# Solar Photovoltaics:
# Fundamental Technology and Applications
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## Lecture-25
## Perovskite Solar cells

Welcome everyone to our course, today we have 6th week first module lecture. We already have started with third generation solar cell. So far we discussed with you about desensitize solar cell and organic solar cell, today we will talk about a one very interesting type of solar cell namely Perovskite solar cell.

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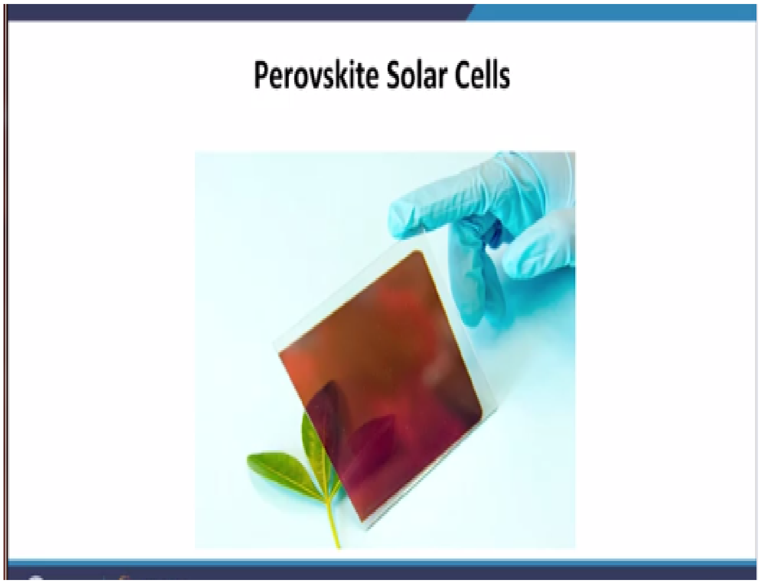

Perovskite Solar Cells

So, the Perovskite solar cell that during the last 10 years it caught the attention of the scientific community as it is efficiency increase all of a sudden from a very desired number to a very high number and this material possess how the properties like tunable band gap, high absorption coefficient. Because of all this excellent photo physical properties, this material is suitable not only for solar cell but also for light emitting diode.

For fabricating photo diodes, for photo detectors as well as different kind of lasers but today we will discuss about the perovskite base solar cells only.

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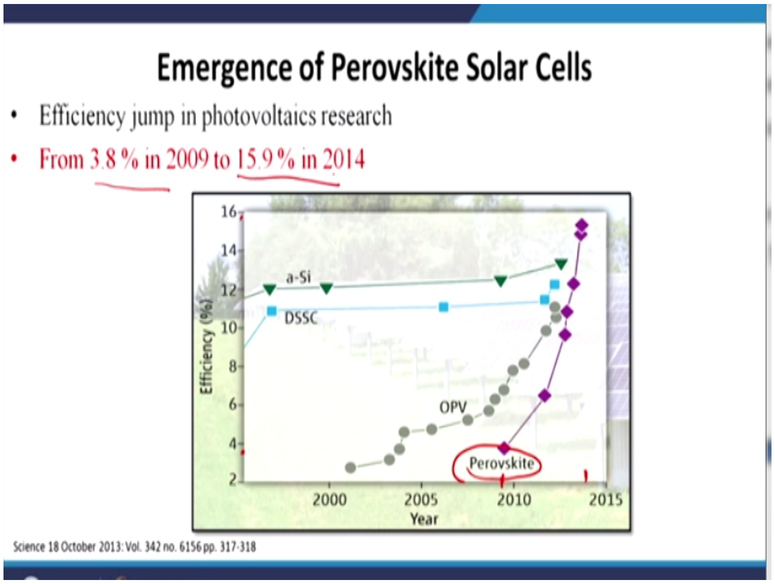

## Emergence of Perovskite Solar Cells

- Efficiency jump in photovoltaics research
- From 3.8 % in 2009 to 15.9 % in 2014

Science 18 October 2013: Vol. 342 no. 6156 pp. 317-318

If you look this graph, this figure which is actually a subset of the (()) (01:36) big efficiency graph. So you can see that we are comparing the efficiency verses year for different generations of the solar cell. Now amorphous silicon solar cell the growth is almost constant, dye-sensitize solar cell the efficiency starting from 10 to 11% it remains almost constants and there is a sudden little bit increase here only.

Organic photovoltaics a steady increase is happening and this have been lead by the discovery of the new materials. Whereas the perovskite material if you look at the growth cage it is the very very steep. So that is why the efficiency started with a very moderate numbers somewhat around 3.8% it rolls to almost about like 15 to 8% in a time period which started from 2008 to 2016. So only in 5 to 6 years of research the efficiency has increasing significantly and this number increasing day by day.

For example today the efficiency of a perovskite solar cell is 22%, so from 3.8% in 2009, 15.9% in 2014, so only 5 years of research, but efficiency enhancement is huge that is why. And even like the efficiency sometimes is comparable to the silicon solar cell efficiency, that is why this material has got the attention of scientific community and lot of people who were working on the sensitizer base solar cell has started working on perovskite based solar cell. But what is this perovskite or what is the name perovskite stands for.

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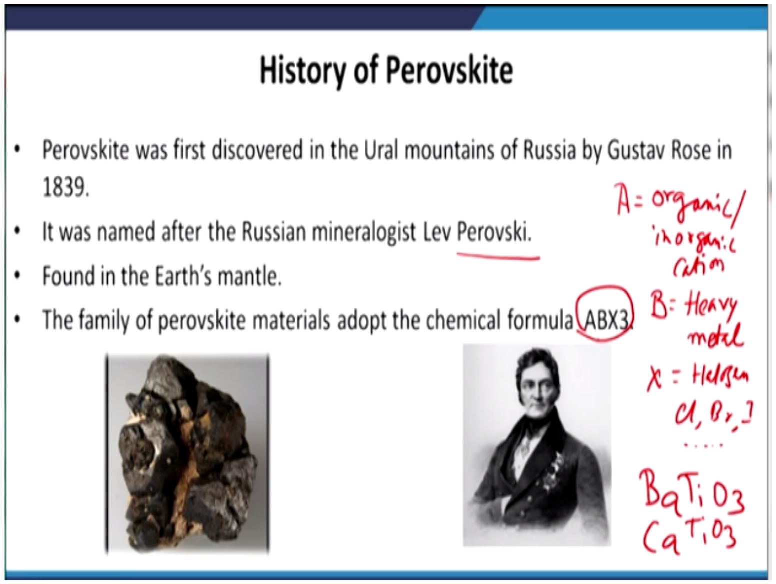

## History of Perovskite

- Perovskite was first discovered in the Ural mountains of Russia by Gustav Rose in 1839.
- It was named after the Russian mineralogist Lev Perovski.
- Found in the Earth's mantle.
- The family of perovskite materials adopt the chemical formula ABX3

A= organic/ inorganic cation

B: Heavy metal

X = Halogen Cl, Br, I .....

$BaTiO_3$

$CaTiO_3$

Perovskite was first discovered in the rural mountains of Russia by Gustav Rose in 1839. So it was named after the Russian mineralogist Lev Perovski. So you can see that from this word perovski the structure name came as a perovskite, it if found in the earth's mantle and the family of perovskite material adopt the chemical formula ABX3. So all those crystal structures or all those materials which have a crystal structure of ABX3 they are called perovskite crystal structure.

Here your A is an organic or an inorganic cation, B is your heavy metal and X is the halogen like chlorine, bromine, iodine etc. So when you have that organic compound as a A cation along with the heavy metal and halogen then we have an organic inorganic hybrid perovskite. When you have an inorganic cation as a A cation along with the heavy metal and the halogen then we have all inorganic perovskite.

Now one of the very very commonly studied inorganic perovskite is barium titanate which we often write as BaTiO3, for example calcium titanate is also widely studied. These are the 2 perovskite material which have been studied extensively for it is ferroelectric properties. And different kind of ferroelectric based material has been fabricated using this 2 perovskite structure but later on people have found that by suitable substitution of the organic cation.

And changing the structure we can always fabricate the perovskite structure with the tunable band gap and once it was realized then the application of the perovskite in the optoelectronics field has started.

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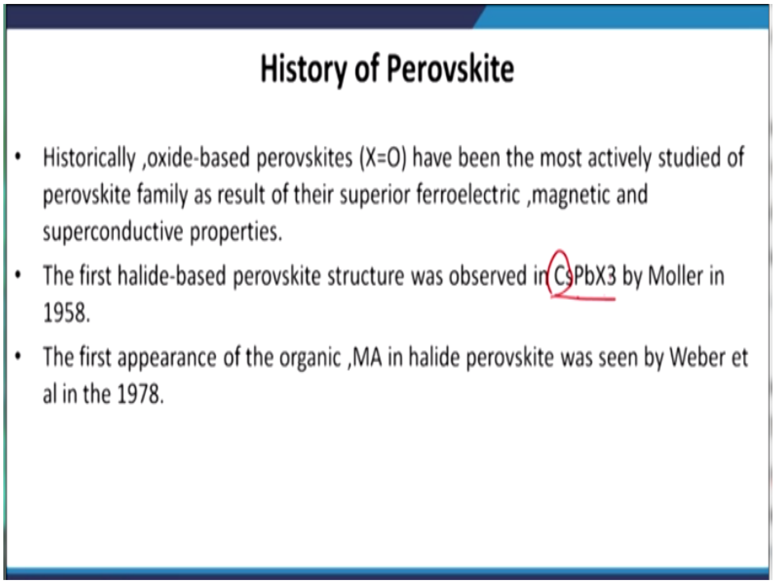

## History of Perovskite

- Historically ,oxide-based perovskites (X=O) have been the most actively studied of perovskite family as result of their superior ferroelectric ,magnetic and superconductive properties.
- The first halide-based perovskite structure was observed in CsPbX3 by Moller in 1958.
- The first appearance of the organic ,MA in halide perovskite was seen by Weber et al in the 1978.

Now historically, oxide-based perovskite have been the most actively studied a perovskite family as a result of their superior ferroelectric, magnetic and super conductive properties. So in the earlier days when super conductivity was in the zenith of it is time there are lot of varieties of the perovskite materials have been studied for the investigation of the room temperature super conductivity. So that is why whenever previously we talk about perovskite.

We usually mean a material which have a very good ferroelectric, magnetic and super conducting properties. The first halide-based perovskite structure was observed in cesium lead halide CspbX3 cesium cs, lead and X3 where X stands for the different halogen compounds by Moller in 1958. The first appearance of the organic MA in halide perovskite was seen by Webster and Weber et al in 1978.

Now why there are so many research, if you look at the number of research papers in this field, it has been exponentially increasing over the last decades. Obviously this material provide us some the advantage over the conventional inorganic materials, so some of the superiorities of the perovskite solar cells are the following.

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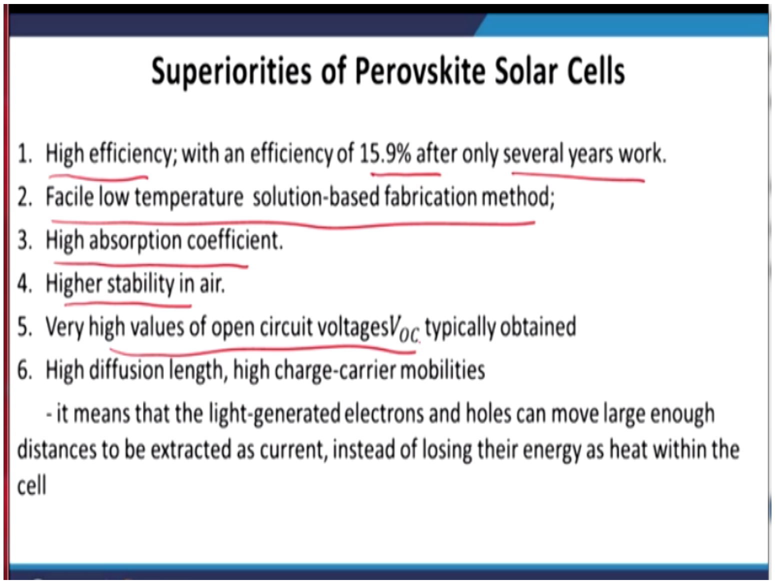

## Superiorities of Perovskite Solar Cells

1. High efficiency; with an efficiency of 15.9% after only several years work.
2. Facile low temperature solution-based fabrication method;
3. High absorption coefficient.
4. Higher stability in air.
5. Very high values of open circuit voltages$V_{OC}$ typically obtained
6. High diffusion length, high charge-carrier mobilities

- it means that the light-generated electrons and holes can move large enough distances to be extracted as current, instead of losing their energy as heat within the cell

First of all the efficiency is high, it is almost as I said 22% and this number is increasing day by day, with an efficiency of 15.9% only after 5 years of research. Now this data 15.9% is a 2015 data and this is for an indication like starting from 2009 to 2015 or 16 is 4, 5 years of research, efficiency increase from 3.8% to 15.9%. But the today's data is 22% and it is increasing every day, facile low temperature solution based fabrications method.

So we can fabricate the perovskite in a solution based approach as well as a vapor based approach. And whenever we process thus solution based perovskite we can even do the sintering or hitting up the film at a low temperature. Now what is the advantage for that, the advantage is that we can fabricate this kind of devices on a flexible printable substrate. So nowadays this flexible or printable large area or roll to roll perovskite modules are coming into the market.

And that has been all the way in possible because in this kind of material we can do a low temperature solution based processing technique. This material has a very absorption coefficient, so in a small thickness. They can absorb lot amount of light, higher stability in air, very high values of open circuit voltage Voc almost around 1.1 electron volt typically we obtain in this kind of solar cell, high diffusion length and high charge carrier mobilities.

So if the diffusion length is high as well as the charge carrier mobilities is high then the electrons and hole can travel the suitable distance to the electrode before they recombine. That is the optimum properties we will loop for designing high efficiency solar cell. It means that the light generated electrons and holes can move large enough distance to be extracted as current, instead of losing their energy as heat within the cell.

So because of this advantage perovskite picked up the research interest of many people, now some general description of the crystal structure of this material are the following.

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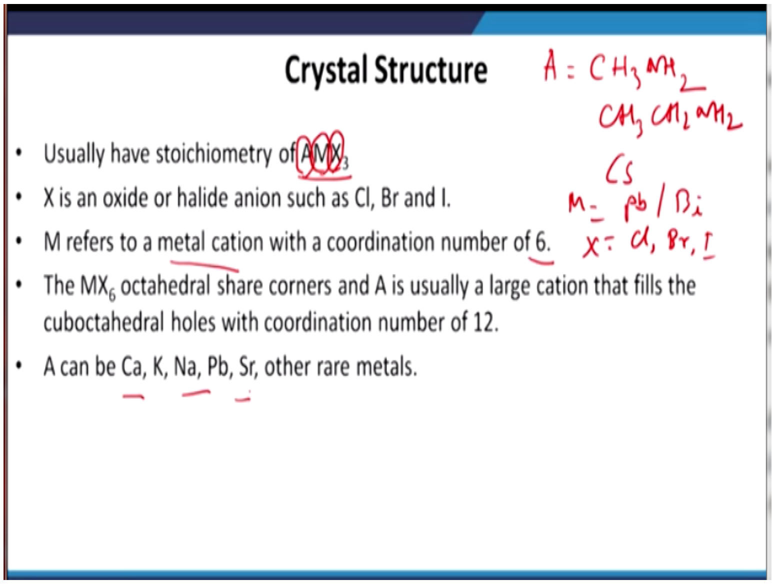

## Crystal Structure

$A = CH_3NH_2$
$CH_3CH_2NH_2$
$Cs$
$M = Pb / Bi$
$X = Cl, Br, I$

- Usually have stoichiometry of $AMX_3$
- X is an oxide or halide anion such as Cl, Br and I.
- M refers to a metal cation with a coordination number of 6.
- The $MX_6$ octahedral share corners and A is usually a large cation that fills the cuboctahedral holes with coordination number of 12.
- A can be Ca, K, Na, Pb, Sr, other rare metals.

Usually this kind of material as a stoichiometric of AMX3 and these are single perovskite. You also have double perovskite structure. So where A as I said this is can be an organic or inorganic cation when I say as an organic cation, for example CH3NH3 or CH3NH2 or it can be CH3CH2NH2. So we can use an organic group or even we can use an inorganic group like cesium, M is a metal cation, so we can use lead as a metal cation or we can use bismuth as a metal cation but commonly lead is very very extensively used.

And X is the halogen that is chlorine, bromine or iodine or a combination of chlorine, bromine and iodine. X is an oxide or halide anion such as chlorine, bromine and iodine, M refers to a metal cation with the coordination number of 6 you cannot pick up any metal, those metal which has a coordination number of 6, they usually substituted in this kind of structure. The MX6 octahedral share corners and A is usually a large cation.

That fills the cuboctahedral holes with coordination number of 12. A can be calcium, potassium, sodium, lead strontium and other rare metals.

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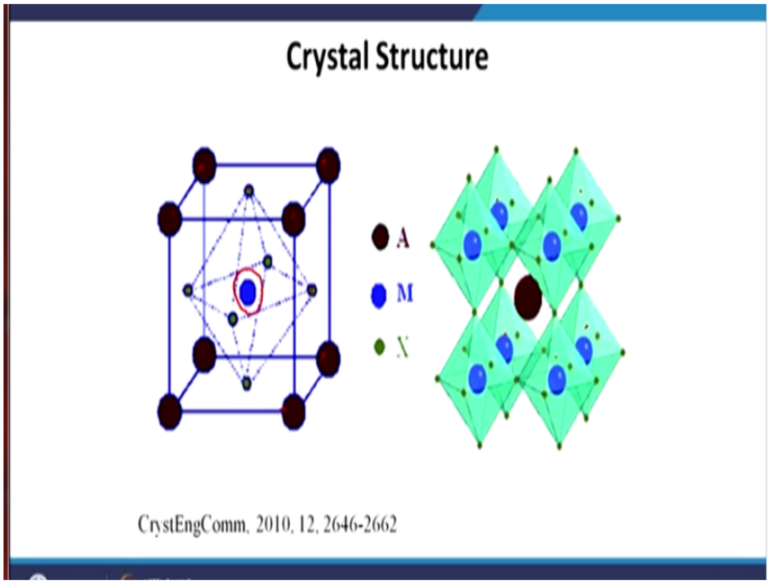

Crystal Structure

CrystEngComm, 2010, 12, 2646-2662

This is a typical crystal structure of a perovskite material where you can see the M is lying at the centre, A is at the corner and the phase centre is occupied by the halogen atoms. So the octahedral has been equally shared by each of this unit cell when surrounded in a 3 dimensional polymer. So even if I look here, so this kind of octahedra they are coordinated with each other to make a joint cuboctahedral geometry and the metal cations sits at the centre of this **cube** cuboctahedral geometry.

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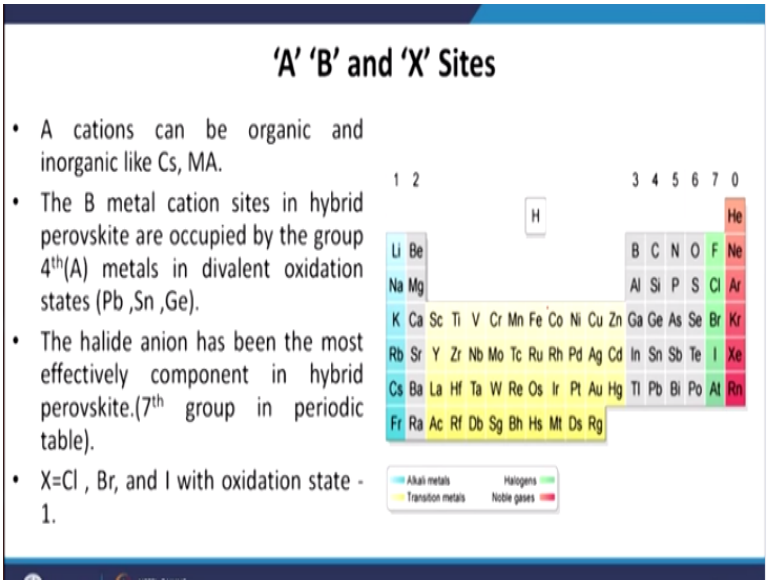

## ‘A’ ‘B’ and ‘X’ Sites

- A cations can be organic and inorganic like Cs, MA.
- The B metal cation sites in hybrid perovskite are occupied by the group 4th(A) metals in divalent oxidation states (Pb ,Sn ,Ge).
- The halide anion has been the most effectively component in hybrid perovskite.(7th group in periodic table).
- X=Cl , Br, and I with oxidation state -1.

| 1 | 2 | | | | | | | | | | | 3 | 4 | 5 | 6 | 7 | 0 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | H | | | | | | | | | | He |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| Fr | Ra | Ac | Rf | Db | Sg | Bh | Hs | Mt | Ds | Rg | | | | | | | |

A cations can be organic and inorganic like cesium or CH3NH2 methyl ammonium, the B metal cation sites in hybrid perovskite are occupied by the group fourth metals in divalent oxide states like lead, tin, germanium. The halide anions has been the most effectively component in hybrid perovskite 7 group in perovskite like chlorine, bromine, iodine with oxidation state of 1.

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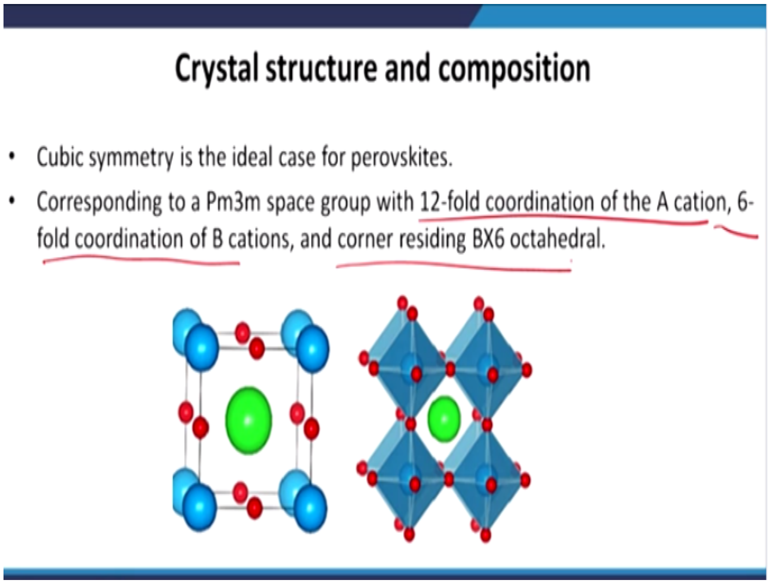

## Crystal structure and composition

- Cubic symmetry is the ideal case for perovskites.
- Corresponding to a Pm3m space group with 12-fold coordination of the A cation, 6-fold coordination of B cations, and corner residing BX6 octahedral.

Crystal symmetry is the ideal case of for perovskite corresponding to a Pm3m space group with 12-fold coordination number of the A cation, 6 pole coordination of the B cation and the corner residing BX6 octahedral. We get this cuboctahedral geometry which is shown in this figure.

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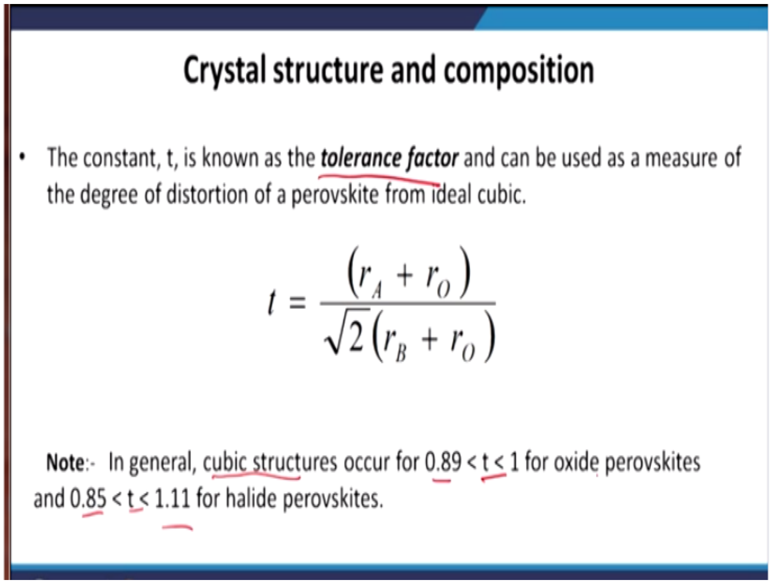

### Crystal structure and composition

- The constant, t, is known as the ***tolerance factor*** and can be used as a measure of the degree of distortion of a perovskite from ideal cubic.

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

**Note**:- In general, cubic structures occur for $0.89 < t \leq 1$ for oxide perovskites and $0.85 < t \leq 1.11$ for halide perovskites.

Now when we synthesize or when we make this perovskite material one important parameters we will look for it, is called the tolerance factor. This constant t is also known as the tolerance factor and can be used as a measure of the degree of distortion of a perovskite from ideal cubic. Now if you look back to the earlier structure, if I go back to the earlier slide you see that in the left hand side we have an ideal cubic structure but right hand side is not an ideal cubic.

So there is a distortion from an ideal crystal structure to the perovskite structure, now this distortions quantitatively represented by the tolerance factor. And the definition of the tolerance factor is t = rA + rO/square root of 2 rB + rO, in general cubic structure occurs for the values of t between 0.89 and 1 and for oxide perovskite the t value is between 0.85 to 1.11 for halide perovskites. Now here rA is the radius of your A cation rB is the radius of your B cation and O is the radius of the O anion.

So when the values of t is between 0.89 and 1 is gives a cubic structure when the values of the t is between 0.85 and 1.11 for halide perovskites it is gives a perovskite structure. So once we fabricate a perovskite structure usually from the stoichiometric ratio we look for the tolerance factor and the tolerance factor has to be satisfied to get it required perovskite structure.

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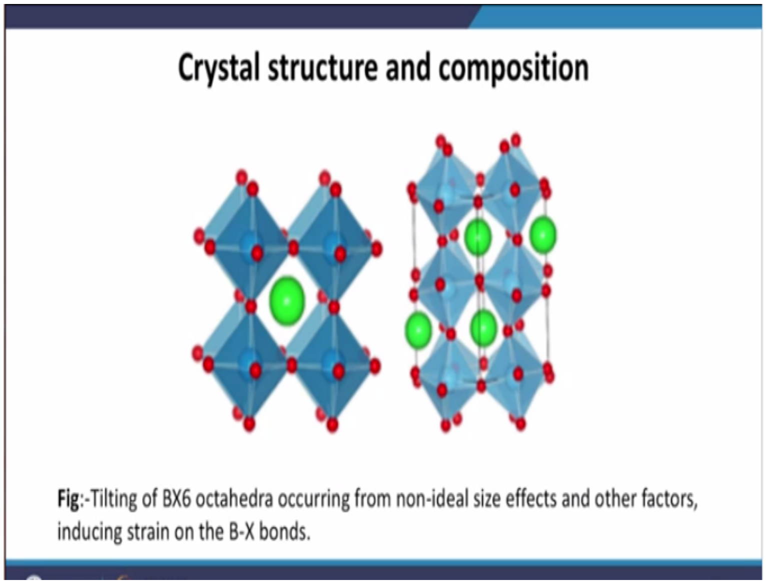

## Crystal structure and composition

Fig:-Tilting of BX6 octahedra occurring from non-ideal size effects and other factors, inducing strain on the B-X bonds.

You can see in this picture the tilting of the BX6 octahedra occurring from non-ideal size effects and other factors inducing strain on the BX6 bonds.

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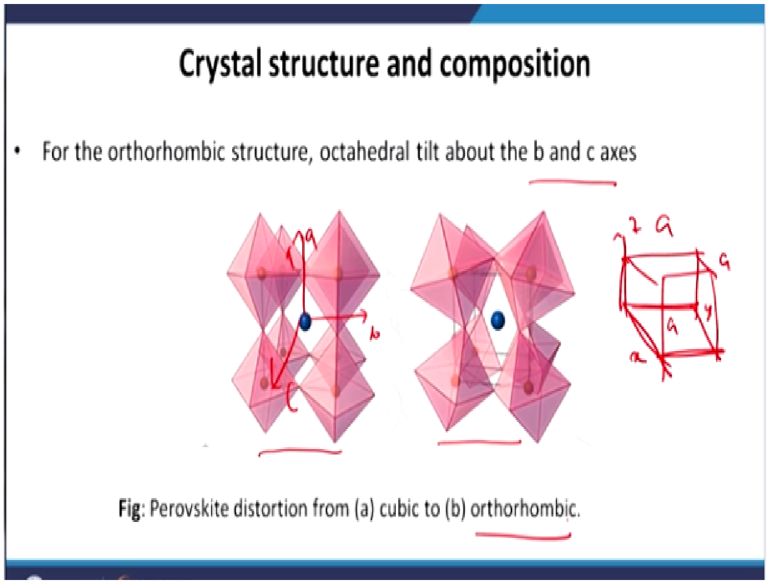

## Crystal structure and composition

- For the orthorhombic structure, octahedral tilt about the b and c axes

Fig: Perovskite distortion from (a) cubic to (b) orthorhombic.

For the orthorhombic structure octahedral tilt about the b and c axis, so if it is an orthorhombic structure then this octahedral this octahedral they tilt around the b and c axis as you can see here. So here this is a perfectly cubic structure but when there is a tilt happens, so you get an orthorhombic structure. And this tilt, if you consider this is as A axis and this as your B axis and the C axis is along the perpendicular to the plane of the paper.

Then we have a twisting or rotation around the b and c axis then the this cube like structure get twisted and you get a orthorhombic structure like that. So for example if you define a cube like this this is not an ideal cube because the length of the cube should equal let us consider that the length is all equal here. Now if this is one of the axis and this is one of the axis and if this is one of the axis and let say this is your x axis this is your y axis and z axis.

Now keeping x fixed, if I rotate this cube with respect to y as well as z direction. So I will induce a strain on the crystal structure. And the resultant geometry you will get is the orthorhombic structure ok, so orthorhombic structure has a less symmetry than the cubic structure.

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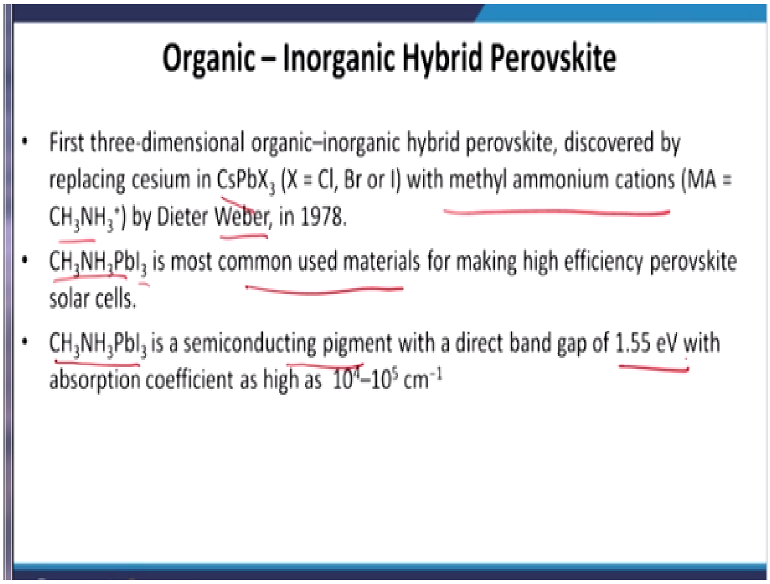

## Organic – Inorganic Hybrid Perovskite

- First three-dimensional organic–inorganic hybrid perovskite, discovered by replacing cesium in $CsPbX_3$ (X = Cl, Br or I) with methyl ammonium cations (MA = $CH_3NH_3^+$) by Dieter Weber, in 1978.
- $CH_3NH_3PbI_3$ is most common used materials for making high efficiency perovskite solar cells.
- $CH_3NH_3PbI_3$ is a semiconducting pigment with a direct band gap of 1.55 eV with absorption coefficient as high as $10^4$–$10^5$ $cm^{-1}$

First 3 dimensional organic-inorganic hybrid perovskite discovered by replacing cesium in CsPbX3 with methyl ammonium cations CH3NH3+. So the first example of the organic-inorganic cation and which is still is used very very progressively and commonly is a MA based perovskite structure, where MA or methyl ammonium is CH3NH3+ and it was discovered by Weber in 1978.

CH3NH3 lead iodide is the most commonly used materials for making high efficiency perovskite solar cell. And there are lot of study on this material, later on people have done different variations of this structure. They have replace this CH3NH3 with CH3NH3NH2 lead iodide3, some people have keep this thing as a same but replace lead with bismuth or tin or germanium.

Some people have replace this iodine with chlorine, bromine or a combination of iodine and chlorine, iodine and bromine or chlorine and bromine these are called (()) (17:22) perovskites.

But still CH3NH3 lead iodide is the most widely and most extensively studied halide perovskite structure. CH3NH3 lead iodide is a semiconducting pigment with a direct band gap of 1.55eV. So CH3NH3 lead iodide is alight absorbing material which has a direct band gap of 1.55eV. And it is absorption coefficient is also very high as high as 10 to the power 4 to 10 to the power 5/centimeter.

So this is almost comparable to an inorganic materials, so because of this high absorption coefficient the light absorptions can happen even in a smaller thickness. We when do not need a micron size thick film lied on inorganic semiconductor to make a suitable device out of this material.

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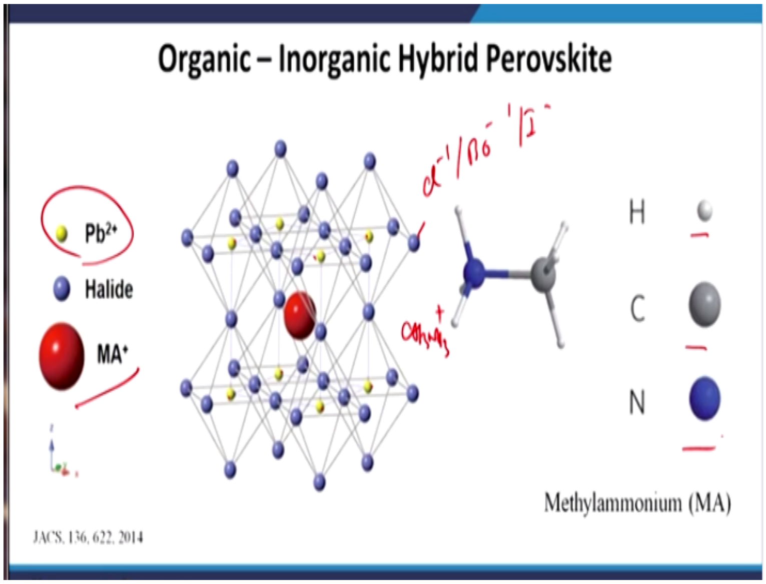

Organic – Inorganic Hybrid Perovskite

JACS, 136, 622, 2014

Let us take a look at the structure of this CH3NH3 lead iodide, where you can see here again we have done this orthorhombic crystal structure and in the centre there is a big MA cation which is CH3NH3+. And these are the halides chlorine, bromine or iodine and these are the this yellow colors circular balls they are the leads Pb2+ ions. And you can see that MA is bigger, another important thing to mention in the perspective is that.

Here in addition to the electronic nature there is an ionic contribution is also happening. Now it has been proposed that this MA cations that percolate or diffuse or migrate in this crystal structure, when light falls on it. This phenomena is commonly known as ion migration. Now because of this ion migration, although there are some debate over it but this is quite and accepted theory now a days.

Now when you have 3 dimensional structure of this perovskite material, now this organic cations or MA cations they start to migrate along the crystal structure. And because of that because of this ion migration the photo stability of the perovskite structure is very very poor. So what does it mean is that if I fabricate a high efficiency perovskite solar cell of 20% efficiency in a control environment. So by control environment I mean where you can control the humidity level and we can control the oxygen level.

In this control environment, for example in a glove box if we can fabricate a perovskite device with an efficiency of 15%. Now if I bring this device in an ambient condition and expose to the light because of this ion migration the 3D structures spontaneously disintegrate to a 2D structure. So now we do not have the required perovskite crystal structure which was responsible for the light absorption, that is why the short circuit current dramatically increase, dramatically decrease and the device become photo degradable.

Here we are showing like you know how the methyl ammonium cation looks like, here you that there is a H, carbon and nitrogen. Now one of this if the this theory is true or if we believe this theory like you know the ion migrates over the crystal structure when the light falls on it. Then the next question is that if I want to increase the stability of this devices, so I need to erased this ion migration or I need to stop the ion migration, so how can I do it.

So one possible solution as you can see from this figure, if this the big red ball is responsible for disintegrating the structure, if I make it more bulky, if I make it larger like this much size. So because of the steric hindrance then this large bulky balls will not be able to move around the structure. So that is exactly achieved if we replace this CH3NH3+ this MA cations with a longer chain cations.

For example $CH_3NH_2NH_3^+$ or $CH_3CH_2NH_2^+$ is called (()) (21:52) similar way they are gadolinium. So there are long chains alkyl groups or the larger cations one can replace but there is a limit for that provided it satisfy the tolerance factor. One can make this kind of ion migration as small as possible. Similarly people have been tried to replace this halide anion like for chlorine instead of a chlorine they mix the mixture of the 2 anions like chlorine and bromine or chlorine or iodine, or bromine or iodine.

And this is called mixed halide perovskite and these approach where one can play around with the different cationic sides as well as different anionic sides to enhance the stability of the perovskite structure is called compositional mapping. In a compositional mapping we keep the tolerance factor in the mind, so that the perovskite structure is still retained but we change the organic sides we permute the organic sides as well as we permute the anionic sides, so that the ion migration can be hindered or stopped.

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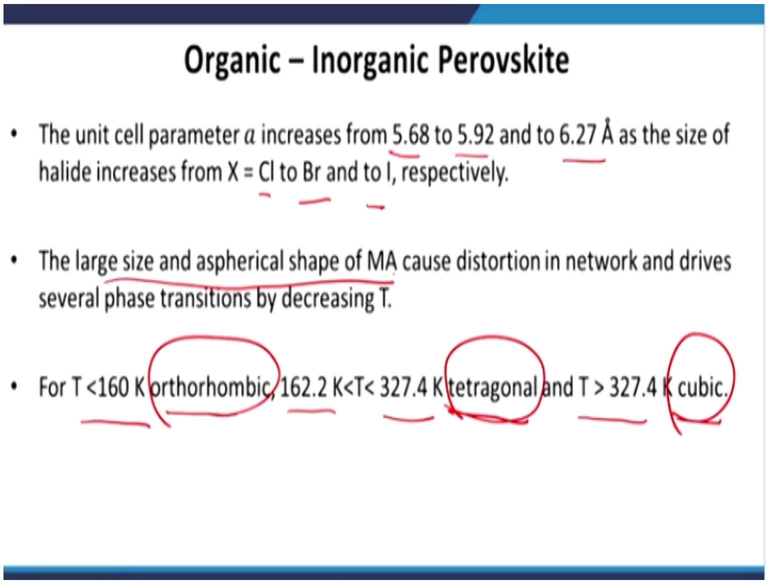

## Organic – Inorganic Perovskite

- The unit cell parameter $a$ increases from 5.68 to 5.92 and to 6.27 Å as the size of halide increases from X = Cl to Br and to I, respectively.
- The large size and aspherical shape of MA cause distortion in network and drives several phase transitions by decreasing T.
- For T <160 K orthorhombic, 162.2 K<T< 327.4 K tetragonal and T > 327.4 K cubic.

So because of that the intrinsic instability of the device can be enhanced or the intrinsic photo stability of the device can be enhanced. Organic-inorganic perovskite, the unit cell parameter A increase from 5.68 to 5.92 and to 6.27 Armstrong as the size of the halide increase from chlorine, bromine to iodine. If you change from chlorine to bromine to iodine, so what happens the unit cell parameters change from 5.68 to 5.92 to 6.27 Armstrong.

So the unit cell become larger and larger, the largest side and the aspherical shape of MA cause distortion in the network and drive several phase transition by decreasing T. So this perovskite structure shows a temperature dependent crystal structure. If you change the temperature, so what will happen due to the largest size of this anions and as well as largest size of and the spherical shape of this MA cations, there is a distortion in the crystal network.

And because of the distortions, if the thermodynamic equilibrium is distorted by changing the temperature then different kind of crystal page can be obtained. For example for T<160kelvin we get an orthorhombic crystal structure, whereas for a temperature 162 to 327 kelvin at a room temperature we get tetragonal crystal structure. And at a high temperature T>3327kelvin we get a cubic structure, so same material.

But we get 3 different crystal structure for 3 different temperature, one is tetragonal structure at room temperature, a low temperature orthorhombic structure, at high temperature cubic structure, why there are 3 different structure crystal structure from the same material. Because of the large shape and the a spherical shape of the MA the cause distortion in the crystal geometry. And this distortions actually is responsible for the phase transitions when the temperature change is induced.

So now depending upon what particular kind of crystal structure we are looking for in our practical applications, we can tune the temperature to get that the desired crystal structure.

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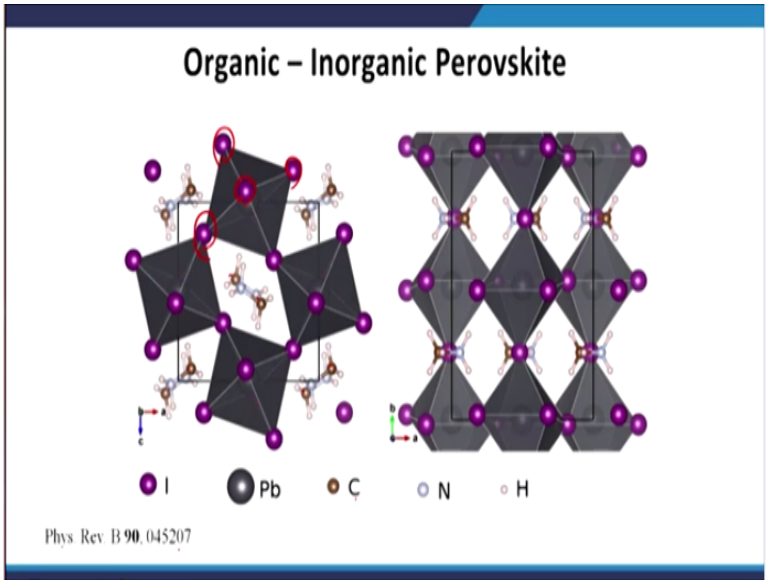

Organic – Inorganic Perovskite

Phys. Rev. B **90**, 045207

For example let us take a look at this organic inorganic perovskite crystal structure, here we have colored the different sides. As you can see this iodine is here right and lead is kind of the big one and the carbon this is here, this is the representative image which have been taken from one of the paper which was published by physical review B. you can read that paper journal to get a more idea on it.

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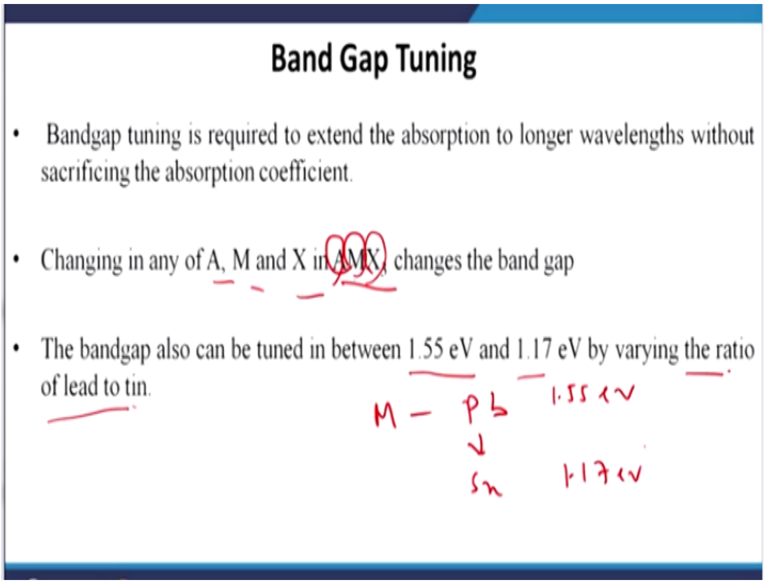

Band Gap Tuning

- Bandgap tuning is required to extend the absorption to longer wavelengths without sacrificing the absorption coefficient.
- Changing in any of A, M and X in AMX$_3$ changes the band gap
- The bandgap also can be tuned in between 1.55 eV and 1.17 eV by varying the ratio of lead to tin.

M – Pb 1.55 eV
↓
Sn 1.17 eV

Now as you mention in the beginning one of the advantage of the perovskite material is the band gap tuning. Band gap tuning is required to extend the absorption to longer wavelengths without sacrificing the absorption coefficient. So consider how good it will be, let us say I have a material where the absorption coefficient remains the same even in UV range and visible range and in near IR range, perovskite provides that opportunity, changing in any of the A, A, M and X in the AMX3 changes the band gap.

So either changing A cation or by changing M or by changing X you can change the band gap why, because once you change these things basically you change the tolerance factor T. If the tolerance factor is change then there is a distortion in the crystal structure and wherever there will be a distortion in the crystal structure there will be different kind of crystal geometry and that is leads to the different kinds of band gap.

For example the band gap can be tuned between 1.55 electron volt and 1.17 electron volt by varying the ratio of lead to tin. So if we go in the M cation if we replace the M from lead to the tin, so if the M is lead to tin then the band gap change from 1.55 electron volt to 1.77 electron volt. So basically if we replace the lead with tin we get a **a** material which low band gap material which can absorb in the near IR range.

So tin should be preferred but the problem with the tin based compound is that it is not very stable. It makes oxide at the ambient temperatures and become very very unstable that is why like you know tin base compound although has a lower band gap. So it is not very useful for fabricating high efficiency device as you mention earlier that the efficiency in a solar cell is a product function it depends upon so many parameters.

It depends upon exciton generation, it depends upon exciton diffusion, it depends upon exciton dissociation as well as charge carrier extraction. Now if one of this process is get suffered or if the morphology of the device is not good, if the photo physics of the device is not good, if the stability of the device is not good even other parameters are optimum then the efficiency should be as small as possible.

So one should optimize or one should try to figure out to while making a solar cell that the all the 4 or 5 parameters get optimized to a similar extent rather than optimizing one parameter to the ultimate and neglecting the other parameters. So that is why even if you go from lead to tin basically what you are gaining is the exciton generation because your band gap is now lower. But now the morphology becomes poor and because of this poor morphology the stability of this device is very very poor.

Now if the device is very very poor in the stability then what is the practical purpose of using the device. So that is why like you know the efficiency ultimately is not very promising or it is not very useful for making commercial product.

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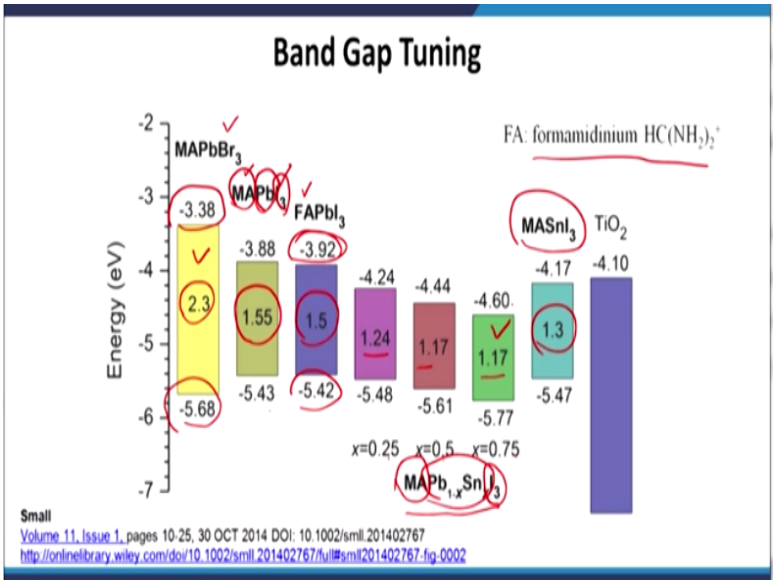

Band Gap Tuning

FA: formamidinium $HC(NH_2)_2^+$

Small
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http://onlinelibrary.wiley.com/doi/10.1002/smll.201402767/full#smll201402767-fig-0002

This is an extensive graph which is showing how we can do the band gap tuning by changing the cation ratio and the halide ratio. For example you see that this is MAPbI3 which has a HOMO energy level at -5.43 and a LUMO energy level of -3.88 with a band gap of 1.55 electron volt it is a direct band gap semiconductor. If I go to MAPbBr3, so what I have done here I replace the iodine with the bromine, so the positions of the HOMO and LUMO level changes and the band gap increased 2.3electron volt.

On the other hand instead of replacing the anionic side let us replace this cationic side MA, if you replace MA with the longer chain FA CH3NH2 CH3CH2NH2. Then the positions of the HOMO and LUMO level this is the HOMO level and this the LUMO level that also further changes and band gap decrease to 1.5electron volt and the stability also increase ok. So similarly if you change the halogen ratio for the same compound FAPbI3, if you change the X or halogen ration to 0.25 to 0.5 to 0.75 in a compound MAPbSnI3.

You see that here we are taking a ration instead of so what in this compound we are doing, we are keeping the halide ion is the same. And we are keeping the anionic side same, in this 2 cases we have change the anionic side and we have change the cationic side. Now we keep both of them same but we are changing now this part lead and Sn changing the ratio and ratio we are changing from 0.25 to 0.5 to 0.75.

And how does the band gap is changing 1.24 electron volt to 1.17 electron volt to 1.17 electron volt that is really becoming close and close to the silicon band gap. Even if you use a compound like MASnI3 I mention that the band gap of 1.3electron volt can be achieved, where this FA is the formamidinium HC HCNH2 2+, where in the MA that was only 1+. So what is the lesson we learnt from this graph, so either by changing this cationic site or by anionic site or by this metallic sites.

We can tune the band gap from 2.3 electron volt all the way to 1.17 electron volt, this method is called the compositional mapping. So only thing we have to keep in mind while we are changing this thing we have to keep the tolerance factor, so that ultimately we get a perovskite crystal structure either we have to get a orthorhombic or tetragonal or cubic structure. So we need to have a perovskite crystal structure but we can change as long as we can get a 3D perovskite crystal structure.

And what the gain we will get, the gain will get is in their efficiency number because the band gap tunes, if the band gap changes then the exciton generation efficiency also changes and that gives to the high efficiency solar cell.

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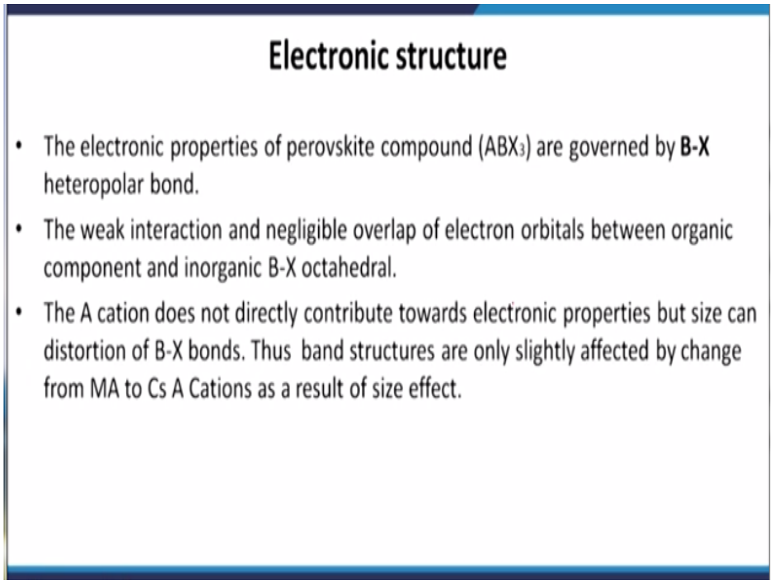

## Electronic structure

- The electronic properties of perovskite compound ($ABX_3$) are governed by **B-X** heteropolar bond.
- The weak interaction and negligible overlap of electron orbitals between organic component and inorganic B-X octahedral.
- The A cation does not directly contribute towards electronic properties but size can distortion of B-X bonds. Thus band structures are only slightly affected by change from MA to Cs A Cations as a result of size effect.

Now one more things we will study today before we complete this part the electronic structure. The electronic properties of the perovskite compounds ABX3 are governed by B-X heteropolar bond. The weak interaction and negligible overlap of electron orbitals between organic components and inorganic B-X octahedral that is responsible for this. The A cation does not directly contribute towards electronic properties but size can distortion of B-X bonds. Thus band structure only slightly affected by change from MA to cesium A cations as a result of the size effect.

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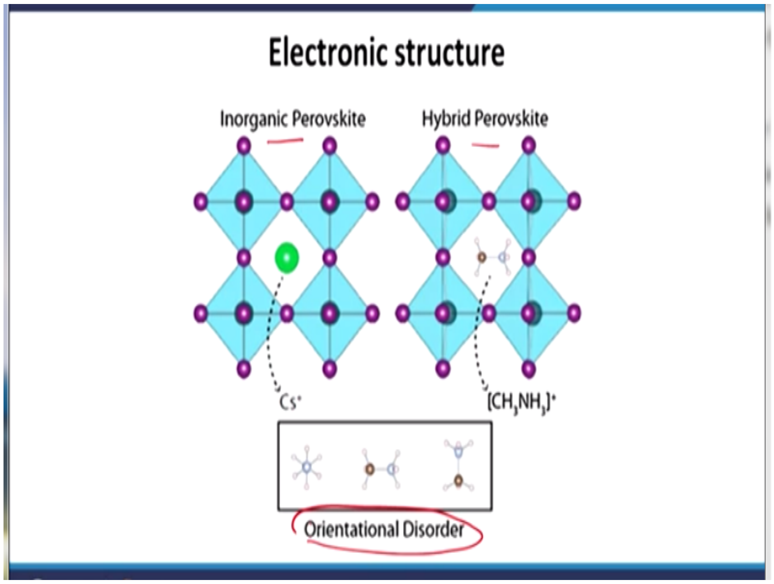

## Electronic structure

For example here you would look at an inorganic perovskite, here you look at a hybrid perovskite. So when you go from here to here, so basically what you observed is the orientational disorder and because of the orientational disorder the electronic properties is also different.

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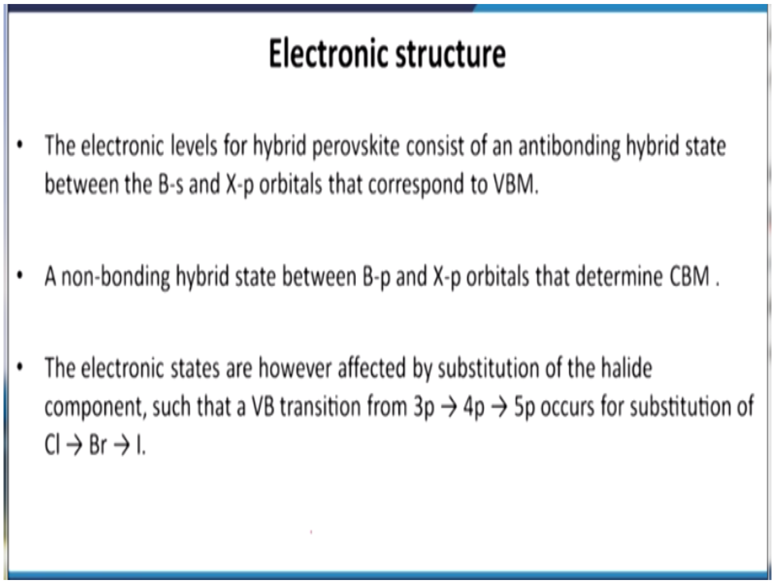

## Electronic structure

- The electronic levels for hybrid perovskite consist of an antibonding hybrid state between the B-s and X-p orbitals that correspond to VBM.
- A non-bonding hybrid state between B-p and X-p orbitals that determine CBM .
- The electronic states are however affected by substitution of the halide component, such that a VB transition from 3p → 4p → 5p occurs for substitution of Cl → Br → I.

The electronic levels for hybrid perovskite consist of an antibonding hybrid state between the B-s and X-p orbitals that corresponds to VBM. In non-bonding hybrid state between B-p and X-p orbitals then determine the conduction band the electronic states are highly affected by substitution of the halide component such that a VB transition from 3p to 4p to 5p occurs for substitution of chlorine to bromine to iodine.

So when we change the anionic site basically the transition between the orbitals is also changing and that is the responsible for the electronic properties changing.

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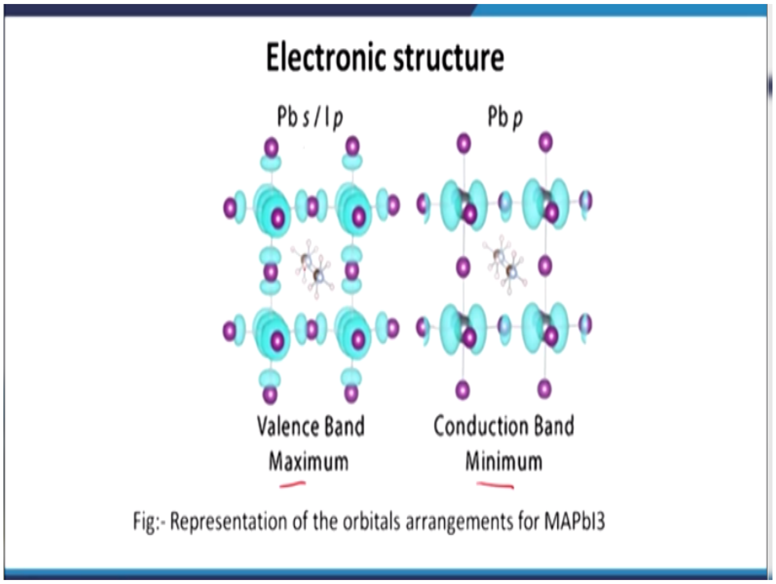

Electronic structure

Fig:- Representation of the orbitals arrangements for MAPbI3

For example here the valence bond maxima the conduction band maxima showing here for the lead where you have s1p orbitals and the Pbp orbitals. Now the orbital arrangements in this 2 case one in the s orbital and this is a p orbital you see that, that is way different in this 2 different geometry. Now as I said that this perovskite material only within a few years of research starting from an efficiency of descent 3.8% is reach today to 22% and that numbers is increasing every day.

So this material has been not only used for solar cell but also used for making light emitting diode for making photo detectors for making lasers. But in our course we will learn about perovskite base solar cell and today what we have learn that, the perovskite has a crystal structure ABX3. And there are some excellent properties of the perovskite material like large absorption coefficient, tunable band gap, solution based synthesis approach.

And because of all this things the perovskite is a choice of the preferred material for making solar cells. And another important aspect of the perovskite we have learn today is that by changing either the A cation or by X anion or by the M sides. We can tune the band gap over a wide range keeping the absorption coefficient same, because of that the optical properties of this material is very very tunable.

Similarly due to the overlap of the band the electronic properties is also tunable and also these material shows a temperature dependent crystal structures. So because of all this good good properties, perovskite materials has been used extensively in fabricating the solar cell in **in** diverse amount of geometry. In the next lecture we will learn about how to fabricate a simple perovskite solar cell or what are the components in a perovskite solar cell what are the role of those components.

And how you can make a perovskite solar cell in the lab, for today's lecture although there are lot of basic review paper and research papers are available online.

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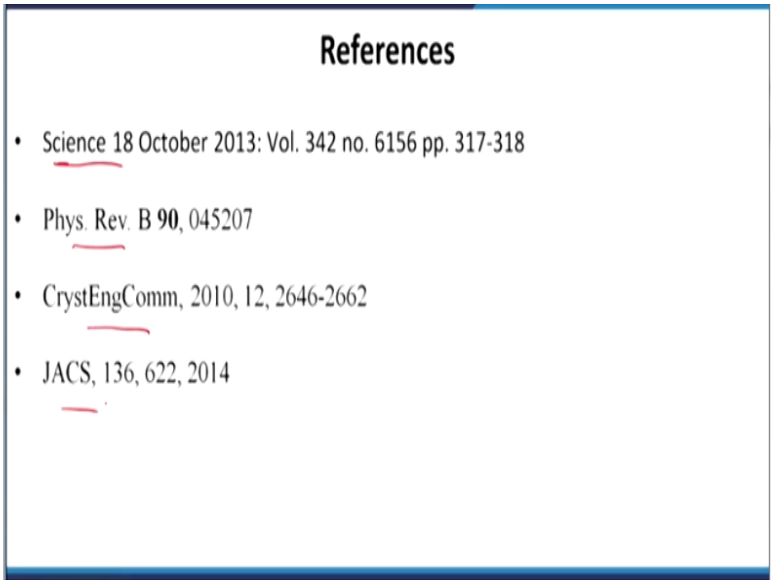

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