# Chemical Crystallography
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## Lecture – 24
## Systematic Absences and Crystallisation Methods

Welcome back to this course of Crystallography. In the previous class, we have learnt about how to construct a reciprocal lattice and how to get the reciprocal lattice drawn for orthorhombic and monoclinic systems. And, we have learnt about some relationship of Bragg's law in reciprocal space. And, then we discussed about the possibility of some systematic absences, we have shown you an animation where we could see that some of the reflections where bright and some of the reflections where dull and they were not some of the reciprocal lattice where dull and they were not making any diffraction which they were crossing the Ewald sphere.

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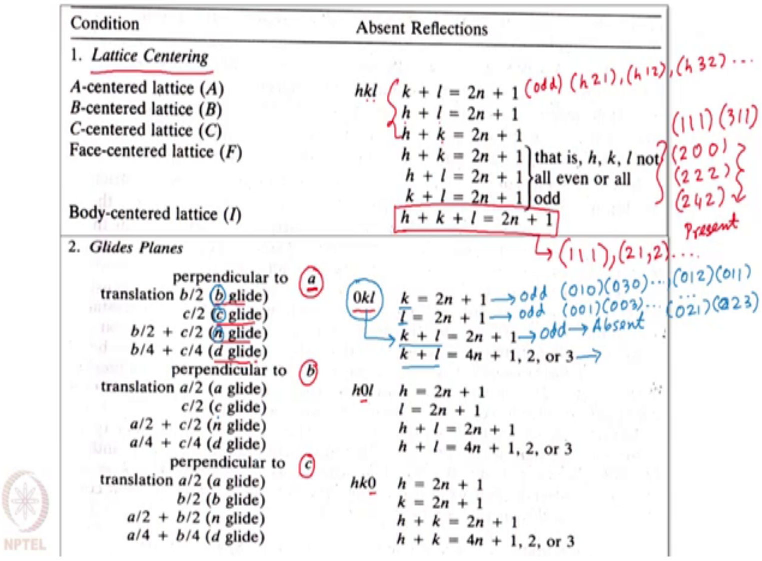

| Condition | | Absent Reflections | |
|---|---|---|---|
| 1. *Lattice Centering* | | | |
| A-centered lattice (A) | hkl | $k + l = 2n + 1$ | (odd) (h21), (h12), (h32) ... |
| B-centered lattice (B) | | $h + l = 2n + 1$ | |
| C-centered lattice (C) | | $h + k = 2n + 1$ | (111) (311) |
| Face-centered lattice (F) | | $h + k = 2n + 1$<br>$h + l = 2n + 1$<br>$k + l = 2n + 1$<br>that is, h, k, l not all even or all odd | (200)<br>(222)<br>(242)<br>Present |
| Body-centered lattice (I) | | $h + k + l = 2n + 1$ | (111), (21,2) ... |
| 2. *Glides Planes* | | | |
| perpendicular to a | | | |
| translation b/2 (b glide) | 0kl | $k = 2n + 1$ | → odd (010)(030) ... (012)(011) |
| c/2 (c glide) | | $l = 2n + 1$ | → odd (001)(003) ... (021)(023) |
| b/2 + c/2 (n glide) | | $k + l = 2n + 1$ | → odd → Absent |
| b/4 + c/4 (d glide) | | $k + l = 4n + 1, 2, \text{ or } 3$ | → |
| perpendicular to b | | | |
| translation a/2 (a glide) | h0l | $h = 2n + 1$ | |
| c/2 (c glide) | | $l = 2n + 1$ | |
| a/2 + c/2 (n glide) | | $h + l = 2n + 1$ | |
| a/4 + c/4 (d glide) | | $h + l = 4n + 1, 2, \text{ or } 3$ | |
| perpendicular to c | | | |
| translation a/2 (a glide) | hk0 | $h = 2n + 1$ | |
| b/2 (b glide) | | $k = 2n + 1$ | |
| a/2 + b/2 (n glide) | | $h + k = 2n + 1$ | |
| a/4 + b/4 (d glide) | | $h + k = 4n + 1, 2, \text{ or } 3$ | |

So, we have discussed about the systematic absence arising out of various lattice centerings and we would like to continue from here. The translational symmetry elements other than the unit translation, for example, the lattice centering right planes and screw axis, they result in to systematic absence conditions for a particular set of h k l reflection.

So, when we are trying to see the reflections which are corresponding to which are we the symmetry element which is a b glide or a c glide or n glide or a d glide which can be perpendicular to a, what could be the systematic absence condition. To understand that we first need to see against which axis the glide is perpendicular. So, when it is perpendicular to a, the Miller indices for the planes which may suffer systematic absence should be 0 k l. So, this 0 comes when it is perpendicular to a, when it is perpendicular to b, it is 0 for k and when it is perpendicular to c 0 comes for the l index.

At the moment, this you may need to memorize because we have not understood how these systematic absence conditions can be derived, but the easier way to remember is this. So, when it when a plane is perpendicular to a the h index is 0, when a plane is perpendicular to b the k index is 0, when a plane is perpendicular to c, the l index is 0 and these set of reflections suffer systematic absences under certain conditions.

So, now when I am saying it is a b glide; that means, the translation is along b. So, now, when we look at this particular reflection which is a set of 0 k l reflection and I am saying that it is a b glide; that means, the translation takes place along b. So, the index which corresponds to b when it is odd the set of reflections are said to be systematically absent; in the same manner when it is a c glide which means we are talking about a translation along c immediately the set of 0 k l reflections with l equal 2 n plus 1. So, n equal to odd becomes systemically absent.

In the same manner; when we say it is n glide and perpendicular to a; that means, the translation happen simultaneously along a and simultaneously along b and c. So, in that case, the sum of the indices k plus l is going to be odd and those reflections are going to be absent. What does it mean? In case of 0 k l set of reflections where 0 1 0, 0 3 0, etcetera or 0 1 2, 0 1 1; all these will be absent for a b glide perpendicular to a. Similarly, 0 0 1, 0 0 3, 0 2 1, 0 2 3, etcetera will be absent in case of c glide perpendicular to a and m glide when the sum is odd the sum of k plus l is odd then it will be absent.

In the same manner, when we talk about a d glide, the systematic absence condition is k plus l equal to 4 n plus 1, 2 or 3 which once again indicates that the sum is odd. So, in the way, one can understand the corresponding a, c, d and n glide perpendicular to b and c which I am not going to explain in this lecture.

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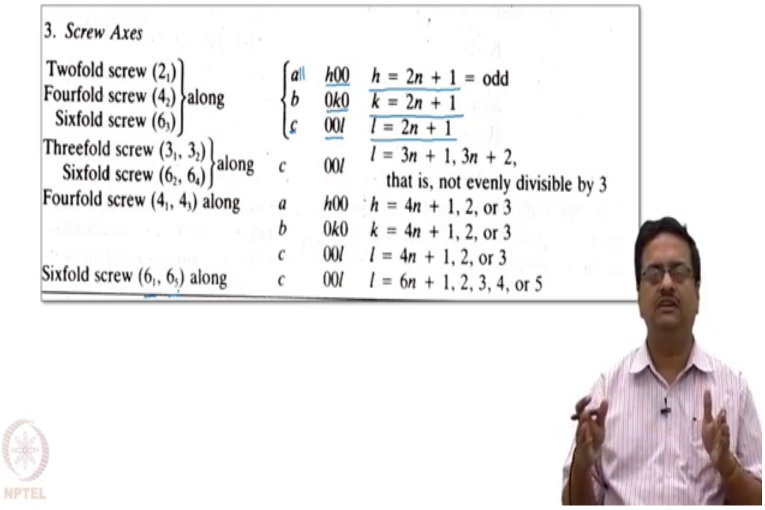

3. *Screw Axes*

| | | | |
|---|---|---|---|
| Twofold screw ($2_1$)<br>Fourfold screw ($4_2$)<br>Sixfold screw ($6_3$) along | $a$ | $h00$ | $h = 2n + 1 = \text{odd}$ |
| | $b$ | $0k0$ | $k = 2n + 1$ |
| | $c$ | $00l$ | $l = 2n + 1$ |
| Threefold screw ($3_1$, $3_2$)<br>Sixfold screw ($6_2$, $6_4$) along | $c$ | $00l$ | $l = 3n + 1, 3n + 2$,<br>that is, not evenly divisible by 3 |
| Fourfold screw ($4_1$, $4_3$) along | $a$ | $h00$ | $h = 4n + 1, 2$, or 3 |
| | $b$ | $0k0$ | $k = 4n + 1, 2$, or 3 |
| | $c$ | $00l$ | $l = 4n + 1, 2$, or 3 |
| Sixfold screw ($6_1$, $6_5$) along | $c$ | $00l$ | $l = 6n + 1, 2, 3, 4$, or 5 |

In the same manner, when we have a screw axis it can be a 2 1 screw to 3 1 screw or whatever any kind of screw axis which is parallel to a, b or c can give rise to systematic absence conditions. So, in this case, if we are taking about a screw axis which is parallel to a, then the reflections that get hampered are set of h 0 0 reflections. So, here one should remember that when I am saying a screw axis it is parallel to one axis either a, b or c. If it is parallel to a then the h index remains k and l becomes 0 because, you are doing a rotation like that which is in the k and l plane and the reflections and the planes and the and the reciprocal lattice points with 0 k and 0 l will fall in this particular row.

So, in that case, the h equal to 2 n plus 1 is the condition for systematic absence in the same way for 2 1 screw parallel to b k is odd and a 2 1 screw parallel to c l is odd and in the same manner, the higher enfold screw axis like 3 1 and 3 2, 6 2 and 6 4, 4 1 and 4 3 are understood in same manner and here again 6 1 and 6 5. So, this is how one can understand the systematic absences that might appear due to different types of non lattice translational symmetry.

That means, it is not unit translation, this translational symmetries are half translation; be it a lattice centering or be it a screw axis or a glide plane, these are the ones which generate the systematic absent reflections in a given crystal structure. So, with this initial background on theory of X-ray diffraction, I would like to change the topic now and we would like to discuss about the crystal growth, the mechanism of crystal growth and how one can grow good quality single crystals, what do you mean by good quality single crystal and things like that with some figures and diagrams.

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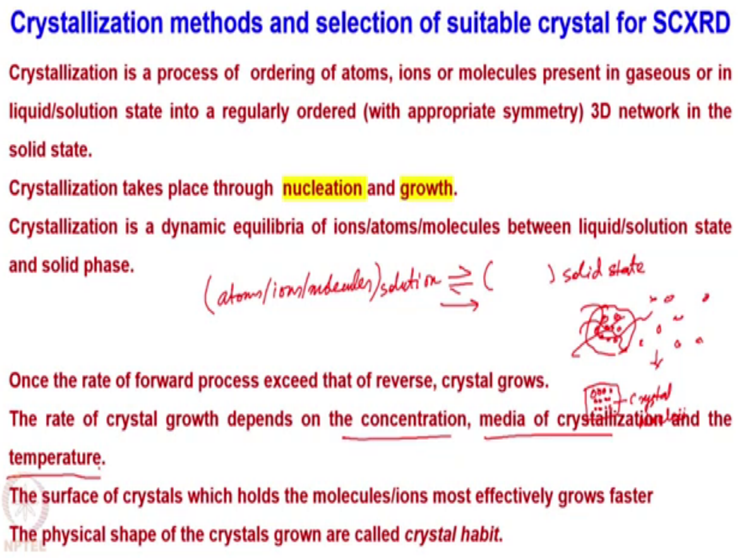

## Crystallization methods and selection of suitable crystal for SCXRD

Crystallization is a process of ordering of atoms, ions or molecules present in gaseous or in liquid/solution state into a regularly ordered (with appropriate symmetry) 3D network in the solid state.

Crystallization takes place through nucleation and growth.

Crystallization is a dynamic equilibria of ions/atoms/molecules between liquid/solution state and solid phase.

$(\text{atoms/ions/molecules})_{\text{solution}} \rightleftharpoons (\quad)_{\text{solid state}}$

$\longrightarrow$

crystal

Once the rate of forward process exceed that of reverse, crystal grows.

The rate of crystal growth depends on the concentration, media of crystallization and the temperature.

The surface of crystals which holds the molecules/ions most effectively grows faster

The physical shape of the crystals grown are called *crystal habit*.

So, now we would like to discuss the crystallization methods and selection of suitable single crystals for X-ray diffraction. The method of crystallization means we are trying to bring a set of atoms group of ions or a group of molecules from its randomly arranged state in either liquid or in gaseous phase to a particularly add ordered and 3 dimensionally translational symmetry followed with other symmetries incorporated in to a network of a solid state. As you know, one can only crystalizes compounds in 230 different ways to generate 230 different space groups, this ordering is very crucial when you start from a gas phase or a liquid state of this of any particular compound.

So, the method of crystallization takes place through two very simple, but highly complicated methods called process is called nucleation and growth. Crystallization is a dynamic equilibrium of irons atoms and molecules between a liquid or a solution state and a solid phase. So, what we have is a set of atoms or ions or molecules in solution and is in equilibrium with the same in solid state and when this equilibria shifts more towards the right, then we end up getting the crystal growth. What happens here is that this atoms ions or molecules try to come together, they start interacting, they start talking to each other using various intermolecular interactions or inter ionic interactions. These interactions can be ionic in nature this can be covalent in nature, this can be non covalent interactions like hydrogen, bonding, etcetera.

So, what can happen is a set of molecules can come closer and form some interaction pair in solution and remember in solution these atoms ions or molecules are always in random motion. So, this group will again break and they will be scattered here and there due to their random motion. So, this process continues and what happens is we try if we try to allow the solvent to evaporate or we try to lower the temperature, in either case, we are trying to increase the concentration of the solute particles in the solution that we want to crystalize.

So, in this process, what happens is that a critical size is achieved with these molecules or ions which then can arrange in appropriate order to form very very tiny crystalline nuclei. And, this crystal nuclear when reaches a critical size, it starts to grow and then we end up getting a significantly large crystals. When we are talking about large crystals we are talking about crystals of size larger than 50 micron and it can be anything big larger than that. So, the rate of crystal growth depends on a various factors like the concentration, the media of crystallization and the temperature of crystallization.

So, higher the concentration of solute faster is the crystallization process, depending on what kind of media we have how these atoms ions or groups of atoms or molecules interact with the media; here we mean by media as the solvents or solvent systems which can form different types of intermolecular interactions with our target molecules or atoms or ions and control the crystallization process.

Temperature has very important role in crystallization. Some compounds crystallizes at higher temperature, some compounds give you very nice good crystal at a much much low temperature like minus 15 minus 20 degree centigrade or even lower. So, we will discuss about some of these crystallization methods in the following slides. The surface of crystals which holds the molecules on ions very firmly are most effective surfaces for crystal growth. So, not every surface of crystal grows evenly, some crystal surface grows much faster than the other surface that can be seen under a microscope.

The physical shape of the crystals grown are called the crystal habit, which means a compound can crystallize in different shapes different geometric shape crystals can be like prisms can be like plates, rods, needles and so on. So, that shape which in which a compound crystallizes is called its habit.

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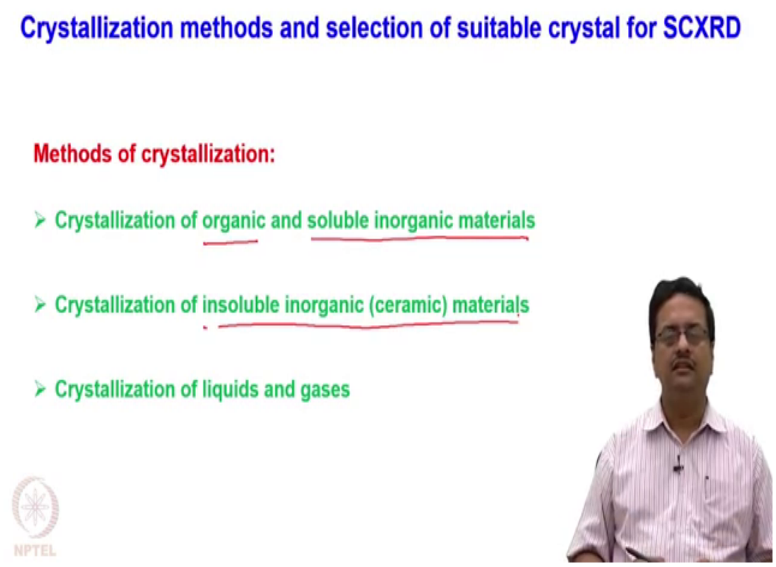

**Crystallization methods and selection of suitable crystal for SCXRD**

**Methods of crystallization:**

- Crystallization of organic and soluble inorganic materials
- Crystallization of insoluble inorganic (ceramic) materials
- Crystallization of liquids and gases

In general, when we deal with different types of materials in the lab, we have different methods with to apply for different types of compounds that we encounter in the lab. In general, in most of the labs we encounter different types of organic and soluble inorganic materials which can be crystallized using a particular type of methods. In some cases, we are trying to generate in soluble in organic ceramic materials or materials which can be crystallized from a solution, but then the compound formed does not dissolve in any solvent and then we can try to crystallize materials which are liquids or gases at ambient conditions. So, let us one by one see, how these different types of materials can be crystallized.

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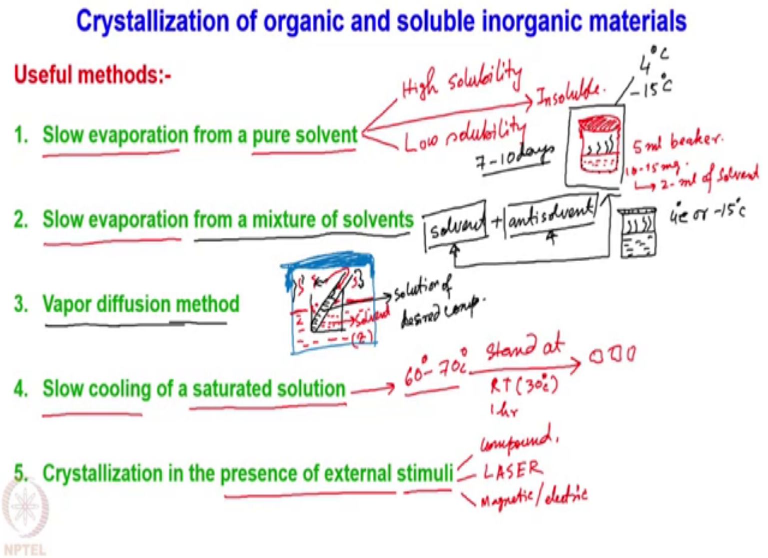

## Crystallization of organic and soluble inorganic materials

**Useful methods:-**

1. Slow evaporation from a pure solvent
2. Slow evaporation from a mixture of solvents
3. Vapor diffusion method
4. Slow cooling of a saturated solution
5. Crystallization in the presence of external stimuli

So, to discuss at the beginning, we let us consider the crystallization of organic and soluble inorganic materials. Mostly, there are 4 to 5 different ways one can crystallize these materials, if you see here in all the cases, we have a slow evaporation or a slow cooling. Why do we need to make the process slow? Because, we would not want to disturbed a system very frequently, we would like them to crystallize as naturally as possible and we do not want the system to be hurried out for crystal growth.

So, when we are trying to crystallize from a pure solvent we need to keep few things in mind. We first need to know what compound we are dealing with, we need to know in want solvent we have high solubility and in which type of solvent we have low solubility and in what kind of solvent, it is insoluble. Depending on the behavior of the target molecule and the interaction with different types of solvents one compound may like a protic solvent; one compound may like aprotic solvent. Some molecules may want solvents which can form strong hydrogen bounds, some molecules which can may like molecules like carbon tetra chloride and so on.

So, we need to know the solubility of our compound in different solvents. So, in that what we try to do is, we try to make a saturated solution in a small crystallization vessel like we try to use a very small crystallization beaker may be a 5 ml beaker. So, in that we take 10 to 15 mg of the product if that is soluble in about 2 ml of solvent.

So, what we are do is we are trying to make a very concentrated solution of the solute in the given solvent in which it dissolves very nicely and then we cover the top of this beaker with a paraffin fill. And we make a few holes, we make a few holes very tiny holes with needles on the cover and allow the solvent to evaporate at a very slow rate. And, then we try to keep this, then we try to keep this beaker in a refrigerator at about either 4 degree centigrade or at about minus 15 degree centigrade. So, that the solvent which is inside evaporates very slowly over a period of 7 to 10 days.

So, on doing this process, what a happens is that with slow evaporation of solvent at a given point of time, the solution reaches saturation with the compound and then the compound slowly comes out of the solvent. The nuclei starts to grow and we at the end of the day may be after a week or so, we end up getting crystals of the compounds ticking on the walls. This method works for a large number of different compounds where a single solvent is good enough for crystallizing these compounds. But there may be situations of difficulty, it may so happen that from a particular solvent we may not end up getting a single crystal, but we may end up getting a polycrystalline powder being deposited from the solution.

So, in that case what we need to do is we use a mixture of solvents, generally a mixture of solvent plus antisolvent means a liquid in which your compound does not dissolve. So, we take a liquid may be suppose di chloromethane in which the compound dissolves completely and cyclohexane or n hexane in which the compound does not dissolve at all. So, we first dissolve the compound in a solvent; in the same manner as we have done it previously and then we add the anti solvent in the same solution and mix them well. So, what we know have is a solution of our compound in a beaker in two different solvents.

So, now what will happen is when this solvent system would slowly evaporate at about 4 degree centigrade or at minus 15 degree centigrade in a freezer, this slow operation process will then be control by the rate of operations of the solvent and antisolvent and a phase equilibrium will be reached. And, under that condition when the solvent is much less in amount and your solute cannot stay in the solvent, it then starts to grow its crystal and there may be some amount of antisolvent still left over in which those crystals will be floating, And, it will be easy to collect those crystals for this particular i solvent mixture.

It may so happen that the two solvents that we have used of course, not in case of dichloromethane and hexane it may be in case of methanol and thf; it can be methanol and di chloromethane or some other combination where the two solvents also interact with each other form some kind of weak hydrogen bond. And, then crystallize along with your compound and form a solvent of that which was not possible when we used a single solvent and we could not crystallize it efficiently.

The second third method that one can use is called a vapor diffusion method. In this once again, we need to use two different solvents. What we do is that we take a smaller beaker, in that we take a test tube filled with a solution of the desired compound, solution of desired compound in a solvent in which the compound dissolves most. And, then we add a second solvent in the outer beaker in which the compound does not dissolve, solvent 2 in which the compound does not dissolve.

Then if we isolate the entire system in a closed container may be in we place it in a larger beaker and convert the top with paraffin film completely and do not allow any hole. So, that the solvent mixture does not evaporate; we can fill the outer part of this larger beaker also with the solvent 2. So, that there is an access of vapor of solvent 2 inside the enclosed container and though that vapor can then slowly diffuse into the test tube in which we have our compound dissolved in the desired solvent.

So, in this process the vapor of this anti solvent can diffuse through a vapor state to the solution in which we have our target solute. And, in the same process simultaneously the solvent which is inside the test tube will evaporate and slowly come out and fill the outer air aerial volume of that container and slowly reduce in volume. So, by this vapor diffusion method the diffusion of vapor of solvent 1 in solvent 2 and solvent 2 in solvent 1 may result into a good quality single crystal growth. This method is many times use full in case of organic compounds. In chemistry teaching laboratories when we try to make some derivatives, we must have learnt how to purify those derivatives by crystallization method.

So, all of you might have done in your undergraduate courses where you have made some particular compound from a starting material and you your teacher has asked you to crystalize by from a solution. What you might have done is you have might have made a saturated solution of the compound in a test tube by slowly or rapidly evaporating the solvent and making in saturated at elevated temperature may be at 60 to 70 degree centigrade and then you might have left it on the rack.

So, standing at room temperature which is about 30 degree centigrade for about 1 hour; in this 1 hour time the saturated solution has cooled from about 70 60 to 70 degree centigrade to about 30 degree centigrade. So, this is a method of cooling of course, uncontrolled, but it is a method of slow cooling, you are not applying any coolant to cool the substance. You are allowing the solution to radiate its heat slowly and as a result of lowering the temperature of a saturated solution, as we know the solubility decreases drastically and we end up getting crystals of the compound in that test tube or a beaker.

One of the recently applied methods of crystallization is in the presence of external stimuli. These external stimuli can be of different types. These external stimuli can be a compound, the crystal of a compound which does not dissolve in your crystallization solution can be dropped in the solution as a surface on which the crystallization can take place, otherwise the crystals may not be growing.

The external stimuli can be laser beam. Recently, there are reports where a solution which is being irradiated with a given laser of a particular wavelength generates a local heating and on withdrawal of that local heating the crystal growth starts. Crystallization can happen in presence of some magnetic field or electric field. These type of crystallizations are done in case of materials which are magnetic in nature or they have some electro dipole movements which gets arranged in a very high electric or magnetic field and then those compounds can crystallize.

So, in today’s lecture, we have initially learnt about the systematic absence are now, to understand the systematic absence conditions. And, then we have discussed about various methods of crystallization of organic and in organic soluble materials which can be dissolved in a solvent or a mixture of solvents and then this can be crystallized.

So, we will continue this in the next lecture.