Solar Photovoltaics: Fundamental Technology and Applications

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Lecture - 30

Single Crystal Solar Cells

Welcome everyone to our Solar Photovoltaics course. Today we are having 6th week 5th module. Now in our 6th week lectures we are discussing about a very important technology of solar cell that is perovskite solar cell and so far if you remember we have discussed about the perovskite solar cell how to fabricate a perovskite solar cell and some of the parameters related to the stability of the perovskite solar cell.

Now I mention that a perovskite solar cell this is very interesting materials for study because its efficiency is very, very high and the material cost is low, but while discussing in terms of stability we have seen that the morphology plays a very important role in determining the stability of this devices. Now what do you mean by the morphology. So by morphology we mean a uniform pinhole free continuous thin film.

So what we have happen if we have lot of pinholes. Now this pinholes are defect states or trap states. So if there are lot of pinholes or the defect or trap states in the systems then those defect states or trap states works like a potential energy minimum and that can lead to the electron hole recombination. So in an ideal case we should as minimum or as small number of defect states in the system.

Now this is achieved by a slightly different fabrication approach by changing the perovskite bulk material to perovskite single crystal solar cell. We will see that perovskite single crystal has a much less number of defect states and nowadays it has been extensively used for making not only for solar cells, but also for making different kind of photo detectors as well as the light emitting diode. So we will discuss about the Perovskite single crystal.

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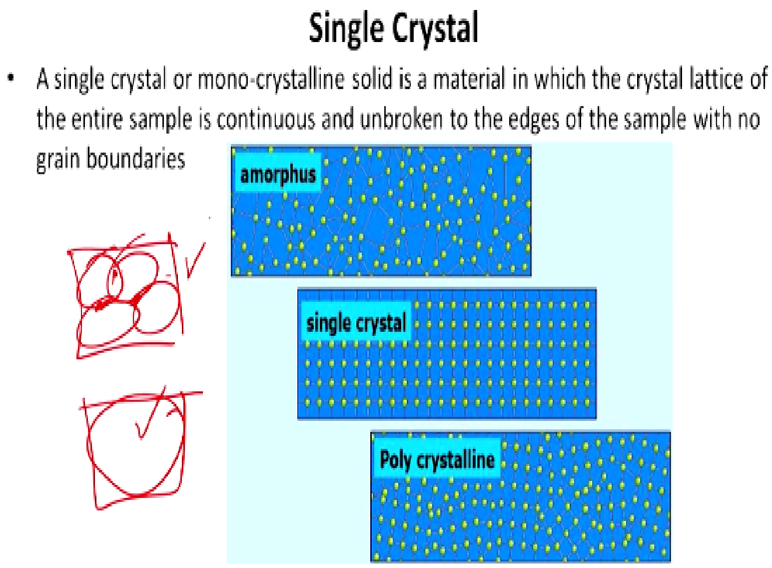

Single Crystal

- A single crystal or mono-crystalline solid is a material in which the crystal lattice of the entire sample is continuous and unbroken to the edges of the sample with no grain boundaries

So what is single crystal? A single crystal or monocrystalline solid is a material in which the crystal lattice of the entire sample is continuous and unbroken to the edges of the sample with no grain boundaries. So let us say this is an amorphus material. Let us say I have a chalk in my hand which we use for writing in the board. So chalk is an example of a amorphus material there is no symmetry in the crystal structure.

Now if you put a crystal structure symmetry so if you have a periodic arrangement of the lattice point which is arranged by the atoms and (()) (02:52) then we will get a periodic lattice. Now this periodic structure can be such that it is a continuous and unbroken to the age of the sample like single crystal or it can be not continuous and the same pattern is not followed everywhere like a polycrystalline material.

For example, like you know let us say I have this 2 square box I have drawn not both of them are a crystalline material, but one of the material has lot of crystal grains here. So if there are many crystal grains then there will be lot of this grain boundaries are there. In another case the whole this rectangle is filled by one circle like that or one domain size like that. So this is a single crystal, this is a polycrystalline material.

So the crystalline material can be further polycrystalline or a single crystalline material. Single crystal material is continuous and unbroken to the edge of the samples with no grain boundaries.

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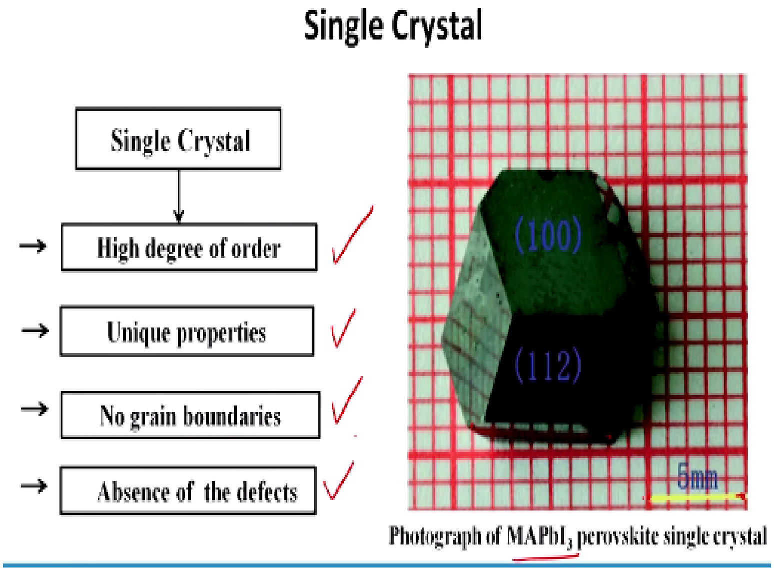

Single Crystal

Single Crystal

- → High degree of order ✓
- → Unique properties ✓
- → No grain boundaries ✓
- → Absence of the defects ✓

Photograph of $MAPbI_3$ perovskite single crystal

We can start the single crystal material or we can fabricate the perovskite single crystal material starting with our common perovskite source MAPbI3 also and this figure is an example of Perovskite single crystal which is made from the MAPbI3 and we have put it on a graphic paper to show you that the dimension of the perovskite single crystal you can see that this scale bar this yellow line from here is 5 millimeter.

And this crystal is from here to here this is quite large it is almost 8 millimeter along the length and this phase are 100 phase or 112 phase. These are the miller indices of the crystal structure. So single crystal they have a high degree of order. They have a unique properties very often it is different from their bulk counterpart, no grain boundaries so usually they do not have a grain boundaries and absence of the defects.

We expect the number of trap states or defect states is much, much small in comparison to a polycrystalline bulk counterpart. So single crystalline materials obviously offer us some advantage in terms of the degree of crystallinity, high degree of order, no grain boundaries. If there is no grain boundaries since perovskite has a free charge carrier dynamics so the charge carrier can easily be corrected so it gives a high efficiency and as well as unique properties. Like all other crystal growth perovskite single crystal growth also follow two step.

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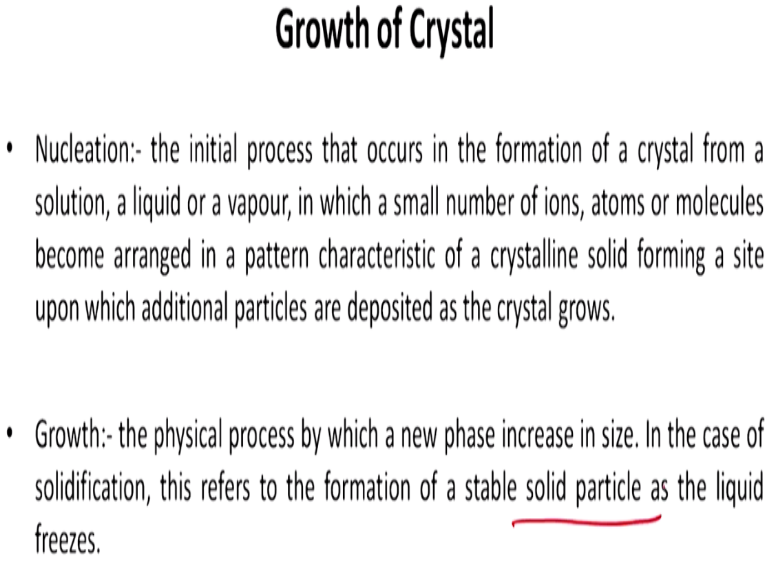

Growth of Crystal

- Nucleation:- the initial process that occurs in the formation of a crystal from a solution, a liquid or a vapour, in which a small number of ions, atoms or molecules become arranged in a pattern characteristic of a crystalline solid forming a site upon which additional particles are deposited as the crystal grows.

- Growth:- the physical process by which a new phase increase in size. In the case of solidification, this refers to the formation of a stable solid particle as the liquid freezes.

One is nucleation another is the growth. We will discuss about the 2 different phase what is nucleation. The nucleation is the initial process that occurs in the formation of a crystal form a solution. A liquid or a vapor in which a small number of ions, atoms or molecules became arranged in a pattern characteristics of a crystalline solid forming a site upon which additional particles are deposited as the crystal grows. So basically this is a seed forming phenomena.

We start from a solution liquid or vapor in which a small number of ions, atoms are molecules become arranged in a pattern and that pattern will be characteristics of the crystalline solid forming a site upon which additional particle can be deposited in the next stage for the crystal growth. Second stage is the crystal growth. The physical process by which a new phase increase in size.

In the case of solidification this refers to the formation of a stable solid particle as the liquid freeze.

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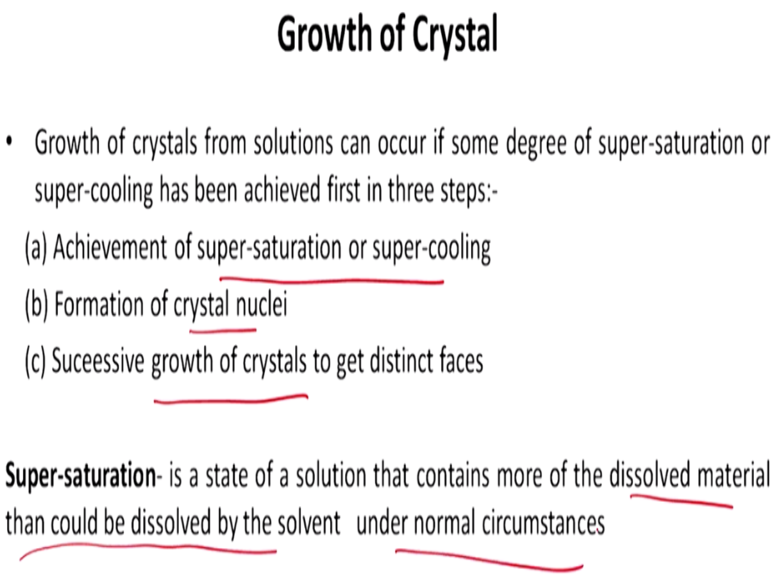

Growth of Crystal

- Growth of crystals from solutions can occur if some degree of super-saturation or super-cooling has been achieved first in three steps:-
  (a) Achievement of super-saturation or super-cooling
  (b) Formation of crystal nuclei
  (c) Suceessive growth of crystals to get distinct faces

Super-saturation- is a state of a solution that contains more of the dissolved material than could be dissolved by the solvent under normal circumstances

Growth of crystal from solution can occur if some degree of super saturation or super cooling has been achieved first in 3 steps. Achievement of super saturation or super cooling, formation of crystal nuclei, successful growth of crystal to get distinguish. So there are 3 steps one is the achievement of the super-saturation or super-cooling then the crystal nuclei is formed and finally on top of the crystal nuclei the growth of the crystal starts.

Super saturation is a state of solution that contains more of the dissolved material then that can be dissolved by the solvent under normal circumstances. For example, let us say I have a glass of water and I want to dissolve sugar in it. So you pour one teaspoon full of sugar into one glass of water 250 ml glass of water okay so the sugar will be dissolved completely in the completely you stir it with a spoon.

Now let us say you wanted to dissolve some more sugar into it. So you add 2 or 3 more teaspoon full of the sugar so it will be dissolved, but let us say you wanted to dissolve 500 gram of sugar in 250 ml of water so then what will happen. There will be a limit until which you can keep on dissolving the sugar and beyond that particular limit if you add even one more grain of sugar molecule all the sugar will come outside the solution.

So that critical stage you reached that is called the super-saturation. So at the normal temperature when the solution is keeping or dissolving the maximum amount of solute inside it then it is a super-saturation condition.

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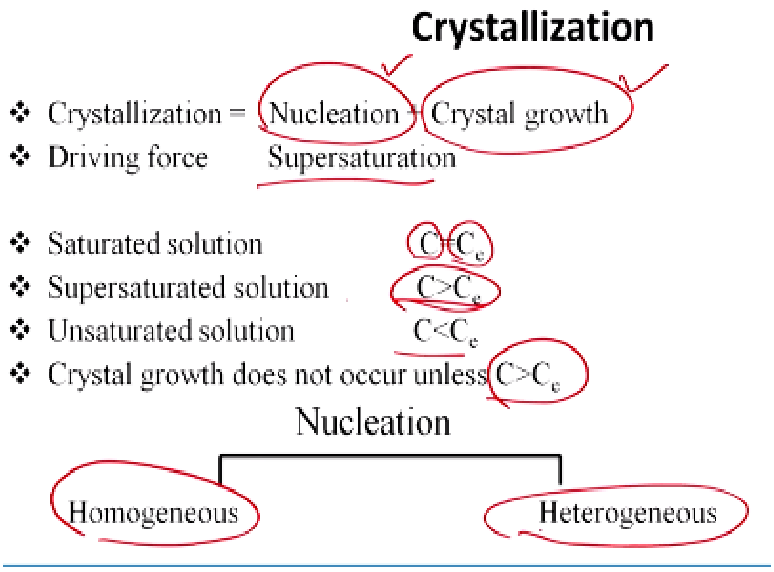

Crystallization

- Crystallization = Nucleation + Crystal growth
- Driving force Supersaturation
- Saturated solution $C=C_e$
- Supersaturated solution $C>C_e$
- Unsaturated solution $C<C_e$
- Crystal growth does not occur unless $C>C_e$

Nucleation

Homogeneous Heterogeneous

Crystallization is actually the simultaneous process of the nucleation followed by the crystal growth. First there is a nucleation and which is followed by the crystal growth and the driving force is super saturation. Saturated solution, supersaturated solution, unsaturated solution and crystal grows. So there are 4 different condition is there. In a saturated solution the concentration C=critical concentration Ce.

Critical concentration means that is a maximum amount of the solute you can dissolve in the solution beyond which if you even add one particular grain of the sugar molecule all the sugar will come outside the water that is your super saturation condition that is your critical concentration. Now the concentration C if it is= critical concentration then you have a saturated solution.

When C>C it is a supersaturated solution when C<C it is an unsaturated solution and crystal growth does not occur unless C>C. So basically we need to have a supersaturated solution to get a crystal growth. Now this nucleation that can be categorized either as a homogeneous nucleation or a heterogeneous nucleation we will discuss this 2 things in the next slide.

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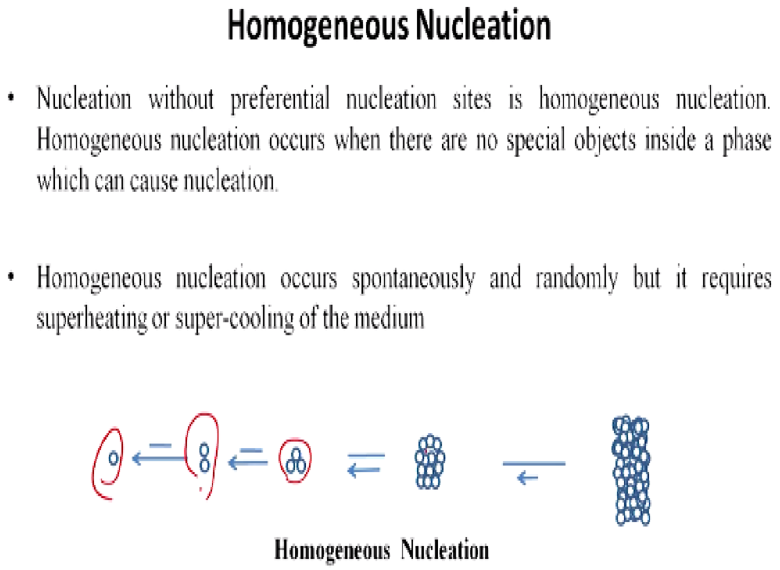

Homogeneous Nucleation

- Nucleation without preferential nucleation sites is homogeneous nucleation. Homogeneous nucleation occurs when there are no special objects inside a phase which can cause nucleation.
- Homogeneous nucleation occurs spontaneously and randomly but it requires superheating or super-cooling of the medium

Homogeneous Nucleation

So homogenous nucleation this is the nucleation without preferential nucleation sites is homogenous nucleation. Homogenous nucleation occurs when there are no special objects inside a phase which can cause nucleation. So basically nucleation without preferential nucleation site that is the homogenous nucleation. Homogenous nucleation occurs spontaneously and randomly, but it requires superheating or super-cooling of the medium.

For example, you can look at this cartoon how we are forming the homogenous nucleation in the figure. So we had one molecule from there we get 2 then we get 3 so this is going spontaneously and randomly and then we have made a cluster finally we have a large crystal. So starting from the 1 we get first 2 then 3, but when I come from 2 to 3 is there any preferential growth direction no.

The second surface has grown on the top of the first circle, but the third circle has grown just below this. And when we come to the 4th lecture this has grown randomly and this growth is also spontaneous. Finally, like you know if everything like you know grows in a very random fashion grows like this then you call it as a homogenous nucleation.

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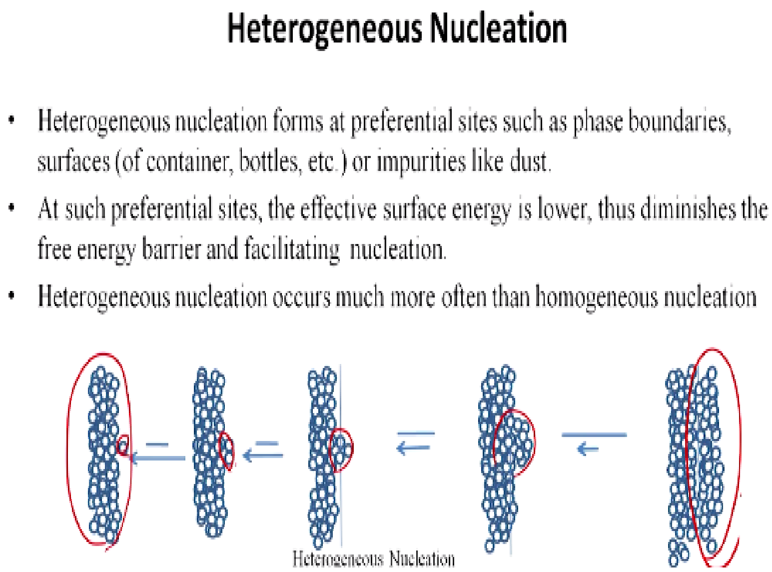

Heterogeneous Nucleation

- Heterogeneous nucleation forms at preferential sites such as phase boundaries, surfaces (of container, bottles, etc.) or impurities like dust.
- At such preferential sites, the effective surface energy is lower, thus diminishes the free energy barrier and facilitating nucleation.
- Heterogeneous nucleation occurs much more often than homogeneous nucleation

Whereas in heterogeneous nucleation that forms a preferential site such as phase boundaries, surface of containers, bottle etcetera or impurities like dust. So then need some other substrate on which the heterogeneous nucleation can start. At such preferential sites the effective surface energy is lower. Thus diminish the free energy barrier and facilitating nucleation.

So whenever you have a preferential site the surface barrier energy is lower at those preferential sites. If the surface energy is lower than the free energy barriers that prevents the nucleation to start that can be overcome and the nucleation process starts. So all this nucleation and the growth process can also be described in terms of the phase diagram. Homogeneous nucleation occurs much more often heterogeneous nucleation occurs much more often than homogeneous nucleation.

So in a heterogeneous nucleation so we need a site to grow here there is a either an interface or grain boundary or a dust particle on which you see that particle has started growing. Now it has grown and finally it has grown like this. So this is very, very common. If we have a seed on which we wanted to grow our crystal so we put the seed in a supersaturated solution and we allow them to super cool or super heat.

So then according to the preferential site orientation either like atoms or molecules or ion can grow on top of that there will be a preferred orientation of preferred direction of the growth and that you call as a heterogeneous nucleation and that is very, very common. For homogenous nucleation we do not need a preferential site.

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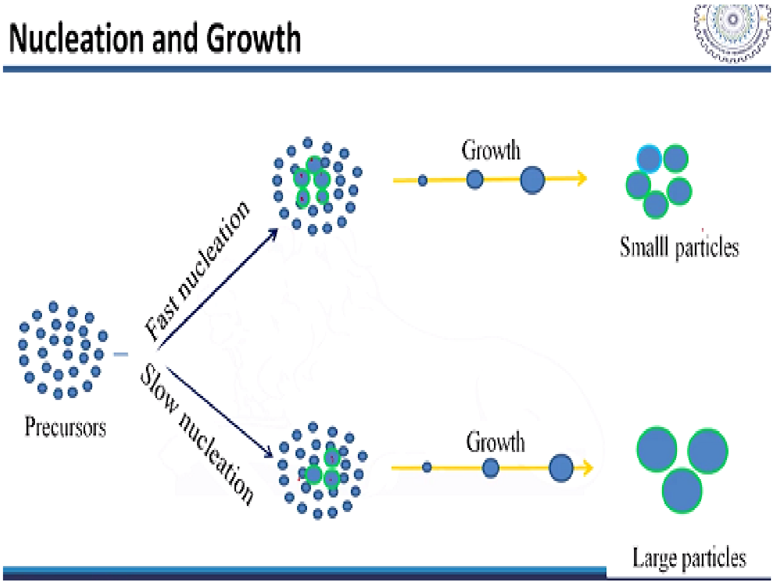

Nucleation and Growth

Now let us look at this animation for the nucleation and the growth process. So now I have precursor solutions from the precursor solution if the fast nucleation happens then we get a sites like this the solid circle and if you have a slow nucleation then the number of sites is less than the fast nucleation process. So the nucleated site in the fast nucleation here you can see the solid blue circle 1, 2, 3, 4, 5 we have drawn, but here we have drawn 1, 2, 3.

So the number of the nucleated sites in the slow nucleation is smaller than the fast nucleation. Now let us allow them both of them to grow. Another important difference if you can look between the fast nucleation and the slow nucleation here the size distribution is smaller and random. Here size distribution is larger and uniform why because you are doing a slow nucleation to control the kinetics of the process.

You allow enough time the systems to undergo a small, small (()) (13:24) state. So then you have a better control over the size and the uniformity of the crystal orientation. Now starting from the fast nucleation if I allow them to grow so basically what will happen it will becomes larger and larger over the time and I will get a smaller particle, but from the slow nucleation if we allow them to growth so we will get a large particles.

So starting from the precursor solution the fast process is the nucleation. Nucleation is the growth of a pattern it can be homogenous or heterogeneous nucleation and from the nucleated site the growth starts. If I have a fast nucleation, then we will get a smaller particle. If I have a slow nucleation we will have a larger particle. So if I wanted to get a larger particles or large domain size in our crystal then we should allow it for a slow nucleation.

If we wanted to have a large number of small domain size, then we will allow the crystal for a fast nucleation.

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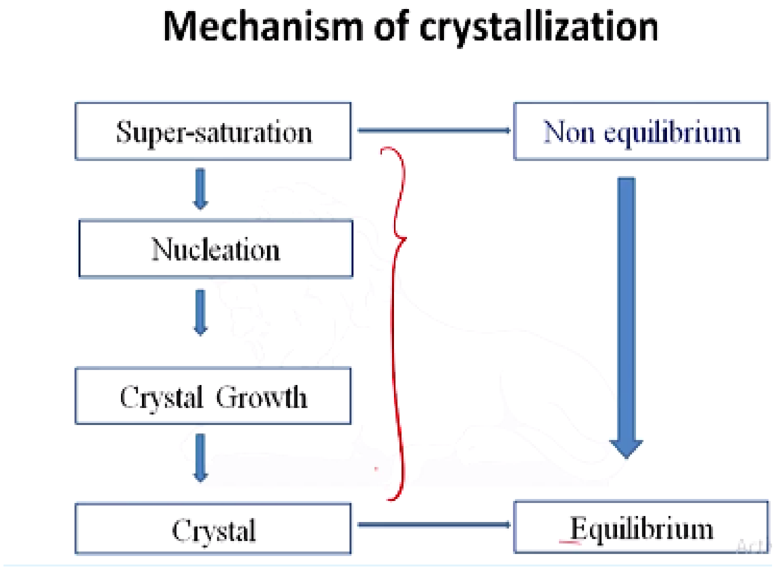

Mechanism of crystallization

Super-saturation

Nucleation

Crystal Growth

Crystal

Non equilibrium

Equilibrium

So mechanism of the crystallizations now summarize like the following. First you have a super saturation, super saturation that leads to the nucleation. Nucleation leads to the crystal growth and crystal growth leads to the crystal and finally it reach to an equilibrium system. If there is no super saturation, then it will be non equilibrium finally over the time it will also reach a equilibrium system.

So these are the states which is involved in the crystal growth process. The first we have a supersaturated condition which can leads to the nucleation which leads to the crystal growth which leads to the crystal structure formation and it is a equilibrated structure.

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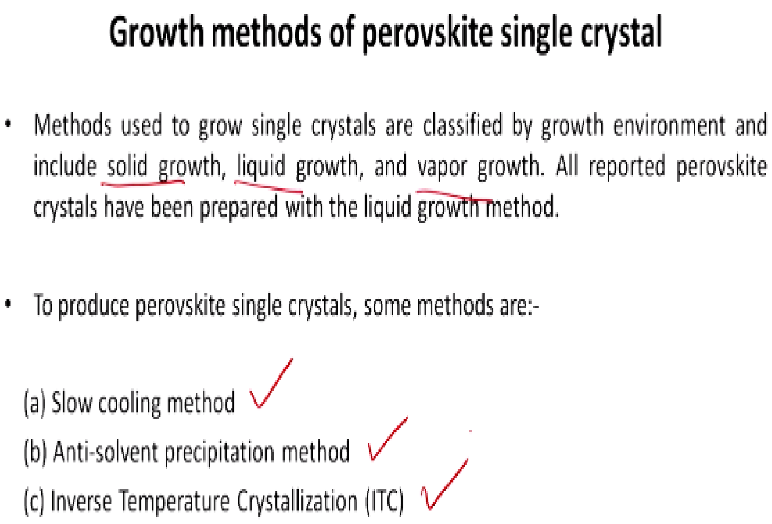

Growth methods of perovskite single crystal

- Methods used to grow single crystals are classified by growth environment and include solid growth, liquid growth, and vapor growth. All reported perovskite crystals have been prepared with the liquid growth method.
- To produce perovskite single crystals, some methods are:-

(a) Slow cooling method ✓
(b) Anti-solvent precipitation method ✓
(c) Inverse Temperature Crystallization (ITC) ✓

Keeping this general mechanism in mind let us look at the growth mechanism and growth methods of the perovskite single crystal. Methods used to grow single crystals are classified by the growth environment and includes solid growth, liquid growth and vapor growth. Now if you grow a perovskite crystals in a solid state it is a solid growth. If you grow them in a liquid state it is a liquid growth. If you grow them in a vapor phase it is a vapor growth.

All reported perovskite crystals have been prepared with the liquid growth method. To produce perovskite single crystal some of the popular methods which have been used in the literature are the slow cooling method, anti solvent precipitation method and inverse temperature crystallization method or ITC.

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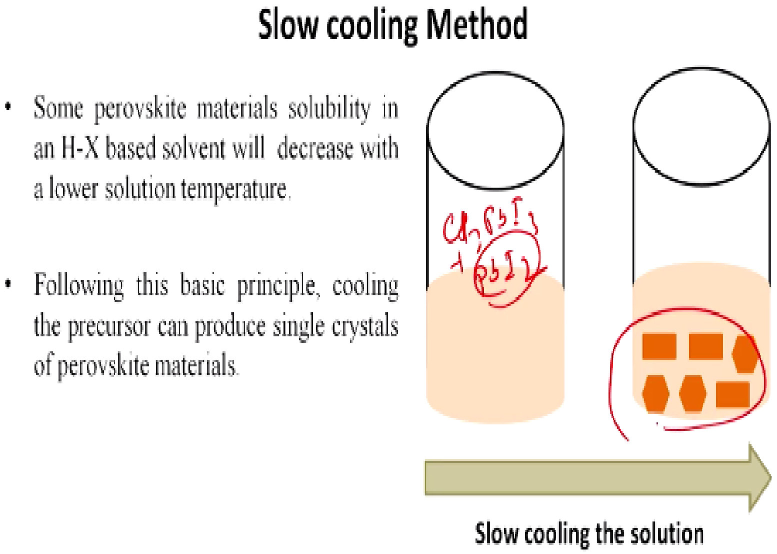

Slow cooling Method

- Some perovskite materials solubility in an H-X based solvent will decrease with a lower solution temperature.
- Following this basic principle, cooling the precursor can produce single crystals of perovskite materials.

Let us discuss like you know this methods in a slow cooling method what we do here. We have been shown in this figure some perovskite material solubility in H-X based solvent will decrease with a lower solution temperature. Following this basic principle, cooling the precursor can produce single crystal of perovskite material. So basically what will happen like you know in this solvent let I put CH3 lead iodide.

And I put lead iodide also as a precursor material. So what will happen so if I cool it very, very slowly. So some of this compound their solubility will decrease. If the solubility decrease at low temperature they will start forming the crystals like this. So the slow cooling can also lead to the crystal formation.

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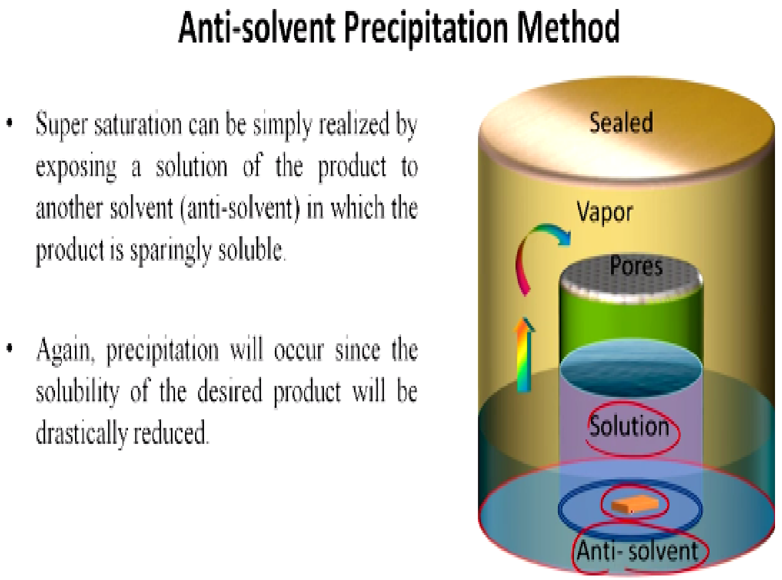

Anti-solvent Precipitation Method

- Super saturation can be simply realized by exposing a solution of the product to another solvent (anti-solvent) in which the product is sparingly soluble.
- Again, precipitation will occur since the solubility of the desired product will be drastically reduced.

Anti-solvent precipitation method as the name suggests we have to use an anti-solvent, anti-solvent means a solvent where the perovskites precursor does not dissolve. You look at this figure here super saturation can be simplified realized by exposing a solution of the product to another solvent anti-solvent in which the product is sparingly soluble. So we have a solution here in this beaker and then what we are doing we are putting an anti-solvent.

Now in anti-solvent this material does not dissolve. So this product is sparingly soluble in the anti-solvent. So what will happen after sometimes precipitation. Again precipitation will occur since the solubility of the desired product will be drastically reduced. So whole the chamber has been sealed. So first we dissolve the solution the precursor in a good organic solvent.

And then we slowly adding the anti-solvent to this material so the solubility will be decreased of the precursor and it will get precipitated at the bottom surface and we can collect the crystals so this method is called the anti-solvent precipitation method.

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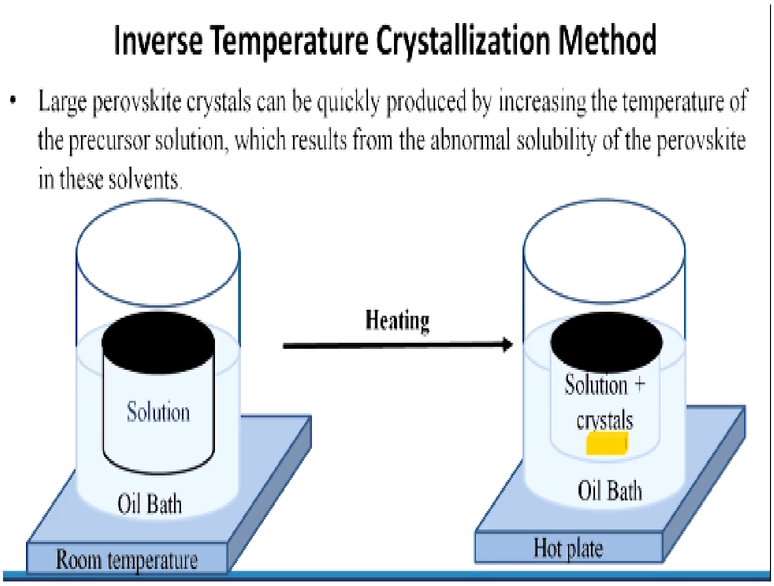

Inverse Temperature Crystallization Method

- Large perovskite crystals can be quickly produced by increasing the temperature of the precursor solution, which results from the abnormal solubility of the perovskite in these solvents.

Then the ITC inverse temperature crystallization method. Large perovskites crystal can be quickly produced by increasing the temperature of the precursor solution which results from the abnormal solubility of the perovskites in this solvent. So what happens like you know you take a perovskites solutions in a oil bath which is kept on a room temperature and you heat it if you heat it so basically what you will get a solution+ the crystal this is called the inverse temperature crystallizations.

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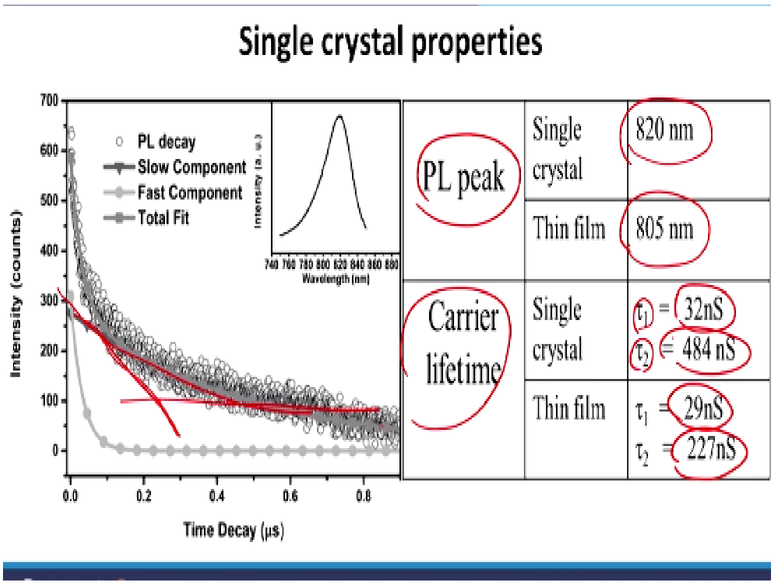

Single crystal properties

PL peak	Single crystal	820 nm
	Thin film	805 nm
Carrier lifetime	Single crystal	τ_1 = 32nS τ_2 = 484 nS
	Thin film	τ_1 = 29nS τ_2 = 227nS

Now when I say that single crystal show some abnormal properties or some distinctive features in comparison to their bulk counterpart. So what do you mean by those properties you look in terms of the thin film and the single crystal in terms of its Photoluminescence properties PL stands for Photoluminescence and in terms of the carrier lifetime. Now if I look at the Photoluminescence peak the single crystal show the Photoluminescence peak at 820 nanometer whereas the thin film show that 805 nanometer so there is a rate shifting happens.

This rate shifting can always or can be attributed to the less number of defects or trap states in the system. What about the lifetime, what is lifetime? When you excite an electron to the ground state to the excited state it can stay in the excited state for some time and after that it will relax back to the ground state. Now the time it spends in the excited state that is the excited state lifetime.

So the lifetime has 2 components one is the slow component another is the fast component. A thin film perovskites solar cell has a lifetime in the order of 29 nanosecond and another lifetime is 227 nanosecond whereas the perovskites single crystal has a lifetime of 32 nanosecond and 484 nanosecond. You look at this photoluminescence decay from this curve this experiment is called transient decay experiment or femtosecond or time fluorescence decay.

So we have a femtosecond laser beam we excite the material, we allow them to excite from the ground state to the excited state and then we are measuring the decay of the excited state we are measuring the depopulation of the excited state and what we are plotting here the intensity count of the fluorescence versus the decay times. So you can see that the PL decay for a slow component and a fast component is showing like this where the total fit is like this.

Now if I take the total fit like this curve so I can see there are 2 components here I can draw one tangent here and I can draw one tangent here. So this tangent is the first component and this component is the slow component which is here showing like you know there are 2 different lifetime components tau 1 and tau2, but the lifetime is different in case of a thin film than a single crystal or in case of a polycrystalline material to a single crystal.

And the fluorescence peak is different. So what does it means that the radiative recombination lifetime or the radiative recombination is different in this 2 different case. So this is directly related to the trap state or the defect states in the systems. So we claim in the beginning that perovskite single crystal has a less number of trap state or less number of defect states in compulsion to a polycrystalline counterpart that can be proved by doing this experiment.

So far we discussed about a very interesting technology of the third generation solar cell which is believed to pick up as comparable to a silicon solar cell the efficiency of this perovskite solar cell is very high 23% and this number is changing every day. This material has a number of important properties for example a tunable band gap a large absorption coefficient, good solubility.

Because of that we can make this kind of solar cell in a roll-to-roll basis on a flexible or (()) (21:32) substrate we can tune the band gap in this material so that gives us the possibility of making a material which can absorb the light in the near IR range and this material has a free charge carrier decay. So that is the reason we get a very high efficiency with the perovskite solar cell and we have also demonstrated you how to fabricate the perovskite solar cell or what is the device structure of a perovskite solar cell.

Like all other sandwich device in perovskite solar cell the active material which is a Perovskite material that has been sandwiched between a photo anode and cathode and to further enhance the charge carrier transport we usually put the transport layer, electron transport layer and hole transport layer or the blocking layer, electron blocking layer and hole blocking layer in the vicinity of the perovskite so that we form an interface.

Now this interface also plays an important role when defining the efficiency of the perovskite solar cell. Now we have learnt that although the efficiency of the perovskite solar cell is very high there are 2 important problems needs to be solved in this case. One is the toxicity due to the lead and the second is the stability. We have shown you about the golden triangle and we have talked about that.

Whenever you want to bring about any technology for example like photovoltaic technology in the market the 3 parameter has to be simultaneously optimized. One is it efficiency second is its cost and third is the lifetime of the stability. If the efficiency is very high cost is very low, but the lifetime is not as promising then that is not a good news. Perovskite solar cell has a comparable efficiency like a silicon solar cell 23%.

Its cost is almost half sometimes one-third or one-third than the silicon technology when you talk about roll to roll production, but in lifetime is very limited in comparison to the silicon solar cell. Silicon solar panel when install it can run easily 20 to 25 years, but perovskite solar cell can run only 1 year on its peak efficiency. So there are lot of work has to be done to improve the stability of the perovskite solar cell.

And there are lot of work is ongoing to improve the stability of the perovskite solar cell. Now in terms of stability we have seen that there are 3 major source of instability. One is the photo instability which can be attributed to the ion migration, there are thermal instability and there are moisture instability. To prevent that most of the time perovskite solar cell is fabricated in a (()) (24:17) control environment where you can control the oxygen level and humidity level.

Oxygen and humidity together they degrade the perovskite into an irreversible products and the 3D structure spontaneously disintegrates into a 2D component structures. So the 2D structure is not good for transport of the charge carrier so you lose significantly your efficiency. Another important factor is that here there are ions are there organic cation and this organic cations upon the light exposure this spontaneously move or migrate along the crystal structure.

A phenomena commonly known as the ion migration. Now we have seen that by using compositional mapping or by changing the cationic site or by changing the anionic site or a be a suitably permutation, combination of the cationic and anionic site. We not only can tune the band gap, but we can also enhance the photo stability and the thermal stability. In addition to that to prevent the environmental degradation we put encapsulate a barrier layer to protect our solar cell.

Still there are lots of efforts and research is ongoing to make a roll-to-roll high efficient perovskite solar module. Now in this context we have also introduce the idea of the perovskite single crystal like all other single crystal here we expect to have very less number of defect states or trap states and one in ideal case one crystal domain. Now if there is a one crystal domain with a no grain boundary.

Then the source of the charge recombination gets suppressed and that is expected to increase the short circuit current. We have seen that in terms of the photoluminescence properties in terms of the steady state and time resolved photoluminescence property there is a significant difference between the bulk polycrystalline perovskite and single crystal perovskite material. We can calculate and find out the number of trap states and defects states in a perovskite single crystal by doing fluorescence time resolved experiment.

We have seen that there are 3 different methods for growth of the perovskite single crystal from the solution like slow cooling, inverse temperature crystallizations and also anti solvent method and we have also learned that the crystallizations is different by the super saturation followed by the nucleation and the crystal growth. And we also discussed that perovskite single crystal.

Because of the superior optoelectronic properties and less number of defect and trap states is very, very useful for not only making solar cell, but also for photo detectors, light emitting diodes and lasers. Now there are tremendous amount of research is ongoing on the bulk perovskite, 2D quasi-perovskite or 3D quasi perovskite, double perovskite solar cell, perovskite single crystal and perovskite silicon tandem solar cell to bring this technology commercially available for everyone.

So this is a very important upcoming technology and lot of people are therefore working ont his technology and those days are not very far we will have a perovskite high efficiency stable perovskite module in the market. Now there are lot of excellent research paper and reviews on the perovskite solar cell you will find online like for the single crystal.

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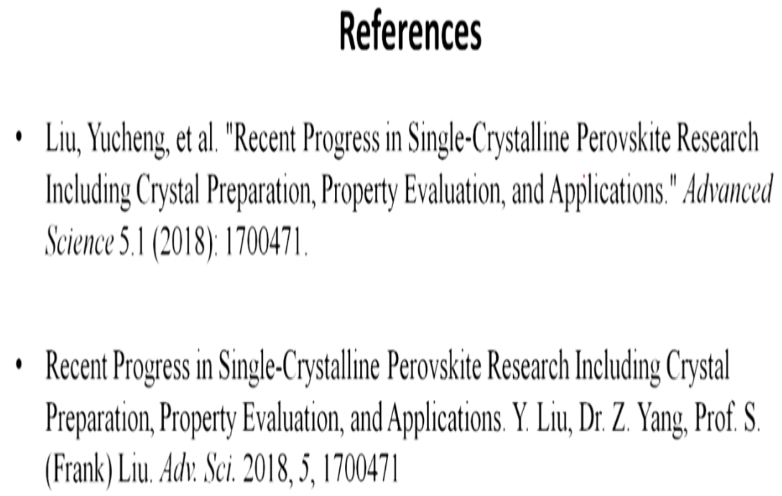

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- Recent Progress in Single-Crystalline Perovskite Research Including Crystal Preparation, Property Evaluation, and Applications. Y. Liu, Dr. Z. Yang, Prof. S. (Frank) Liu. *Adv. Sci.* 2018, *5*, 1700471

You can look at the references like this Liu Yucheng et al. Recent progress in single crystal perovskite research including crystal preparation, property evaluation and application and the recent progress in the single crystal perovskite research including crystal preparation, property evaluation by Y. Liu. So apart from this 2 reference also there are lot of research papers and reviews papers available in the literature on the perovskite single crystal.

And as a whole on the perovskite materials and you can get an in depth idea and understanding about that. So I hope that this perovskite solar cell you have learned and enjoyed this technology and we need to do lot of work still to make this solar cell technology a commercially viable technology. Thank you very much for your attention.