. Research interest on the stability studies is growing rapidly to resolve the stability problem for perovskite solar cells. So there is no thermodynamic limit, there is no fundamental physics problem that we cannot optimize the efficiency and the stability at the same time scale.

So we need to do more research to understand what is the source of the instability, so that we can address that by material science or by suitable engineering for materials properties and we can achieve the high efficiency and the high stability at the same time. And that is why lot of nowadays research is driven for making a high efficiency as well as highly stable perovskite solar cell while addressing the stability choosing perovskite solar cell.

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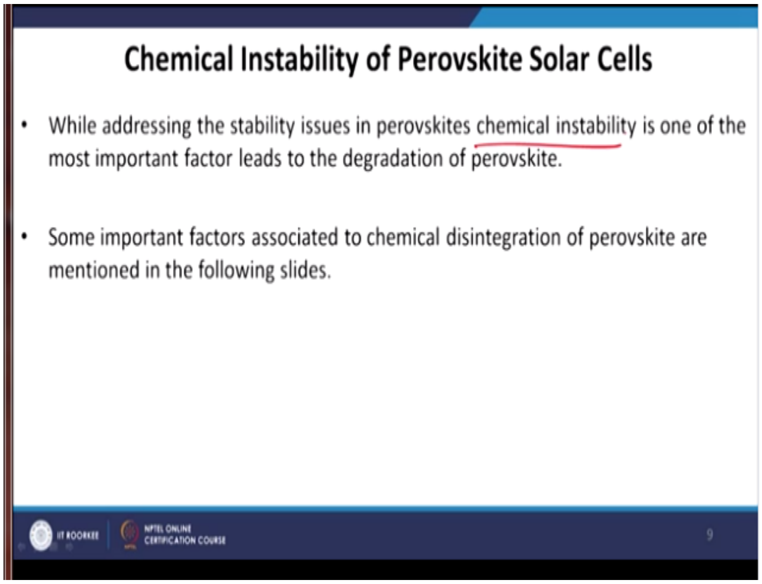

Chemical Instability of Perovskite Solar Cells

- While addressing the stability issues in perovskites chemical instability is one of the most important factor leads to the degradation of perovskite.
- Some important factors associated to chemical disintegration of perovskite are mentioned in the following slides.

The one first important aspect is the chemical instability is one of the most important factors that leads to the degradation of perovskite some important factors associated to chemical disintegration of perovskites are mentioned.

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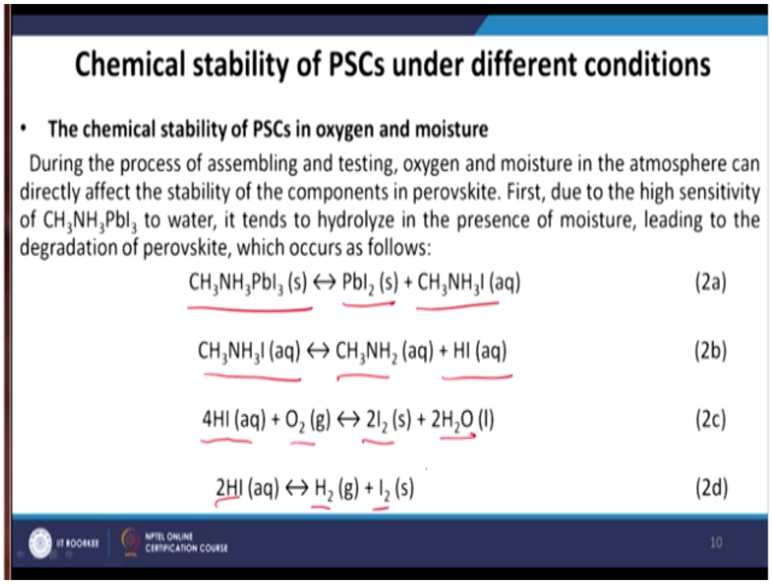

Chemical stability of PSCs under different conditions

- **The chemical stability of PSCs in oxygen and moisture**

During the process of assembling and testing, oxygen and moisture in the atmosphere can directly affect the stability of the components in perovskite. First, due to the high sensitivity of $CH_3NH_3PbI_3$ to water, it tends to hydrolyze in the presence of moisture, leading to the degradation of perovskite, which occurs as follows:

$$\underline{CH_3NH_3PbI_3}\,(s) \leftrightarrow \underline{PbI_2}\,(s) + \underline{CH_3NH_3I}\,(aq) \qquad (2a)$$

$$\underline{CH_3NH_3I}\,(aq) \leftrightarrow \underline{CH_3NH_2}\,(aq) + \underline{HI}\,(aq) \qquad (2b)$$

$$\underline{4HI}\,(aq) + \underline{O_2}\,(g) \leftrightarrow \underline{2I_2}\,(s) + \underline{2H_2O}\,(l) \qquad (2c)$$

$$\underline{2HI}\,(aq) \leftrightarrow \underline{H_2}\,(g) + \underline{I_2}\,(s) \qquad (2d)$$

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So in this successive reactions we are talking about how the perovskite material undergoes the different kind of disintegration materials. During the process of assembly and testing oxygen and the moisture in the atmosphere can directly affect the stability of the components in perovskite, first due to the high sensitivity of CH3NH3 lead iodide to water it tends to hydrolyze in the presence of moisture.

Leading to the degradation of perovskite which can be formalized for the following reaction mechanism. Let us say I have CH3NH3 lead iodide which is a solid compound S stands for the solid. Now what it will do it will absorb the water H2O and it will disintegrate to lead iodide + CH3NH3I which is a solid which is a aqueous medium. Now this aqueous CH3NH3I so that undergoes disintegration to CH3NH2 in aqueous material + hydro iodic acid this is also aqueous.

Now this hydro iodic acid they reacts with the oxygen to get iodine and water and the hydroiodic acid can also disintegrate itself to hydrogen and iodide. So whenever this CH3NH3I which is a solid compound it **it** looks at the moisture when it sees the moisture of the water vapor is disintegrates to lead iodide and CH3NH3I, CH3NH3I now disintegrate to Ch3NH2+HI, HI in the presence of oxygen next I2+H2O and HI disintegrates to hydrogen and iodine.

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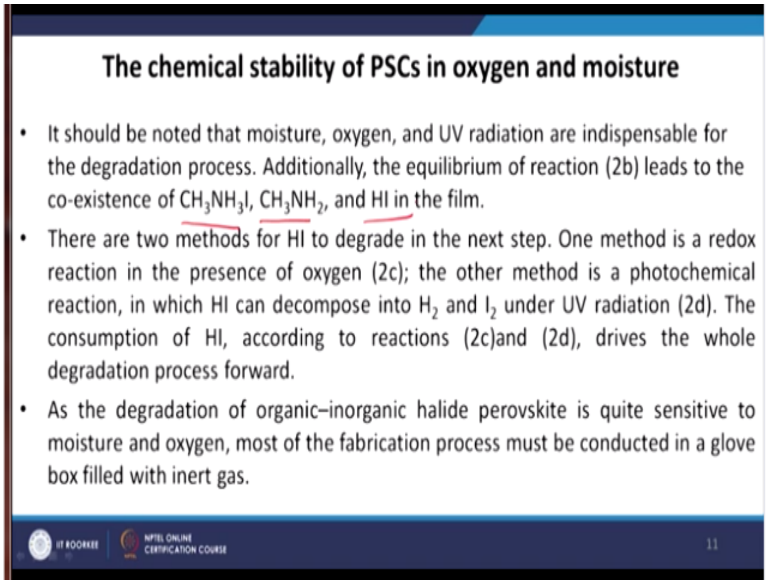

The chemical stability of PSCs in oxygen and moisture

- It should be noted that moisture, oxygen, and UV radiation are indispensable for the degradation process. Additionally, the equilibrium of reaction (2b) leads to the co-existence of CH_3NH_3I, CH_3NH_2, and HI in the film.
- There are two methods for HI to degrade in the next step. One method is a redox reaction in the presence of oxygen (2c); the other method is a photochemical reaction, in which HI can decompose into H_2 and I_2 under UV radiation (2d). The consumption of HI, according to reactions (2c)and (2d), drives the whole degradation process forward.
- As the degradation of organic–inorganic halide perovskite is quite sensitive to moisture and oxygen, most of the fabrication process must be conducted in a glove box filled with inert gas.

It should be noted that the moisture oxygen and UV radiation at indispensable for the degradation process. Additionally the equilibrium of reaction leads to the co-existence of CH3NH3I, CheNh2 and HI in the films. So basically when I expose the film to the moisture we get both CH3NH3I, CH3NH2 and HI in the film. So the 3D structure has now disintegrates to it is individual components.

There are 2 methods for HI to degrade in the next step, one method is a redox reaction in the presence of the oxygens, so HI can react in the presence of the oxygens. The other method is a photochemical reaction in which HI can decomposing to H2 and I2 under UV radiation. So now when you scan the solar cell you have to scan all the wavelength. Now when I scan that then it is also exposed to the UV light now the UV light can degrade the HI to the hydrogen and iodine, these were photochemical reaction.

Now the consumption of HI according to the reaction 2c and 2d dives the hole degradation process forward. Now once the HI has been degraded either to H and I or HI has been oxidized in the presence of the oxygen. Then the hole kinetics moves towards the right and it actually leads to the further disintegration of the perovskite material. As the degradation of organic, inorganic halide perovskite is quite sensitive to the moisture and oxygen.

Most of the fabrication process must be conducted in a glove box filled with inner gas. Now what is a glove box, a glove box is an environmental chamber where you can control the humidity level and oxygen level. So since the perovskite material is very very sensitive to the moisture level or the humidity level, so or the water contact. So we have to fabricate the device in a control environment away from like you know water vapor or away from any kind of moisture.

So that is done by fabricating the perovskite solar cell in a glove box but again the problem is that once you make it in a glove box then what will happen when I bring it outside again it will can undergo the similar kind of degradation kinetics.

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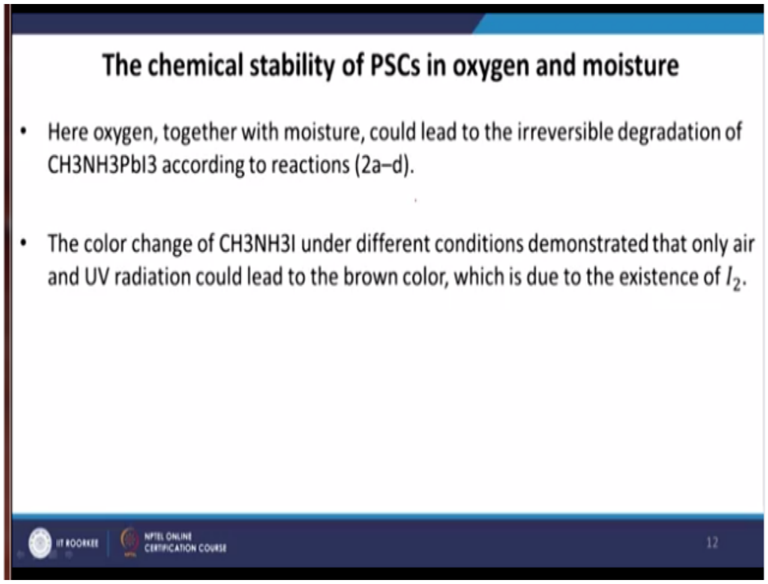

The chemical stability of PSCs in oxygen and moisture

- Here oxygen, together with moisture, could lead to the irreversible degradation of CH3NH3PbI3 according to reactions (2a–d).
- The color change of CH3NH3I under different conditions demonstrated that only air and UV radiation could lead to the brown color, which is due to the existence of I_2.

Here oxygen together with the moisture could lead to the irreversible degradation of the CH3NH3 lead iodide according to the reaction 2a and 2d. So we have both oxygen we have both moisture see if I have both moisture and oxygen you see that the CH3NH3I finally disintegrate to hydrogen iodine some CH3NH3I HI all these compound. And sometimes if both are them are present then this reaction is irreversible, this reaction is irreversible degradation.

The color change of CH3NH3I under different condition demonstrate that only air and UV radiation could lead to the brown color which is due to the existence of the iodine. So when you expose a CH3NH3 lead iodide film to the ambient condition for quite a sometime you will see the black color film has been convert to brown color. And that is because you have iodine in the system now because of the iodine the film has been convert to the black to the brown color, so it is no longer a perovskite crystal structure now.

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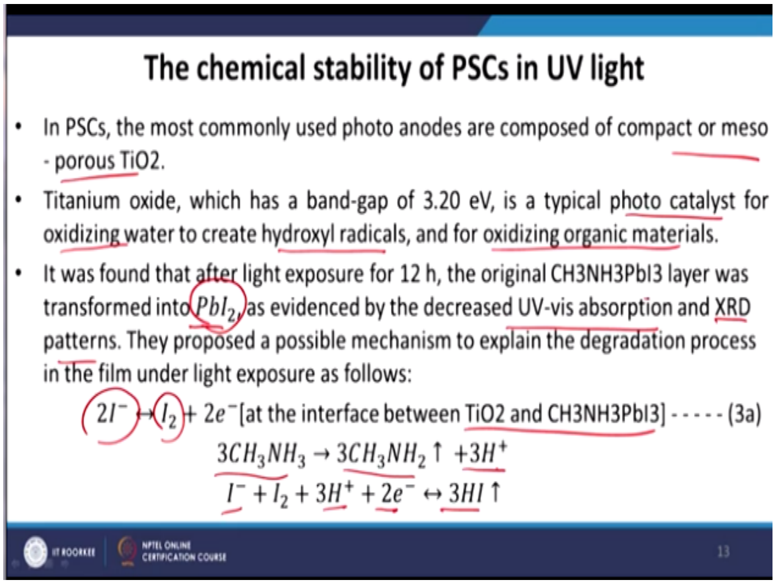

The chemical stability of PSCs in UV light

- In PSCs, the most commonly used photo anodes are composed of compact or meso - porous TiO2.
- Titanium oxide, which has a band-gap of 3.20 eV, is a typical photo catalyst for oxidizing water to create hydroxyl radicals, and for oxidizing organic materials.
- It was found that after light exposure for 12 h, the original CH3NH3PbI3 layer was transformed into PbI_2, as evidenced by the decreased UV-vis absorption and XRD patterns. They proposed a possible mechanism to explain the degradation process in the film under light exposure as follows:

$2I^- \leftrightarrow I_2 + 2e^-$ [at the interface between TiO2 and CH3NH3PbI3] - - - - - (3a)

$$3CH_3NH_3 \rightarrow 3CH_3NH_2\uparrow + 3H^+$$

$$I^- + I_2 + 3H^+ + 2e^- \leftrightarrow 3HI\uparrow$$

In perovskite solar cell the most commonly used photoanodes are composed of compact or mesoporous TIO2. So as you have learnt earlier that we can make the perovskite solar cell either in a PIM geometry or in a NIP geometry we call them as a (()) (29:09). So in a PIM geometry we put P.PSS on top the ITO substrate and we put some spiro emitted or dope spiro emitted on the top surface of the perovskite before metal contact.

But in an NIP geometry we put titanium dioxide mesoporous titanium dioxide or compact titanium dioxide as a end layer on top of the ITO. And we put some hole transport material like P3HT on the top as a hole transport material. Now the photo anode compost of the mesoporous TiO2 layer titanium dioxide which has a band gap of 3.2 electron volt is a typical photo catalyst for oxidizing water to create hydroxyl radicals and for oxidizing organic molecules.

It was found that after light exposure for 12 hour, the original CH3NH3 lead iodide layer was transformed into lead iodide as evidenced by the decreased UV absorption and XRD patterns. So if you look at the in situ XRD patterns in the presence of moisture, you will see that gradually CH3NH3 lead iodide structure is disintegrating into the lead iodide structure. They proposed a possible mechanism to explain the degradation process in the film under light exposure as follows.

See we have the iodine, iodine 2I- it can goes to I2+2 electron at the interface between TiO2 and CH3NH3I, so basically we are now proving the interface between the mesoporous titanium dioxide and the perovskite active layer. So at the interface, so we have now the iodine+2 electron because TiO2 actually acts like a as you said here is a photo catalyst it can oxidized water to create hydroxyl radicals and oxidizing organic materials.

Now CH3NH3 they further degrades to the CH3NH2 and 3H+ this 3H+ in the presence of the electron and iodine they makes 3 iodide. So CH3NH3 that decompose into CH3NH2+3 H+ proton and that proton further reacts with this iodine to makes the 3 HI.

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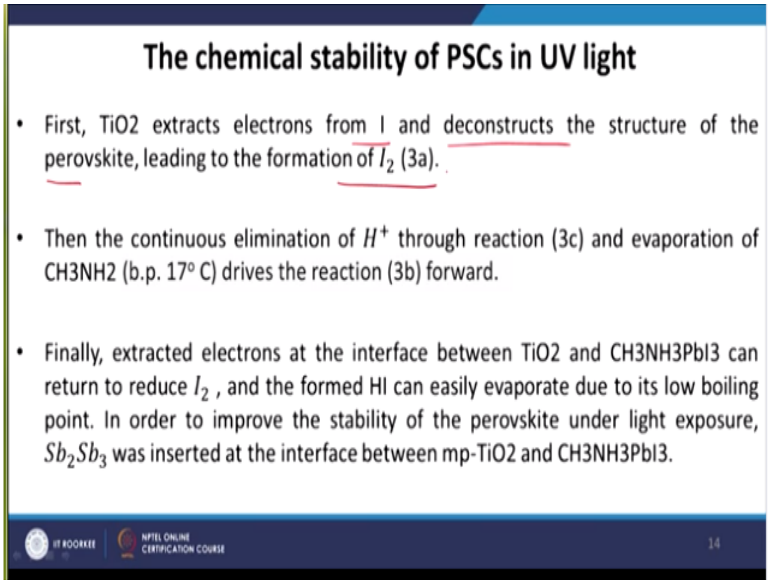

The chemical stability of PSCs in UV light

- First, TiO2 extracts electrons from I and deconstructs the structure of the perovskite, leading to the formation of I_2 (3a).
- Then the continuous elimination of H^+ through reaction (3c) and evaporation of CH3NH2 (b.p. 17° C) drives the reaction (3b) forward.
- Finally, extracted electrons at the interface between TiO2 and CH3NH3PbI3 can return to reduce I_2 , and the formed HI can easily evaporate due to its low boiling point. In order to improve the stability of the perovskite under light exposure, Sb_2Sb_3 was inserted at the interface between mp-TiO2 and CH3NH3PbI3.

First TiO2 extract electrons from iodine and deconstruct the structure of the perovskite leading to the formations of the iodine. So TiO2 is a very known or good electron extractor, so it extracts the electron from iodine and deconstructs the structure of the perovskite leading to the formation of iodine. Then the continuous elimination of H+ through reaction and evaporation of CH3NH2 drives the forward.

Finally extracted electrons at the interface between TiO2 and CH3NH3 lead iodide can return to reduce iodine and the formed HI can easily evaporates due to it is low boiling point. In order to improve the stability of the perovskite under light exposure Sb2Sb3 was inserted at the interface between mesoporous TiO2 and CH3NH3 lead iodide.

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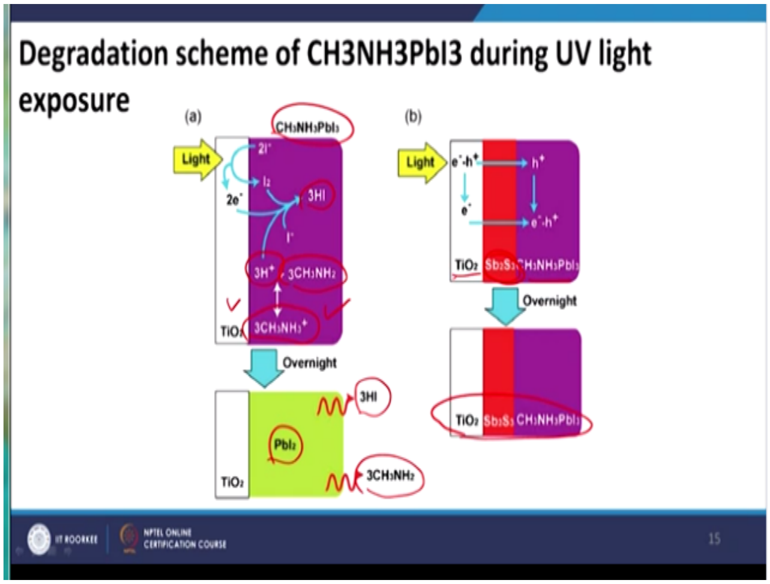

Degradation scheme of CH3NH3PbI3 during UV light exposure

You look at the degradation scheme of CH3NH3 lead iodide during UV light exposure, so what will happen, so of the interface we have the TiO2 and we have this CH3NH3 lead iodide right this CH3NH3 lead iodide and TiO2. Now light generates now light falls on the TiO2 so when light falls on the TiO2, so what will happen TiO2 can grab the electron. So what happens now the iodine the 2I-, so in the presence of the TiO2 now can convert to the iodine I2.

Now this TiO2, so what they do, so if they grabs the electron now we have the proton here, so this proton reacts with the 3CH3NH2 and it makes the cation CH3NH3+ and we generate CHI. But what will happen like in a here overnight so TiO2 if you leave it something like that, so it will disintegrate to 2 components one is 3CHNH2 and another is the lead iodide and lead iodide further it will decompose to the hydro iodic acid, it will vaporize.

This phenomena can be prevented if we put a layer of Sb2S3 a compound in between TiO2 and CH3NH3, what it will do. So the electron hole pair which will be generated here, so electron will be grab by TiO2 and this Sb2S3 will help the hole to pass through this site ok. And this hole can react with the further with the electrons there, so they can prevent degradation. So that is why an ideal stable structure to prevent the decomposition is to put a layer of Sb2S3 in between TiO2 and CH3NH3 lead iodide film.

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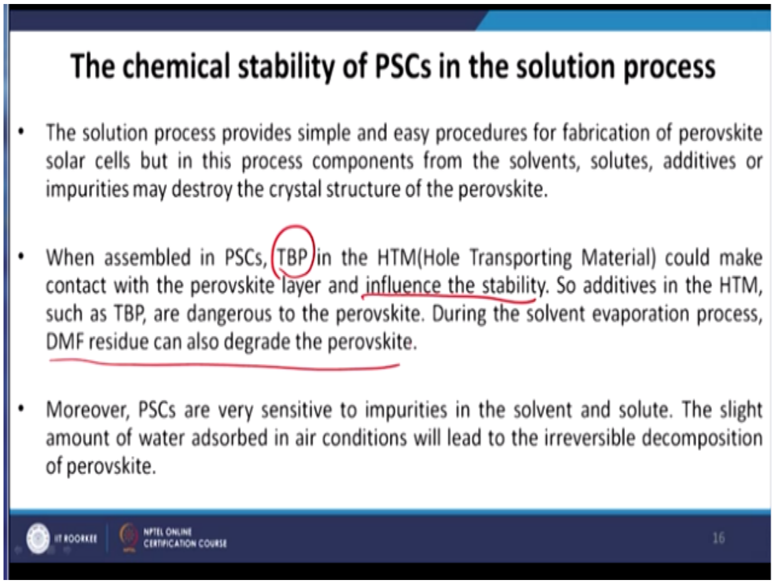

The chemical stability of PSCs in the solution process

- The solution process provides simple and easy procedures for fabrication of perovskite solar cells but in this process components from the solvents, solutes, additives or impurities may destroy the crystal structure of the perovskite.
- When assembled in PSCs, TBP in the HTM(Hole Transporting Material) could make contact with the perovskite layer and influence the stability. So additives in the HTM, such as TBP, are dangerous to the perovskite. During the solvent evaporation process, DMF residue can also degrade the perovskite.
- Moreover, PSCs are very sensitive to impurities in the solvent and solute. The slight amount of water adsorbed in air conditions will lead to the irreversible decomposition of perovskite.

So this is all about interface engineering, now the solution process provides simple and easy procedures for fabrication of perovskite solar cell. But in this process components form the solvents, solutes, additives or impurities may destroy the crystal structure of the perovskite. When assembled in perovskite solar cell tertiary butyl pyridine or TBP in the hole transport material could make contact with the perovskite layer and influence the stability.

So additives in the HTM such as tertiary butyl pyridine just like in TiO2 we said about like Sb2S3 and the Sb2S3 increase the UV stability. Similarly when you use a hole transport material if we use tertiary butyl pyridine, so there also influence the stability. So additives in the HTM such as TBP at dangerous to the perovskite during solvent evaporation process DMF residue can also degrade the perovskite.

Moreover PSCs are very sensitive to impurities in the solvent and solute, the slight amount of water absorbed in the air condition will lead to the irreversible decompositions of perovskite.

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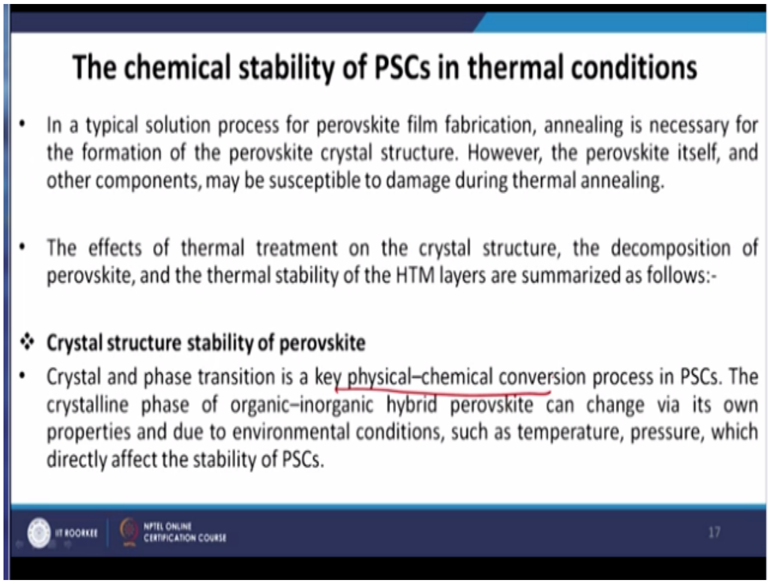

The chemical stability of PSCs in thermal conditions

- In a typical solution process for perovskite film fabrication, annealing is necessary for the formation of the perovskite crystal structure. However, the perovskite itself, and other components, may be susceptible to damage during thermal annealing.
- The effects of thermal treatment on the crystal structure, the decomposition of perovskite, and the thermal stability of the HTM layers are summarized as follows:-

❖ **Crystal structure stability of perovskite**

- Crystal and phase transition is a key physical–chemical conversion process in PSCs. The crystalline phase of organic–inorganic hybrid perovskite can change via its own properties and due to environmental conditions, such as temperature, pressure, which directly affect the stability of PSCs.

In a typical solution process for perovskite film fabrication annealing is necessary for the formation of perovskite crystal structure. So when we mix the lead iodide and CH3NH3I from a DMF solvent to make a perovskite thin film. So what we do after you allow them to react each other to make a perovskite crystal structure we have to heat them at 120 degrees Celsius and this heating process called the annealing and the annealing gives the desired crystal structure.

However the perovskite itself on the other components maybe susceptible to damage during the thermal annealing. But while you are heating it to get the desired crystal structure you can also degrade the perovskite and it is ingredients. The effects of the thermal treatment on the crystal structure the decompositions of the perovskite and the thermal stability of the hole transport layer can be summarized as the following.

First the crystal structure stability of perovskite, crystal and phase transition is a key physio-chemical conversion process in perovskite solar cell. So this is very very important see this is a physical-chemical conversion to the structure change they change to the phase. The crystalline phase of organic-inorganic hybrid perovskite can change by it is own properties and due to the environmental condition such as temperature, pressure which directly affect the stability of the perovskite solar cell.

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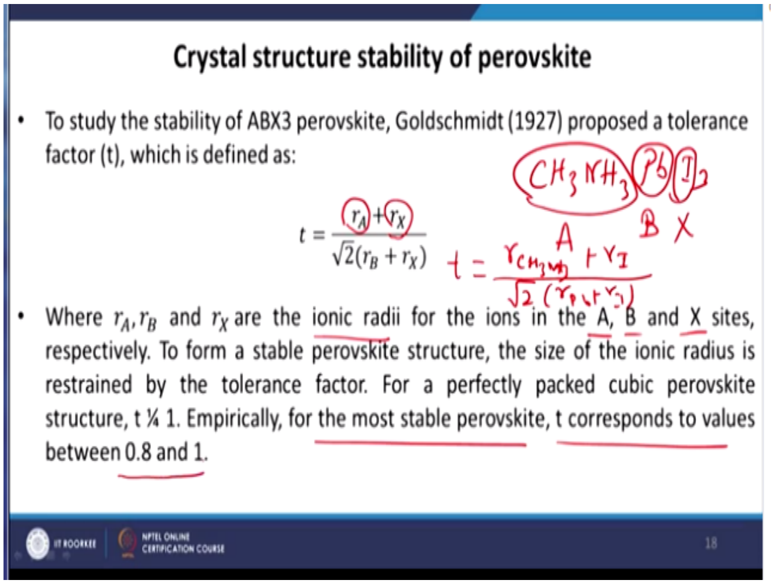

Crystal structure stability of perovskite

- To study the stability of ABX3 perovskite, Goldschmidt (1927) proposed a tolerance factor (t), which is defined as:

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$

$CH_3NH_3\,Pb\,I_3$

A B X

$$t = \frac{r_{CH_3NH_3} + r_I}{\sqrt{2}\,(r_{Pb} + r_I)}$$

- Where r_A, r_B and r_X are the ionic radii for the ions in the A, B and X sites, respectively. To form a stable perovskite structure, the size of the ionic radius is restrained by the tolerance factor. For a perfectly packed cubic perovskite structure, t ¼ 1. Empirically, for the most stable perovskite, t corresponds to values between 0.8 and 1.

To study the stability of ABX3 perovskite, Goldschmidt proposed a tolerance factor which is defined as we have also talked about this earlier. So tolerance factor is the radius of the A if it thus radius of the X/square root of root 2 rB radius of the B+rx halogen. So in our structure CH3NH3 lead iodine right that was the organic-inorganic halide perovskite. So what is A here this is A, what is B here this is B lead and what is X here, so iodine is the X.

So basically if I wanted to write the tolerance factor for this kind of particular structure how you will write it. So t for this kind of NaPbI3 is radius of CH3NH3+the radius of iodine/square root of radius of lead + radius of iodine. So that will give you the (()) (37:42) cubic what kind of crystal structure you did and we have seen that perovskite so the temperature dependant crystal structure.

So what happens if you change the temperature all of this things will change is there (()) (37:56) orientation will change in apart from the factor that they can disintegrate. Here rA, rB and rX of the ionic radii for the ions in the A, B and X sites respectively to form a stable perovskite structure the size of the ionic radius is restrained by the tolerance factor. For a perfectly packed cubic perovskite structure t value is 1/4th to 1.

Empirically for the most stable perovskite structure t corresponds to value between 0.8 and 1. Once you synthesize perovskite material then by XRD analysis or by elemental analysis or by some other advance characterization let us say you measure the ionic radii of the different ions a different components from there you can calculate a tolerance factor. If the tolerance factor value is between 0.8 and 1 then you can say that ok this structure is a stable crystal structure otherwise you have to tune some parameter.

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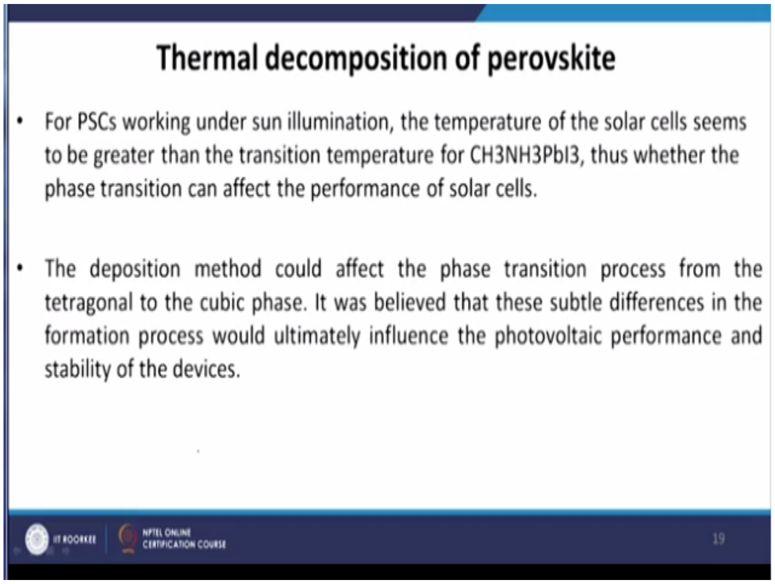

Thermal decomposition of perovskite

- For PSCs working under sun illumination, the temperature of the solar cells seems to be greater than the transition temperature for CH3NH3PbI3, thus whether the phase transition can affect the performance of solar cells.
- The deposition method could affect the phase transition process from the tetragonal to the cubic phase. It was believed that these subtle differences in the formation process would ultimately influence the photovoltaic performance and stability of the devices.

For perovskite solar cells working under sun illumination the temperature of the solar cell seems to be greater than the transition temperature for CH3NH3 lead iodide. So what is transition temperature it is a temperature at which CH3NH3 lead iodide disintegrates to it is ingredient components, thus whether the phase transition can affect the performance of solar cells. The deposition method could affect the phase transition process from the tetragonal to the cubic phase, it was believed that these subtle difference in the formation process would ultimately influence the photovoltaic performance and stability of the device.

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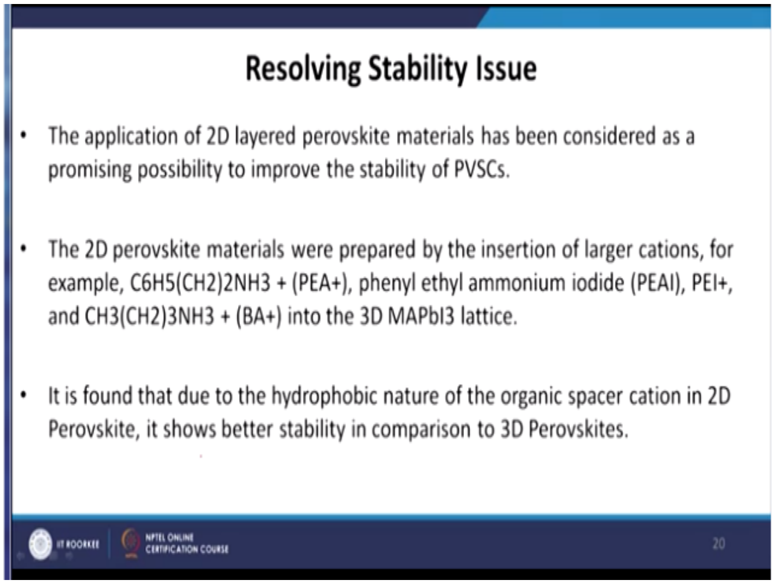

Resolving Stability Issue

- The application of 2D layered perovskite materials has been considered as a promising possibility to improve the stability of PVSCs.
- The 2D perovskite materials were prepared by the insertion of larger cations, for example, C6H5(CH2)2NH3 + (PEA+), phenyl ethyl ammonium iodide (PEAI), PEI+, and CH3(CH2)3NH3 + (BA+) into the 3D MAPbI3 lattice.
- It is found that due to the hydrophobic nature of the organic spacer cation in 2D Perovskite, it shows better stability in comparison to 3D Perovskites.

The application of 2D layered perovskite materials has been considered as a promising solubility to improve the stability of perovskite solar cell. Now instead of this 3D perovskite people are now also talking 2D, 3D quasi perovskite solar cell and also 2D layered perovskite structure, these are more stable but the efficiency is decrease. Because in the 2D perovskite the charge transport is only in one dimension, we have to have a particle dimension charge transport also to increase the efficiency.

The 2D perovskite materials were prepared by the insertion of larger cations, for example C6H5(CH2)2NH3+PEA+ phenyl ethyl ammonium iodide PEI+ and CH3(CH2)3NH3 + barium ion into the 3D MAPbI3 lattice. It is found that due to the hydrophobic nature of the organic spacer cation in 2D perovskite it shows better stability in comparison to the 3D perovskites.

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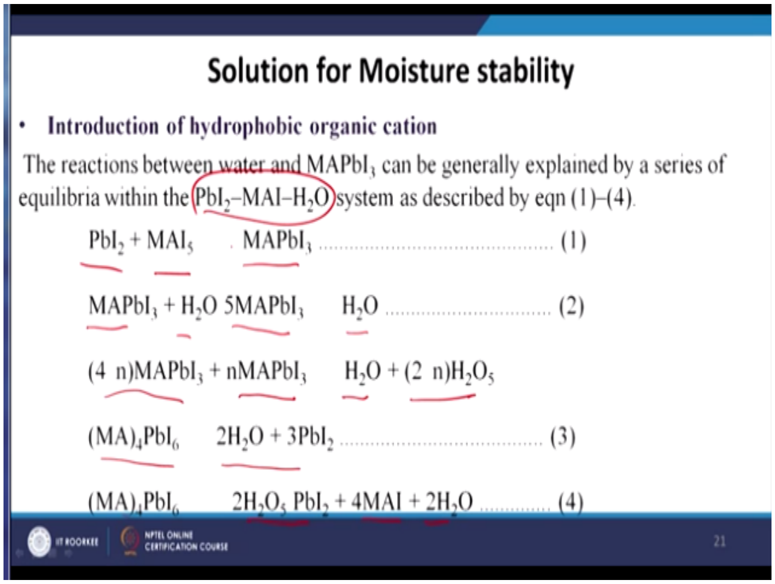

Solution for Moisture stability

- **Introduction of hydrophobic organic cation**

The reactions between water and $MAPbI_3$ can be generally explained by a series of equilibria within the $PbI_2–MAI–H_2O$ system as described by eqn (1)–(4).

$PbI_2 + MAI_5$ $MAPbI_3$ .... (1)

$MAPbI_3 + H_2O$ $5MAPbI_3$ H_2O .... (2)

$(4\ n)MAPbI_3 + nMAPbI_3$ $H_2O + (2\ n)H_2O_5$

$(MA)_4PbI_6$ $2H_2O + 3PbI_2$ .... (3)

$(MA)_4PbI_6$ $2H_2O_5\ PbI_2 + 4MAI + 2H_2O$ .... (4)

So what about solution for moisture stability, introduction of the hydrophobic organic cation, so we have to put a layer of the hydrophobic organic material. The reactions between the MAPbI3 can generally be explained by a series of equilibria within the PbI2-MAI-H2O system. For example if PbI2 and MAI5 they react they can gives to MAPbI3, MAPbI3+H2O.

So it can gives 5MAPbI3 H2O, 4 n MAPbI3+n MAPbI3 that can gives H20+ 2n H2O5, MA4PbI6 +2H2O+3 lead iodide, MA4PbI6 2H2O5PbI2 4MAI 2H2O. These are all equilibrated components and then makes this equilibria systems PbI2-MAI-H2O, these all the intermediates products when you allow the perovskite to reacts with the water molecule.

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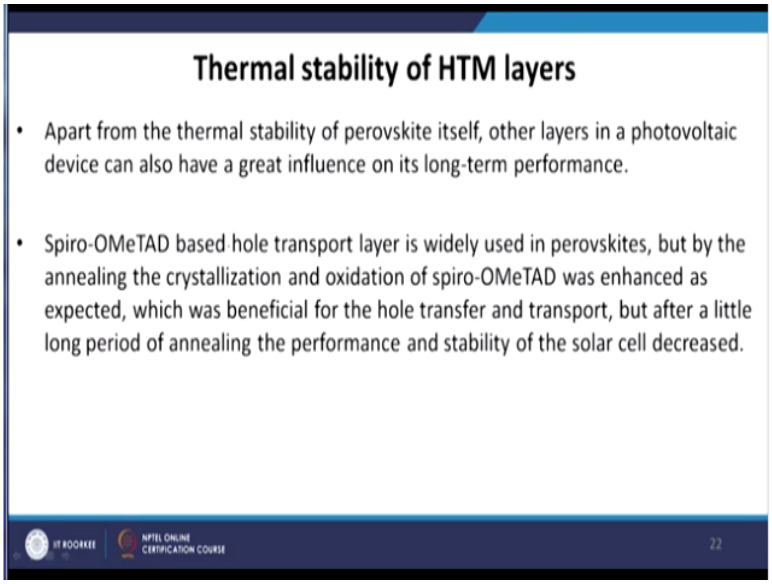

Thermal stability of HTM layers

- Apart from the thermal stability of perovskite itself, other layers in a photovoltaic device can also have a great influence on its long-term performance.
- Spiro-OMeTAD based hole transport layer is widely used in perovskites, but by the annealing the crystallization and oxidation of spiro-OMeTAD was enhanced as expected, which was beneficial for the hole transfer and transport, but after a little long period of annealing the performance and stability of the solar cell decreased.

Apart from the thermal stability of perovskite itself other layers in a perovskite photovoltaic device can also have a great influence on the long term performance. Spiro-OMeTAD based hole transport layer is widely used in perovskite but by the annealing the crystallization and oxidation of spiro-OMeTAD was enhanced as expected which was beneficial for the hole transfer and transport. But after a little long period of annealing the performance and stability of the solar cells decreased.

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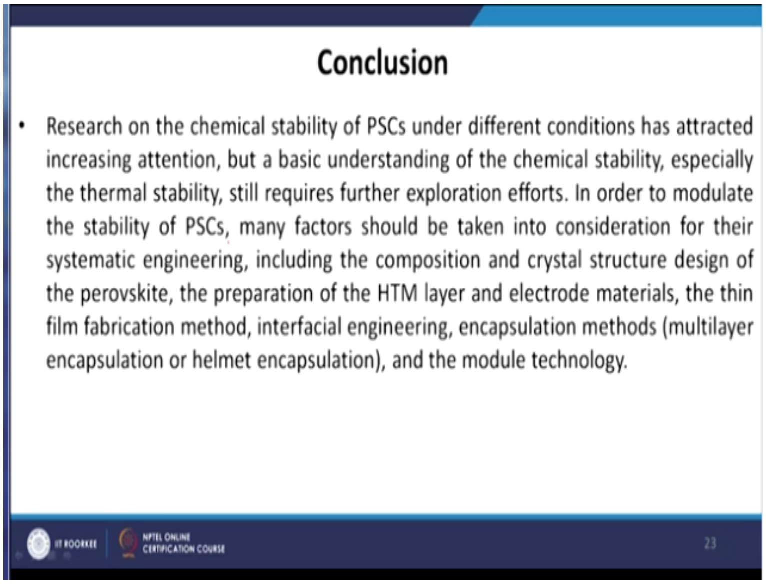

Conclusion

- Research on the chemical stability of PSCs under different conditions has attracted increasing attention, but a basic understanding of the chemical stability, especially the thermal stability, still requires further exploration efforts. In order to modulate the stability of PSCs, many factors should be taken into consideration for their systematic engineering, including the composition and crystal structure design of the perovskite, the preparation of the HTM layer and electrode materials, the thin film fabrication method, interfacial engineering, encapsulation methods (multilayer encapsulation or helmet encapsulation), and the module technology.

So in conclusion research on the chemical stability of perovskite solar cells under different conditions has attracted increasing attention. But a basic understanding of the chemical stability especially the thermal stability still requires further exploration effects. In order to modulate the stability of perovskite solar cells many factors should be taken into consideration for the systematic engineering including the composition and crystal structure designing of the perovskite.

The preparation of the hole transport layer and electrode materials the thin film fabrication method interfacial engineering, encapsulation methods multilayer encapsulation or helmet encapsulation and the module technology. So there are so many factors which can affect the stability of the perovskite solar cells, it can be due to the external factors like moisture or temperature or it can be internal factors like ion migrations.

So we have to do lot of works to address this issues either in terms of a barrier layer of encapsulant layer or either by changing the material properties or either by changing the hole transport layer or either by modifying the perovskite and the transport layer interface. And there are tremendous amount of research is now a days on going to increase the stability of the perovskite alongside the efficiency.

And very soon we will be come across with a perovskite solar module which will also give a high efficiency at the same time very high stability and that is our goal. So for a reference you can look there are lot of research paper and review papers are available in the literature.

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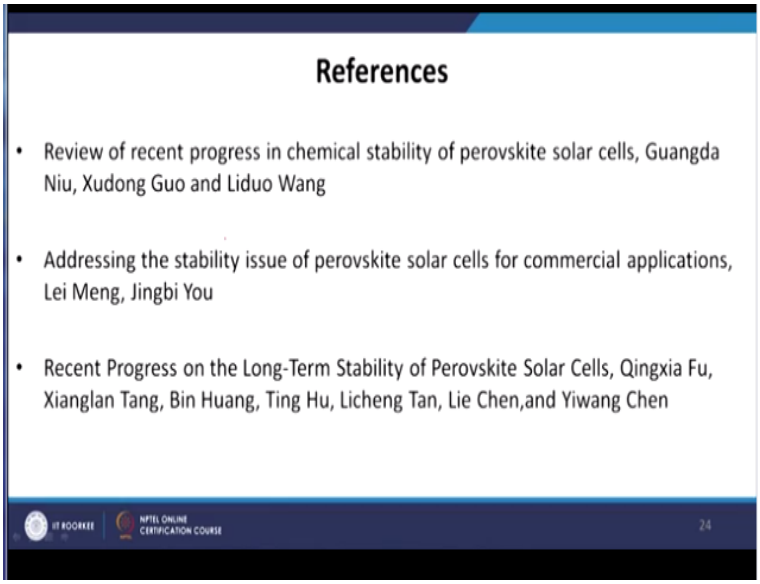

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- Addressing the stability issue of perovskite solar cells for commercial applications, Lei Meng, Jingbi You
- Recent Progress on the Long-Term Stability of Perovskite Solar Cells, Qingxia Fu, Xianglan Tang, Bin Huang, Ting Hu, Licheng Tan, Lie Chen,and Yiwang Chen

Some of them is like review of recent progress in chemical stability of perovskite solar cell by Liduo wang. Addressing the stability of issue of perovskite solar cell for commercial applications by Jingbi You, Recent progress on the long-term stability of perovskite solar cell by Yiwang chen. So these are some of the excellent articles and there are a lot of number of excellent research articles and review papers you will search online.

You can find about some basic introduction to a very in-depth discussion about the stability issue in a perovskite solar cell, thank you very much.