Chemical Crystallography
Prof. Angshuman Roy Choudhury
Department of Chemical Sciences
Indian Institute of Science Education and Research Mohali

Lecture – 25
Specific Method of Crystallisation

Welcome back to the course of Crystallography. As you remember we were discussing in the previous lecture about various methods of crystal growth and in that we talked about the crystallization of organic and soluble inorganic materials. So we need to see the other methods of crystallization.

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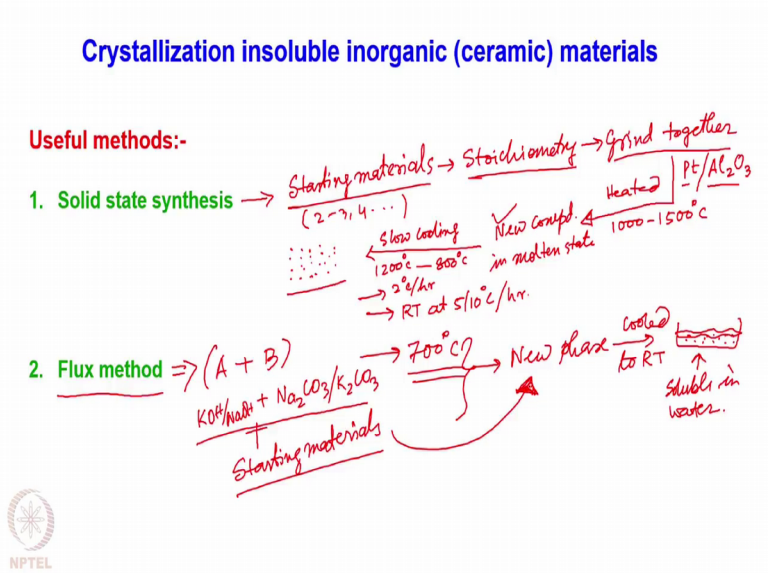

There are large number of different inorganic materials ceramic materials which do not dissolve after they have made from their starting materials.

So, in those cases the crystals are to be grown during their synthesis itself. So, in case of solid state synthesis what one does is that in case of solid state synthesis what one does is the following, you take the starting materials in a given stoichiometry and then grind them together to make an uniform mixture of the starting materials.

This starting materials can be 2 3 or 4 or whatever number of independent compounds and then, this mixtured powdered mixture of starting materials are heated in a furnace at about 1000 to 1500 degree centigrade depending on what kind of starting materials we

have used and depending on their melting points. When these starting materials are heated at such an elevated temperature all of them melt and then they start to interact, remember this heating is done in either platinum crucibles or platinum boats or is done in alumina boats which are stable at those high temperatures.

So, depending on what kind of temperature we are using, we should choose either platinum or alumina. We should not exceed the melting point of platinum while doing this experiment. So, on heating the compounds melt react and form a new phase a new compound is formed in the molten state and that molten liquid is then cooled very slowly from it is reaction temperature which may be 12 1300 degree centigrade to room temperature.

Initially from say about 1200 degree centigrade to about 800 degree centigrade at a rate of 2 degree centigrade per hour which is a very slow cooling rate and then they are cooled to RT at 5 or 10 degree centigrade per hour cooling rate.

So, in this process what happens is inside those platinum boats you generate very tiny crystals of the new phase that was formed in the molten state. As you can imagine this process is a very is a very expensive process and a tedious process to grow these crystals and once these crystals are formed these crystals cannot be dissolved and regrown. If the crystals have not grown suitably for single crystal purpose, one has to reheat this and take it to it is molten state and redo the cooling process very carefully.

So, in order to avoid such very high temperature usage and which becomes very dangerous at some point of time one uses an alternative method which is called a flux method. In this flux method we use a flux of 2 compounds A and B in general it can be KOH or NAOH with sodium carbonate or potassium carbonate as a mixture. So, what happens is this particular mixture melts at about 700 degree centigrade.

So, what we do is we take the same set of starting materials along with the flux material that is a mixture of potassium or sodium hydroxide with potassium or sodium carbonate and then heat it to about 700 degree centigrade. What happens is that the starting materials are ionic in nature this flux melts at about 700 degree centigrade.

So, those ionic compounds then dissolve in the flux at very high temperature like 7 to 800 degree centigrade and then they react and form a new phase and then the flux is once

again cooled to room temperature very slowly and we get a flux with some crystals embedded in that. Mind you the crystals that have formed are now insoluble in water, whereas the solidified flux is still soluble in water.

So, the flux that we have after this reaction mixture can we washed out and the tiny crystalline particles that might have grown from your starting materials which formed a new compound, new phase can be isolated from this mixture. We may have to crystallize materials which are liquids or gases at ambient conditions.

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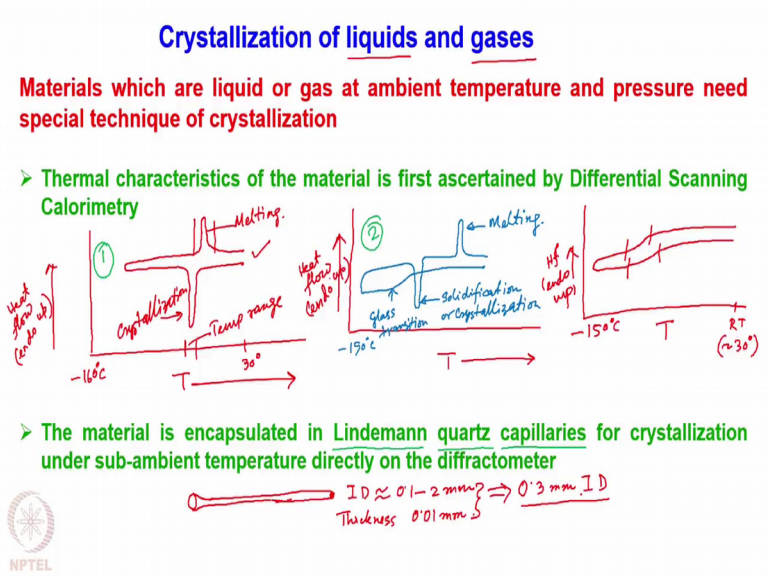

So, to do so one has to use complementary techniques to know their crystallization and solidification behavior. So, to do that what one has to do is to carry out differential scanning Calorimetry experiments to see the behavior of that particular compound on heating and cooling. So, in case of differential scanning Calorimetry, what happens is that we take a substance at a given temperature, we plot temperature in the x axis and heat flow in y axis with endo up which means all the endothermic transitions will have a peak, exothermic transitions will have a deep.

So, now if we start a compound which is liquid at room temperature maybe about 30 degree centigrade and this may be about minus 160 degree centigrade. We need to cool the compound under controlled condition to see at what temperature you see a deep which indicates crystallization and then on warming up from a certain low temperature where the compound melts.

We need to know these behaviors, we need to know the temperature range at which the crystallization took place and the temperature range in which the melting happened. From my previous experience I can share that the liquids that we generally deal with can have 3 different types of DSC patterns.

The first type of liquid is shown here which are very simple, which on cooling from room temperature crystallizes at a temperature just lower than the room temperature can be crystallizing at 0 degree centigrade can be at minus 15 minus 20 maybe minus 30 minus 40 degree centigrade. But there are non liquids, mostly they are all ionic liquids, where the compound the ionic compound does not crystallize when it is cooled rather it goes through a glass transition to a glassy state at a very low temperature which may be about minus 150 degree centigrade. And then when this glassy state is slowly warmed up at a particular temperature while warming it out, it crystallizes and then at a certain temperature above below the room temperature melts.

So, this is a glass transition and this phenomenon is solidification or crystallization and the phenomena here are melting. So, one has to know this behavior beforehand to try to do any crystallization experiment with liquids or gases, we need to know whether they at all form any crystalline phase on cooling or heating. Because, there are materials of the type 3 where if we try to do the same DSC experiment with heat flow endo up, one may end up seeing that the compound forms a glass and then compound the glass melts.

So, in the entire process of cooling and heating down to about minus 150 degree centigrade from room temperature which is maybe about 30 degree centigrade, we do not see any crystallization or solidification behavior. Of course, it is solidifies, but it solidifies as a glass and then slowly the glass once again melts over a range of temperature and we do not get any crystalline phase out of it.

So, if such liquid is encountered, we should not try to crystallize it because they do not tend to form crystal on cooling. So the first 2 types of liquids which is showing some kind of crystallization behavior the liquid of type 1 and the liquid of type 2 can be used for crystallization purpose.

So, this particular liquid is then encapsulated in a special capillary called as Lindemann quartz capillary, you see we are using quartz because we would like to do some heating experiment along with cooling. So, we will use this Lindemann quartz capillaries for

crystallization under sub ambient temperatures directly on the diffractometer. These capillaries are made up of a special glass and are available with various sizes. They look like this a very thin capillary with inner diameter in the range from 0.1 to about 2 millimeter and the thickness of the glass is about 0.01 millimeter; either it is glass or quartz.

So, these capillaries are special capillaries which do not absorb the x rays that we use for x ray diffraction experiment purpose and we use these capillaries to use to do the crystallization of liquids directly on the diffractometer. A good size of the capillary is about 0.3 millimeter internal diameter which is not very small and not very large where the crystal that might be grown inside the capillary may have certain absorption.

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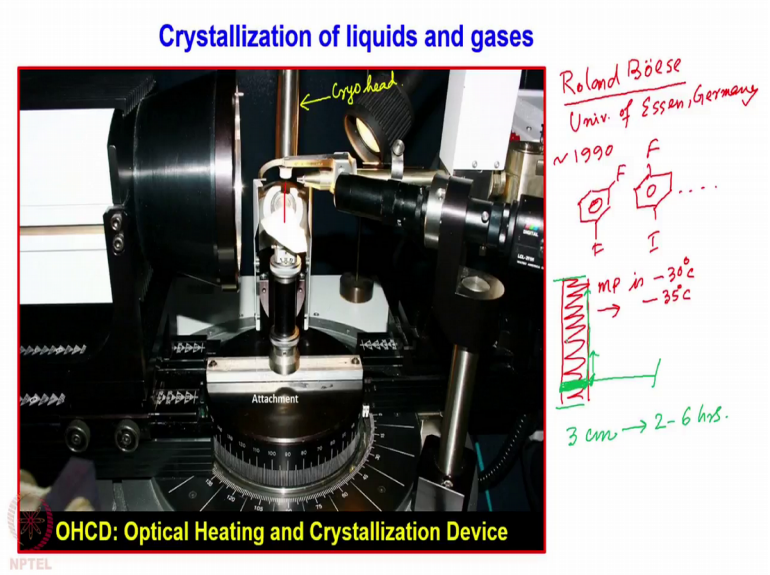

So, this is used done using a particular device which is called which is termed as optical heating and crystallization device, this was introduced by Roland Boese of University of Essen Germany in about 1990. So, what they try to do is they were trying to crystallize a set of fluorinated benzenes di fluorinated benzenes fluoroiodobenzenes and so on which are all liquid at room temperature. So, they wanted to crystallize these materials and study their intermolecular interactions. So, in that process they wanted to make a device which can do crystallization under controlled cooling and heating.

So, what it does is in this particular figure we have a capillary which is mounted on a diffractometer which is mounted here on the diffractometer and at the top you have a

cooling device. We have cryo head which supplies cold stream of liquid nitrogen or rather cold stream of nitrogen gas and then crystallizes the material or solidifies the material inside the capillary which is mounted here.

So, now what happens is when the compound crystallizes inside the capillary, it forms a poly crystalline material and then that poly crystalline material we know melts at a certain temperature from our differential scanning Calorimetry experiment. So, suppose if the melting point is minus 30 degree centigrade, we want the capillary to about minus 35 degree centigrade that is just 5 degree below the melting point and then the equipment is equipped this equipment optical heating and crystallization device is a laser assisted device. Where the laser beam can be focused at 1 point of the capillary using a reflecting mirror and then by moving the mirror upwards the laser beam can be moved along the length of the capillary.

So, with a high control on the laser power one can melt a small narrow zone of this capillary keeping the lower and upper ends solid and then if somebody moves these molten zone upwards by moving the mirror slowly by moving the laser upwards, the molten zone moves up and the lower zone again recrystallizes and this process is done several times. And if suppose the length of this capillary is about 3 centimeter, the laser beam is moves or travels this 3 centimeter distance in 2 to 6 hours.

So, the slow movement of the liquid zone ensures crystal growth inside the capillary as a single crystal. What is a single crystal? We will get to see in next few slides. So, in this process one can crystallize materials which are liquid at room temperature one can form good single crystals out of it and then do the data collection on those crystals.

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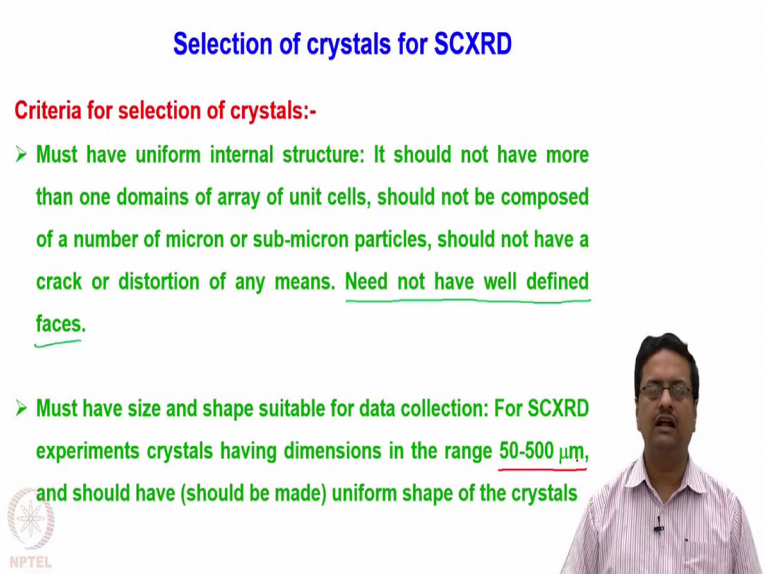

Now, we need to understand when we have grown different types of crystals from various methods that we have used, we have learned till now how to identify a good single crystal for diffraction data collection. So, we need to know the criteria of selection of crystals.

To start with the crystal must have uniform internal structure it should not have more than 1 domain of array of unit cells. So, all the unit cells should be arranged as regularly as possible in all the 3 directions. Should not be composed of a large number of micron sized particles joined together because, in that case those particles will be individual crystals oriented in random direction and they will then diffract in all possible directions and will not be able to index the pattern if it is a composite of large number of tiny micron sized crystals. One should remember that the crystals need not have well defined faces, the external faces may not be well defined, one should be able to cut the crystal under microscope and exposed some of the faces and then try to see it under the microscope.

For any single crystal application we need the crystal to have a certain size, for single crystal measurements we should have crystals ranging from 50 to 500 micron and should have uniform shape of the crystal. If the crystal is by default not of uniform shape, then one must use suitable cutting devices like razor blades to cut it into proper shape and size for diffraction experiment.

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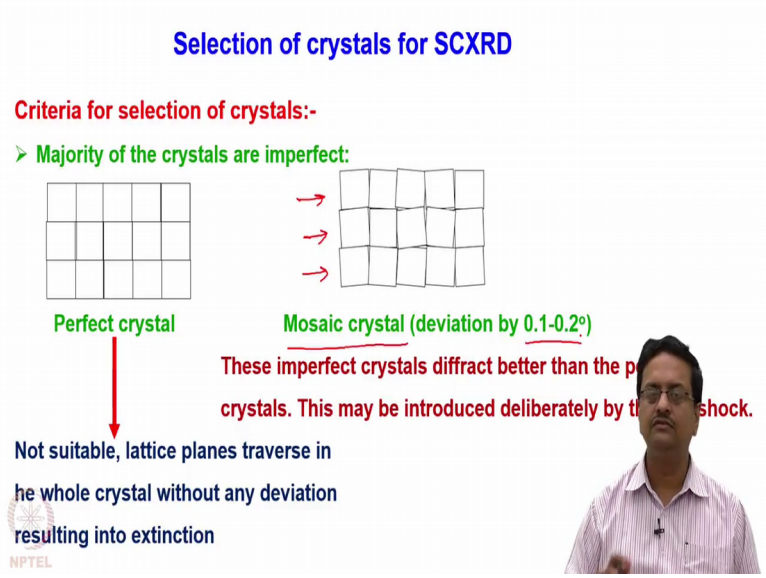

Whatever crystals we grow are imperfect in one sense, if all the unit cells are arranged in a very very uniform manner as we shown here, we call it as a perfect crystal which means it is not suitable because the lattice planes travel traverse in the whole crystal without any deviation and that may end up in extinction. Because, the diffraction from one set of parallel planes going in a particular direction may get internally reflected and come back and there may be extinction coming out of that.

So, a crystal which is slightly imperfect we call it as mosaic crystals, where you can see here the unit cells that are present are not perfectly aligned but they are slightly misaligned and this misalignment is about point one to 0.2 degree. And this gives rise to a mosaic crystal which is then useful for single crystal x ray diffraction.

So, these imperfect crystals diffract better than the perfect crystals and this imperfection can be introduced by a thermal shock. So, if we take a crystal and then suddenly dip it in liquid nitrogen reduce the temperature from room temperature to low temperature very suddenly and then bring it back to room temperature you may introduce these imperfections in that.

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Once we have grown single crystals of different sizes, one must look at it under optical microscope with polarizer and analyzer present in that. When we try to rotate the crystal about an axis and polarized light is passed through it or we change the angle of rotation of the analyzer, the crystal should either appear uniformly dark or uniformly bright or should show one color uniformly throughout the crystal.

It should not show multiple colors at different regions of the crystal or it should not so simultaneously bright and dark regions and the crystal under one particular condition of the analyzer and polarizer. So, crystals with more than one domain would appear dark and light simultaneously or may show multiple color with one particular settings of analyzer and polarizer.

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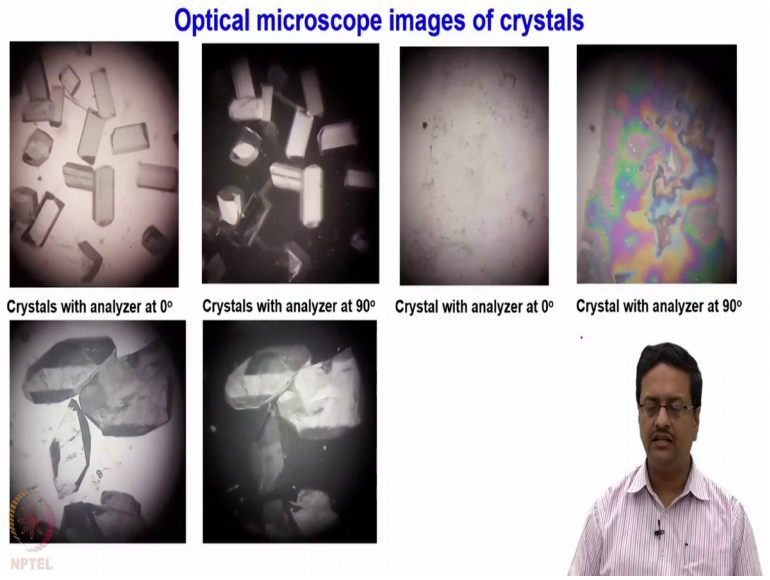

Let us see with some examples here on the first picture, what we have is the image of a set of crystals, with the background bright which means the analyzer is kept at 0 degree and the light is passing through both outside the crystal and through inside the crystal.

So, now when we rotate the analyzer by 90 degree, the light that is passing through the bottom glass is not passing through the analyzer because now the analyzer is 90 degree rotated. So, the light that is passing through the bottom glass surface is now blocked by the analyzer and what we see is the crystal which was looking very nice transparent here is now totally dark.

So that means this is a bright and dark and here it is bright transparent when there will analyze is at 0, here it is brighter and transparent when it is with analyzer 90 degree. So, these are good crystals which one should look for any X ray diffraction analysis. In the upper 2 figures what we are now pointing out, you can see the crystals have a particular shape these are rectangular parallelepiped shapes and these crystals are well faceted as well, so the crystals have different faces exposed outward.

In the figures shown here at the bottom we have a different set of crystals which are of irregular shapes as you can see they are large blocks of crystals, but they do not have any particular shape and some of them have some surface is exposed. And once again when it is looked at with the analyzer at 0 degree, you can see the light coming from the sides and passing through the crystal and giving you a transparent view of the crystal.

Whereas, when we have go to the bright field when it is the analyzer is at 90 degree, the lights is not passing through the outside of the crystal and the crystal also does not allow any passage of light.

These indicate that this is showing extinction of light passing through it extinction of polarized light passing through it. The images on the top right are crystals of bad type. That means, in case of bright field the crystal looks fine because it is transparent it looks nice. But when we rotate the analyzer by 90 degree what we end up seeing is that different regions of the crystal has different color, which means that the unit cells oriented around different directions are not following the arrangement that should be a ideal for a crystal the unit cells may be arranged like this for some time.

Then it is arranged in a different direction, then it is arranged in different direction then it goes like that and it may be. So, that the unit cells are like this up to some point and then they unit cells are like tilted at some point, then the unit cell is further tilted, then unit cell may be inverted and gone like that.

So, there are several such domains with different orientations of the unit cells maybe the axis is totally rotated about a different direction and it gives rise to a non homogeneous single crystal and in case in polarized light those domains show up as green purple yellow blue and so on. So, by looking under microscope one should choose which is a good crystal which is a bad crystal and based on that one can decide what should be mounted for x ray diffraction purpose.

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So, once we have identified the crystals it should have suitable size and suitable shape for data collection. As I have already indicated in one of the previous slides the crystal should have size from 50 to 500 micron and should have or should be made of uniform shape. Why do we need to make it uniform shape? Because the crystal which is placed in front of the beam also absorbs the incident radiation, so if the crystal has non uniform shape.

Suppose one dimension is much larger compared to other dimension for example crystal feature needle like shape. So, the length along the needle is maybe 400 micron where the thickness of the needle is 50 micron, then the absorption of x ray is when the crystal is like this is much higher compared to the absorption of x rays. When the crystal is meeting the x ray at 90 degree and in general the x ray beam is collimated to a circular spot of diameter 0.5 mm that means 500 micron or sometimes slightly bigger.

So, the crystal that we choose must be smaller than the diameter of the beam. So, if the x ray beam is 0.5 millimeter which may be like this, the crystal that we choose must be smaller than the beam. So, that the entire crystal is immersed in the beam.

So, generally we try to choose crystals of size 0.1 to 0.3 millimeter in all the dimensions for appropriate alignment and data collection on single crystal diffractometers. We will talk about this single crystal x ray diffractometer and it is geometry in the future classes Today we would like to concentrate here on the absorption of x rays. When we use any

crystal with a certain number of different elements present in it, every element has a particular amount of absorption of x rays and the amount of absorption depends on the size of crystal as well and that is why we generally use small crystals to avoid any significant absorption. Here this simple expression is very important to understand the absorption of x rays.

This expression is I equal to I 0 e to the power minus mu tau, this I is the intensity of the direct beam after passing through the crystal, I 0 is the intensity of the direct incident beam before passing through the crystal, tau is the thickness or path length of the absorber or the path length in a through which the x ray beam is going in case of this particular crystal and mu is called the linear absorption coefficient.

So, this term mu is very important depending on the wavelength and crystal size the value of mu would changes that is linear absorption coefficient increases with increase in the size and in general size in general and decreases with decrease in wavelength. So that means, a compound if we try to collect the data using copper radiation, we will have a certain value of mu. If we do a data collection using molybdenum which is a much smaller wavelength, we will have much less absorption; that means it will have much more penetration.

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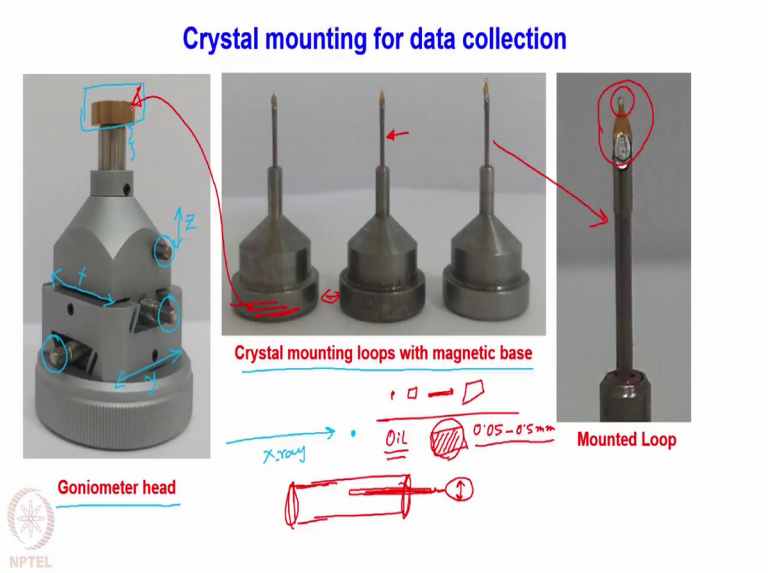

For crystal mounting we use a set of tools, here on the left we I am showing a photograph of a small attachment which is called the Goniometer head. This Goniometer

head is placed on top of the Goniometer of a diffractometer and the crystal is mounted using magnetic sample holders which are shown on the right hand side figure and the crystal is mounted here.

Once we try to mount the crystal directly on by on the diffractometer with these Goniometer head, the crystal has to be aligned in the x ray beam. So, to do that this Goniometer head has 3 screws one is here which allow you to increase or decrease the height of this goniometer head. So, that controls this height here is a screw which can be rotated to move the goniometer head along the direction of x. If this direction is z and if this is x then we have a third screw here which is used to move the crystal in the (Refer Time: 35:53) another perpendicular direction which may be y.

So, by those 3 screws, one can adjust the crystal in height, one can adjust it is orientation x and one can adjust the orientation y. So, in this way one can align the crystal in the x ray beam at a central position because, when we discuss about x ray data collection. We will see that we will be moving this crystal about different axis and during that movement we do not want the crystal to be going out of that x ray beam.

Here we have photographs of some mounting loops which are having a magnetic base, this is the magnetic base that we have which can be fitted on top here with a magnetic attachment and then at the tip, we have a metal pin which is now shown here in a zoom condition and at the tip of that pin we have a polymer film with a small loop. So, the crystal that we have chosen which may be of some shape, which may be needle, which may be block, which may be a thin plate whatever is mounted on that loop using some very thick oil.

So, that oil uses it is surface tension to stick the crystal to that loop. So, the loop is like this and you choose a crystal suitable to the loop or you choose a suitable loop for a particular crystal that we have got and these loops are available of all the sizes from 0.05 to 0.5 mm in diameter. Using those one can mount these crystals on the diffractometer. If we do not have these loops, there are other types of loops that one can use which is also available as from various suppliers, where you have very fine metal tube and at the tip you have a nylon loop which looks like that. This is a nylon thread which is actually bend tend to end twisted several turns and the twisted end is then inserted inside this thin metal tube and sealed with glue and this also is available with a given size.

So, those loops can be mounted on slightly thicker brush pins and then those brush pins can be mounted on the diffractometer instead of the magnetic base and one can collect data. So, by selecting good crystals by cutting them into proper shape and size and then by mounting it on these loop we put it put those crystals on top of a goniometer head. How do we know that it is a good single crystal until and unless we shine x rays to it and see the diffraction we do not know whether it is a good crystal or a bad crystal.

So, what is then done is that we take the goniometer head with the crystal we mount it on the diffractometer and then the axis about which the crystal is mounted we term it as the phi axis of a diffractometer. So, what we do is we rotate the crystal about 360 degree about phi, by keeping the x ray on for about 1 minute or 2 minutes depending on the size of the crystal and we keep on recording what all is getting diffracted from that particular crystal. So, we call this image that is recorded using 2 dimensional detector is called the rotation photographer.

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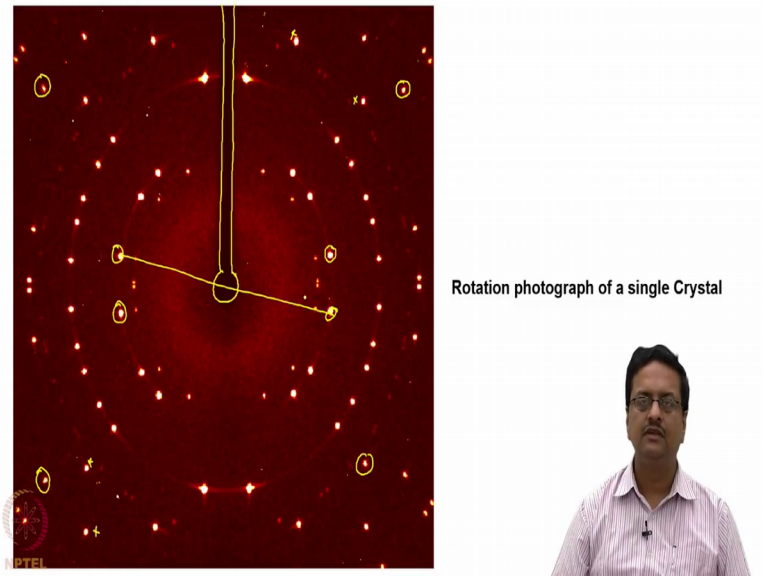

So, here what we have is an excellent rotation photograph from a single crystal. You see here this is a 2 dimensional image where the bright spots are diffraction spots and there is a dark spot or a dark region in the middle which is like that is the shadow of the beam stock.

That means in front of the x ray beam you have a block of lead, which stops the direct beam from falling to the diffractometer falling to the detector and prevents the damage of

the detector. And now what we see these bright spots are all centro symmetrically related. As I indicated in one of my previous lectures that the rotation photograph of a crystal is always centro symmetric irrespective of whether it is a Centrosymmetric or noncentro symmetric structure. In this particular rotation photograph you can verify that the all the spots that are observed in this image have a center of inversion related spot on the other side.

Just you take few examples this is inverted here this point is inverted there, this part is inverted here this part is inverted here and so on. So, all these parts which we look at there is inverted at some point. So, a nice rotation photograph like this indicates that the crystal that we have chosen is extremely good quality and one should be able to collect a data out of it. In case if we had seen concentric rings about the beam stop coming out of the crystal that we have mounted, we should conclude that it is not a single crystal rather it is a poly crystalline lump or poly crystalline particulate matter and is not suitable for x ray diffraction.

So, in today's lecture we have learned how to crystallize a few difficult things like liquids and gases and then we have discussed about how to choose a single crystal under microscope, how to mount it what are the different tools for mounting and how do we test whether it is a good single crystal or if it is just a poly crystalline material. So, in the next lecture we will continue and learn how to do a data collection using modern diffractometer.