Chemical Crystallography

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

Lecture - 55
Powder X-Ray Diffractometer Lab Demonstration

Welcome back to the course of Chemical Crystallography. Today we are in the powder X-ray Diffractometer room, where we will be showing you; how a powder X-ray diffraction data is recorded, how the sample is prepared, and how we can process the data using a computer software program. So, to start with I will first show; what are the required things for a sample preparation. So, what we need is a mortar and pestle.

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This is agate mortar and pestle which is made up of a stone and this stone is very hard for when we grind the sample here. This does not make any scratch on the stone and no sample gets stuck to this stone, during the sample preparation process. So, once we have powder the sample using this mortar and pestle.

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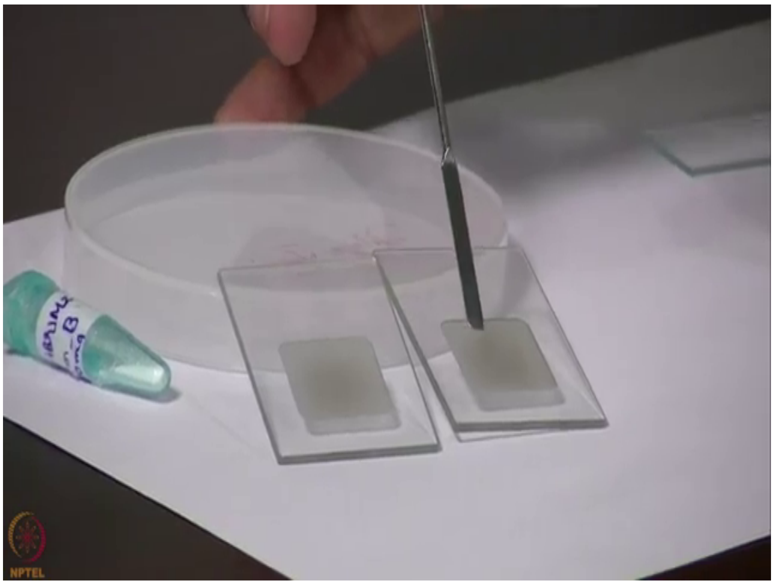

We need to transfer them to this sample plates. So, these are the sample plates on which we need to spread our samples. You can see that the central region in these plates are each and these each plates have different depth.

So, depending on the amount of sample that we have we should choose a particular sample plate. So, that we fill the entire group here with our sample. So, these plates come with different depth like 0.1, 0.2, and 0.5 millimeter depth. And the size is about one and a half centimeter in square. Technically one has to fill the entire square with sample, but in case we do not have enough amount of sample, what we need, is we just fill the central zone of the sample plate and place it under diffractometer.

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To make the sample we transfer the cystallized material, it may be nice crystals. So, this is a poly crystalline powder.

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And we need to grind it gently to a uniform particle size.

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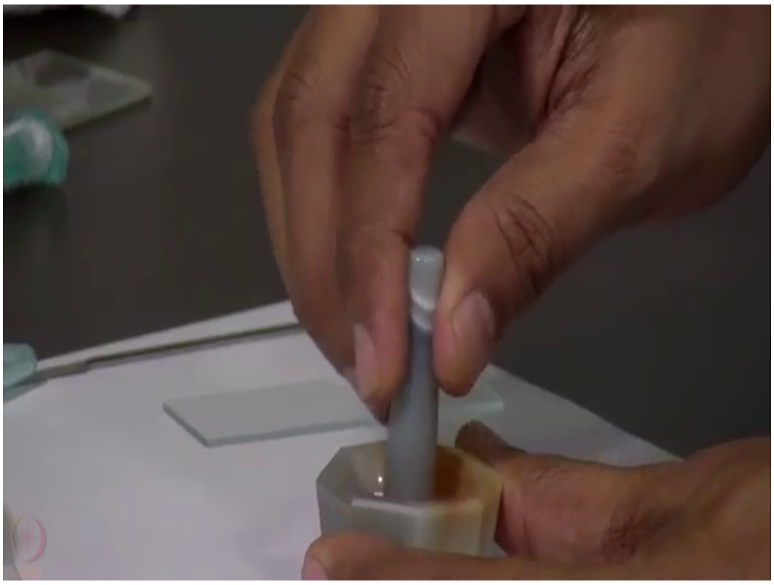

This grinding should be done very carefully and harsh grinding may lead to conversion of the sample to a different form. In case the sample contains some solvent it may so, happen that during this grinding if we apply too much of pressure the solvent can evaporate and lead to a different crystal structure than the starting material.

So, we need to then scoop out this sample, you see that while I am scratching the surface of this stone is not getting scratched. Since, we have very little sample; in this case we need to choose one of these one of these plates which has the lesser depth. So, this plate which I can feel with my finger has a lesser depth this is about point 1 mm depth sample plate. So, we should place the sample in the central zone of this plate.

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We can scratch it further to take the remaining amount of sample that is there inside the mortar and pestle this mortar.

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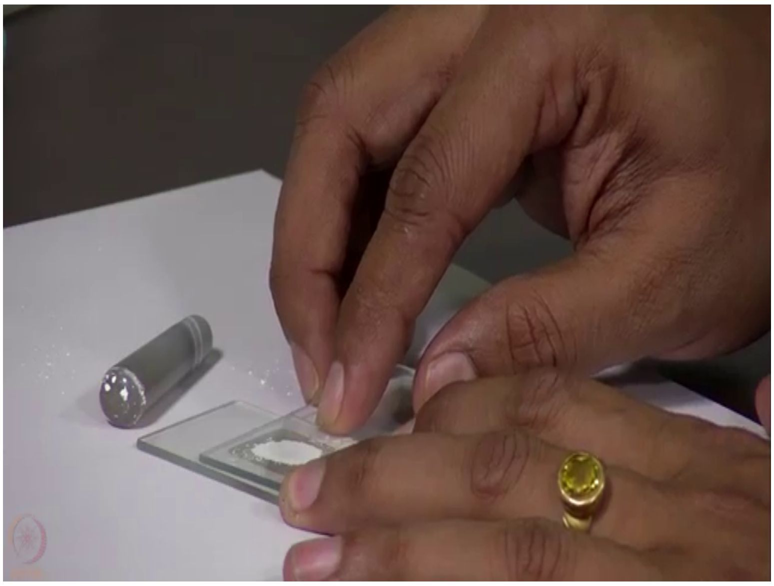

So, now what we need to do is to bring the sample to the center, because we do not have large amount of sample we have made a heap at the center. And then we need to make it flat from the top using a glass plate. So, that the top surface is flat and the sample is uniformly spread in the center. So now, this sample is ready for recording powder X-ray diffraction data we need to clean the side. So, that the excess sample is not getting contaminated on the diffractometer.

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So, what we will do on the diffractometer is we will place this sample in front of the X-ray beam. And then we will make the sample rotate like this at one hundred and 20 RMP so that the entire sample leaves you evenly exposed. Because the beam that we have here is a line focus, which means the beam is like a line which is like this. And then if we rotate this sample we have below the beam the entire sample gets exposed to that beam.

So, this removes any special orientation effect that might be there in those micro crystalline particles. So, this is the powder X-ray diffractometer which we use to record the powder diffractograms.

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So, when we try to open the door we press the button and then open the door. What we have here?

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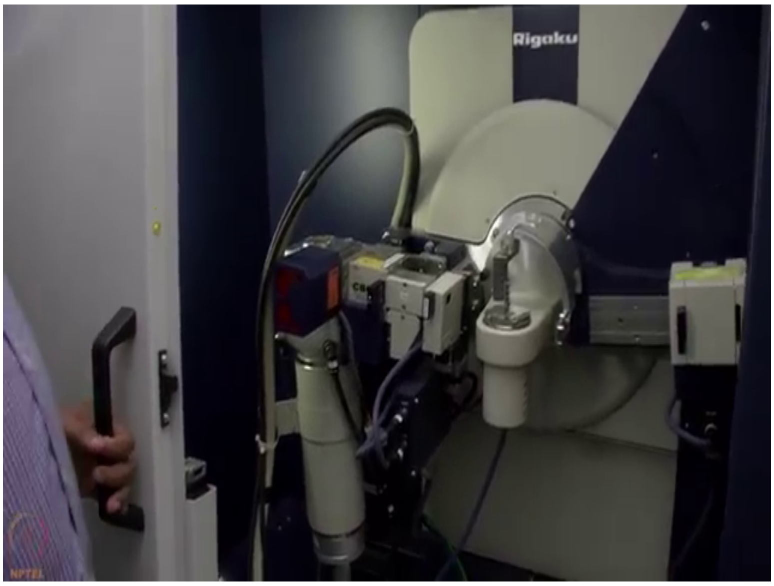

Are the equipment with the X-ray tube detector and the sample stage? On the left hand side here we have the X-ray tube mounted. This is mounted from top and you can probably see that this is a copper based X-ray source which is written here as copper.

So, that tube is giving you copper k alpha and k beta radiation out of it. So, when the beam comes out this is the optics where it is called the cross beam optics it then makes the beam in a linear fashion. And then we have some slits here this is a black brant a no slip it is written as BB

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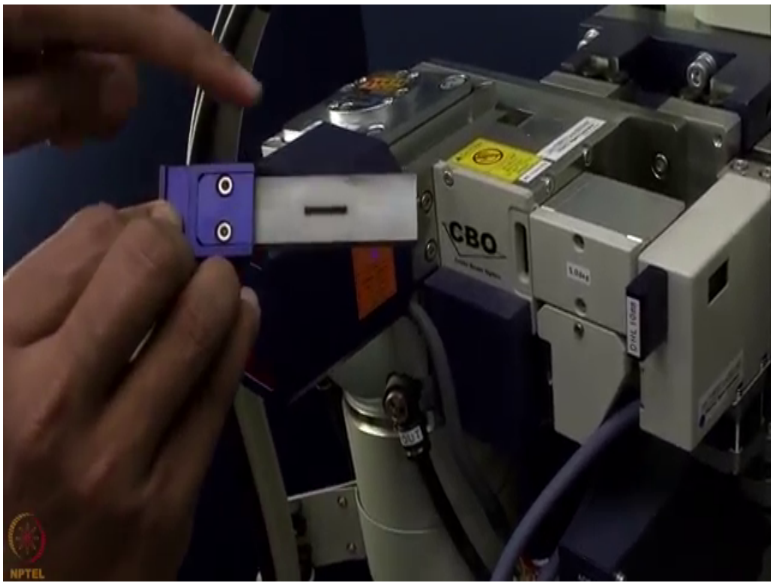

So, the beam passes through that opening zone making it as a line focus source. Then we have some solar slits here, we have a height limiting switch here which limits the size of the beam to 10 millimeter as we can see here is a 10 millimeter slit.

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This lid can be made smaller in case of very small amount of sample.

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This is the sample stage which can be rotated like this during the experiment it rotates which then makes the sample uniformly exposed to the beam, and it removes all possible preferred orientation effects. The X-ray beam comes from the left hand side, gets diffracted from the sample placed on this plate here. And then gets diffracted and gets recorded.

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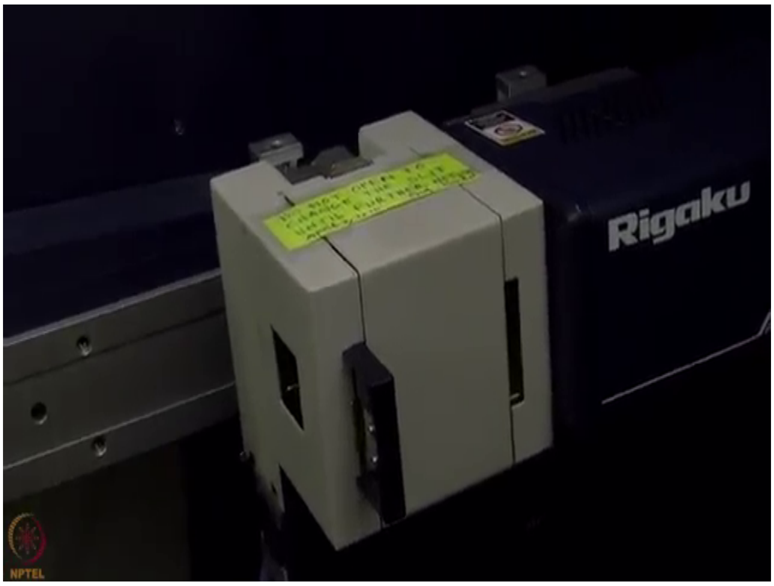

On the detector which is be written Rigaku at the back that is the detector for X-ray here. So, before this sample before the X-ray beam it goes to the detector we have a beam stop here. That beam stopper stops the direct beam from going to the sword going to the detector. Because the direct beam is very high intensity and it may spoil the detector and that is why we should have a beam stop. So, in this X-ray tube we need to pull the anode which is at the back of this tube.

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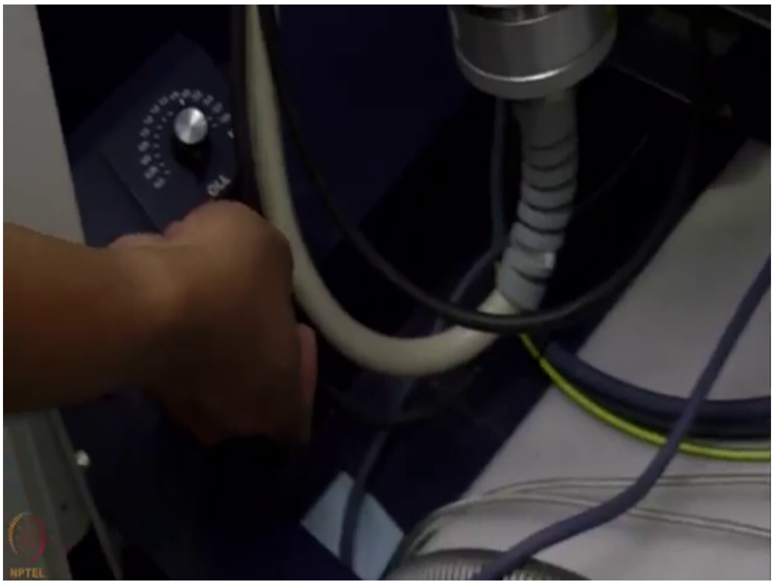

So, to pull that anode we have water supply coming through these tubes which are here. So, this is the tube through which the hot water is going back and then is a tube inside here through which the water cold water is coming in. So, we have the chiller in a different room, which cools the water to about 16 to 17 degree centigrade. And then runs it through the tube at about 4 liter per minute flow rate. So, that the cold water comes gives the back side of the anode takes that heat and goes out to the chiller.

This chiller is an important part of any X-ray diffractometer which has to be maintained at the prescribed temperature for this order diffractometer we maintain it as 16 degree centigrade. When the X-ray data is going on we will see that this particular red light will be on which indicates that the shutter is open. When we are keeping the door open; that means, the shutter is closed. So, although X-ray is generated inside that tube that X-ray is not coming out to this chamber until and unless the shutter is open. And one cannot open the shutter without closing the door. So, when we start recording a data we will showed you that when the shutter is open, this red light will be blowing.

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That red light the red light on the top indicates that X-ray is on which means the tube is on and it is producing x ray. So, in case there is a red light on that it indicates that the X-ray is on. If there is any failure and a generator has stopped working that red light will be switched off. Here in this chamber once again we have some solar slits and what we have before the solar slit is a nickel filter.

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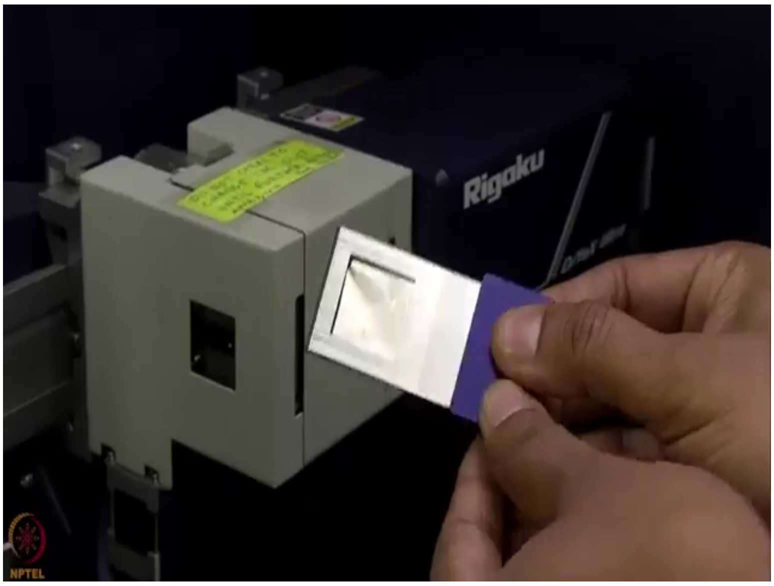

This nickel filter is used to remove the k beta component of the copper radiation and one reaches the detector is just the copper k alpha. So, this diffractometer works in a theta geometry; So that means, here the X-ray source and the detector will go simultaneously upwards.

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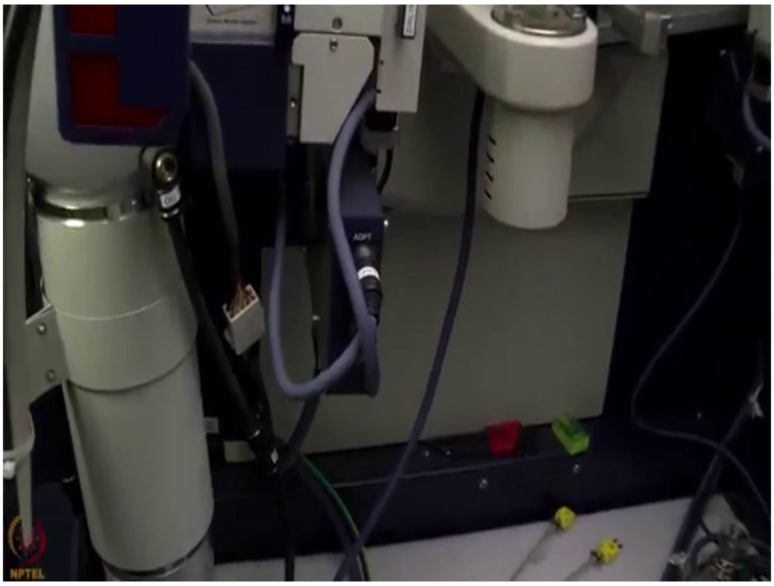

In this case this works on a theta theta geometry. So, I have the X-ray beam coming from my right hand side and the detector is on my left hand side and during the measurement both the detector and the source goes up slowly. So, this is called the theta theta geometry. The other geometry that is possible is a theta 2 theta geometry.

Where the source is kept fixed both the sample and the detector moves upwards. And that is a different geometry possible for X-ray diffraction powder; X-ray diffraction measurement. So, now I am going to place the sample on the diffractometer we need to we need to remove this dummy plate which is another sample plate.

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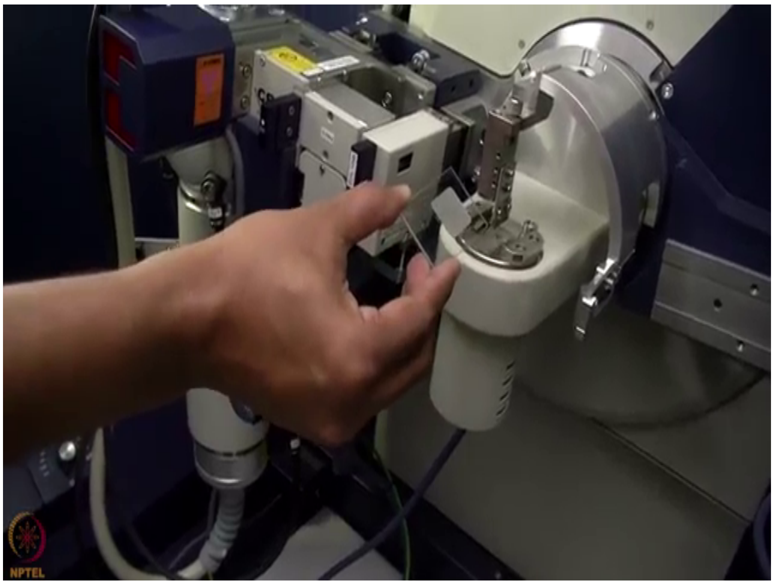

We now place the sample here.

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So, this sample is now placed in the middle portion if we see that here at this point the X-ray beam will come and heat. As a result if we will rotate the sample during the measurement it will expose the entire sample to the beam. So, we need to close the door because we cannot run X-ray diffractometers with the doors open for safety reasons. We should not be exposed to these x rays during the experiment.

So, when we close the door we are safe to operate the instrument and the door is locked. So, what happens inside this X-ray beam comes from left gets diffracted on the sample and gets recorded. And in the front we have a glass door through which we can observe or monitor the process of this data recording.

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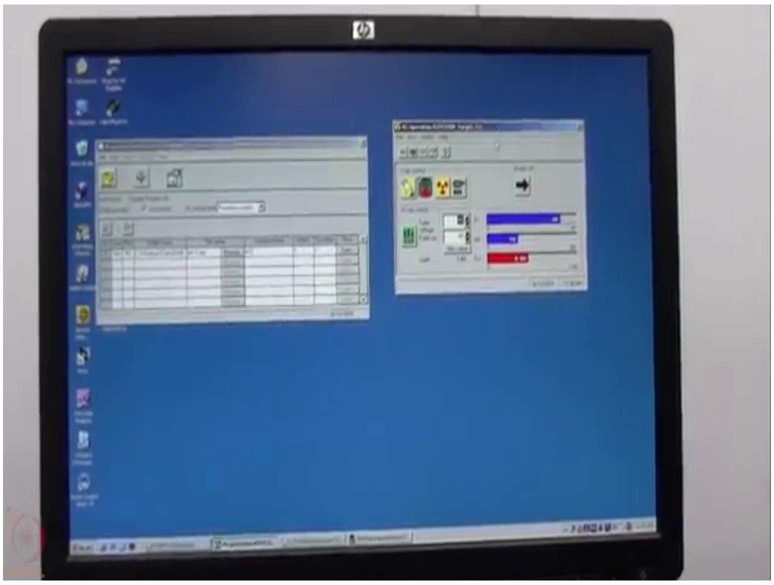

So, in this window we can see that the X-ray is on and we are operating it at 40 kilo volt and 40 milliamps of power which is equivalent to 1.6 kilowatt. So now, we need to set up the data collection strategy. As we normally do we referred the X-ray powder, X-ray diffraction data from 3 degree to about 50 degree into theta.

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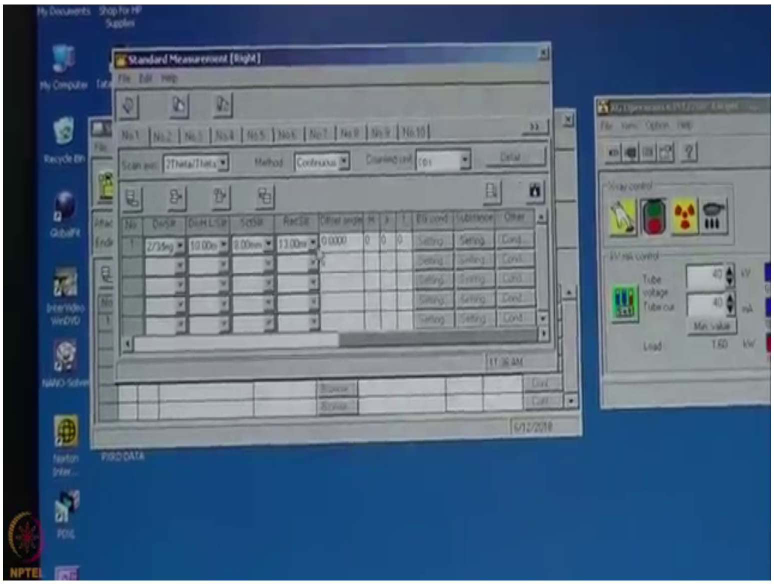

This is a sampling width which means at the interval of 0.02 degree there will be a data recorded there will be a point. And we need to decide on the speed scan speed of data collection. In general we do it for 5 or 10 degree per minute, but in case we have a small amount of sample we do it at a slower rate. So, normally the slower they can be about 1 or 2 degree per minute.

So, for today's sample I am going to do it for 5 degree per minute scan speed. Change the current here to 40 milliamps and these are the default settings of different slits that I have shown on the diffractometer, and as long as we do not change the slits we do not change of these numbers. So, this is the window and we set up the data collection strategy and from here.

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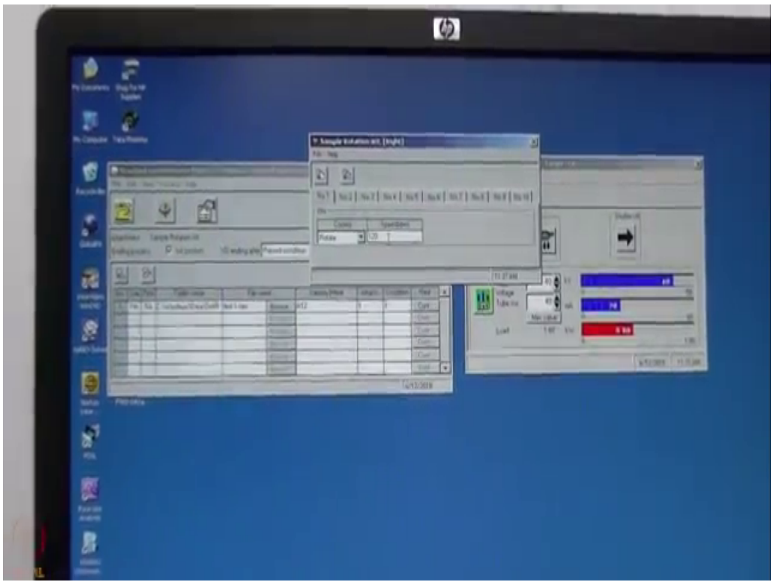

We ascertain that the sample will be rotated by 120 RPM during the data collection. That means, the sample will rotate in an horizontal load in the direction at 120RPM during the entire span of data collection. So now, we need to give a name of our sample.

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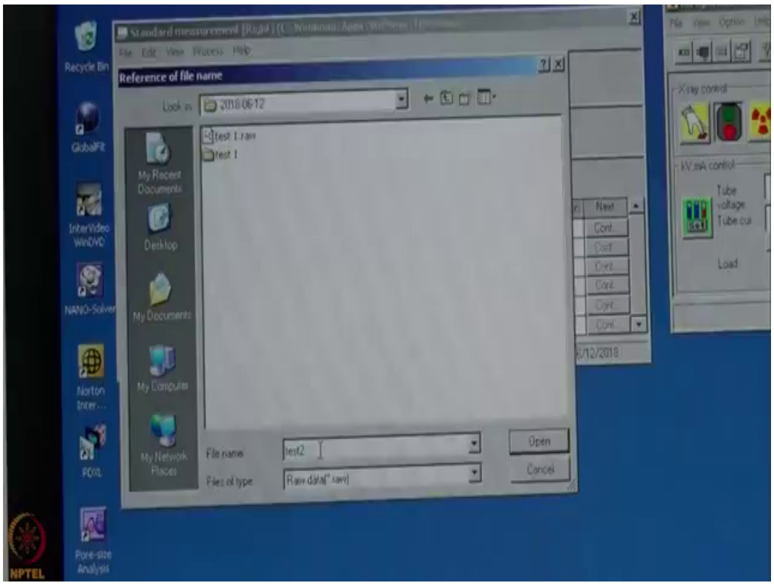

So, we can give it a name as test 2.2 and say it test 2 and then on clicking this yellow button it will start executing the measurement. And it will show how the pattern is coming.

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So, here you can see that during the measurement the sample is rotating at 120 RPM on the sample stage. And the data is getting recorded on the computer which is going to be shown.

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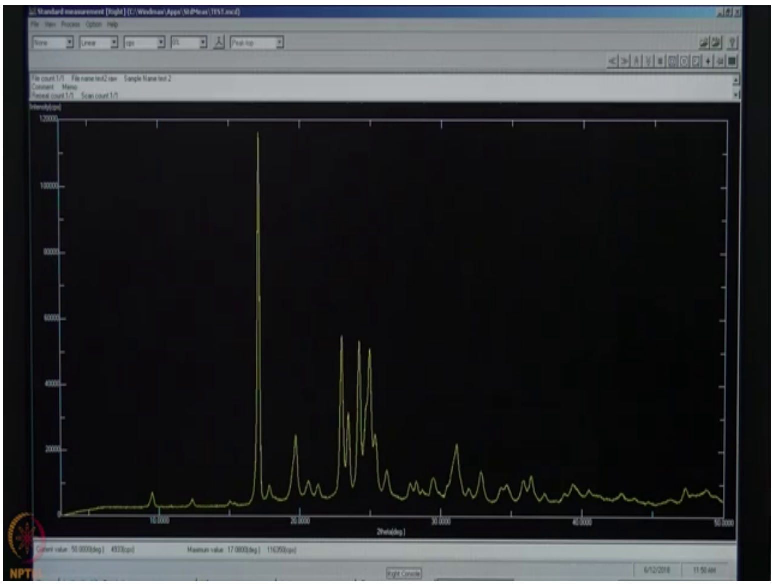

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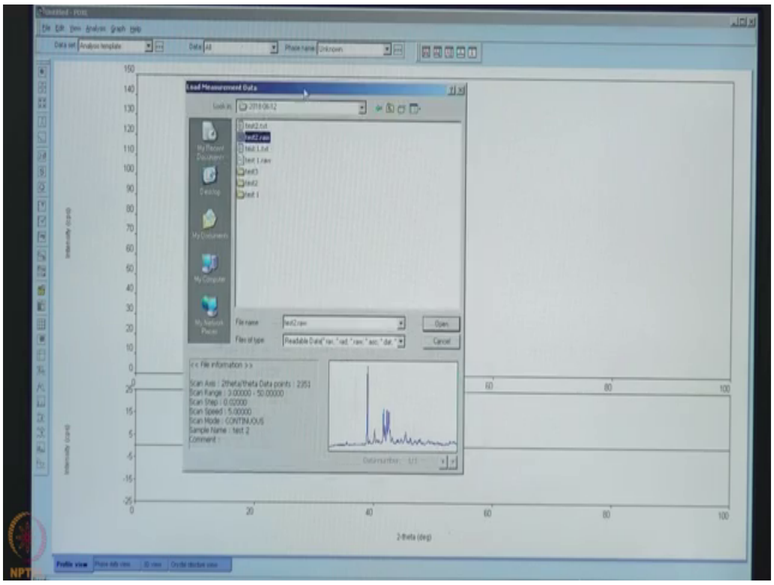

Look in: 2018-06-12

File name: test2.raw

Files of type: Readable Data(*.ras, *.rad, *.raw, *.asc, *.dat, *

<< File information >>

Scan Axis : 2theta/theta Data points : 2351
Scan Range : 3.00000 - 50.00000
Scan Step : 0.02000
Scan Speed : 5.00000
Scan Mode : CONTINUOUS
Sample Name : test 2
Comment :

Now, we are going to analyze the data using the software available with this diffractometer. This software is called PD excel so we were going to open the raw file in this software.

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So, what here is done is that it is off; it has opened the powdered X-ray diffraction data that we have just recorded. And we have a few tools to examine the data, if we try to see the background how it is.

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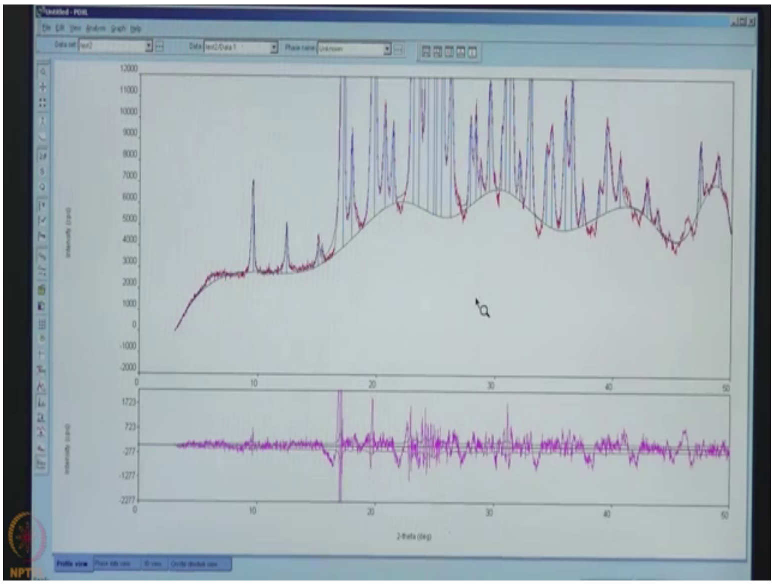

We only need to expand that region and we see that the background is not really flat, but the background is wavy in nature. So, this wavy background indicates probably the sample is not fully dry; it may be having some solvent in it. And it is not a very good sample for powder X-ray measurement purposes. What we can see here is that of course, we have sharp peaks.

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As we can see if we expand this region one can see the peaks are single.

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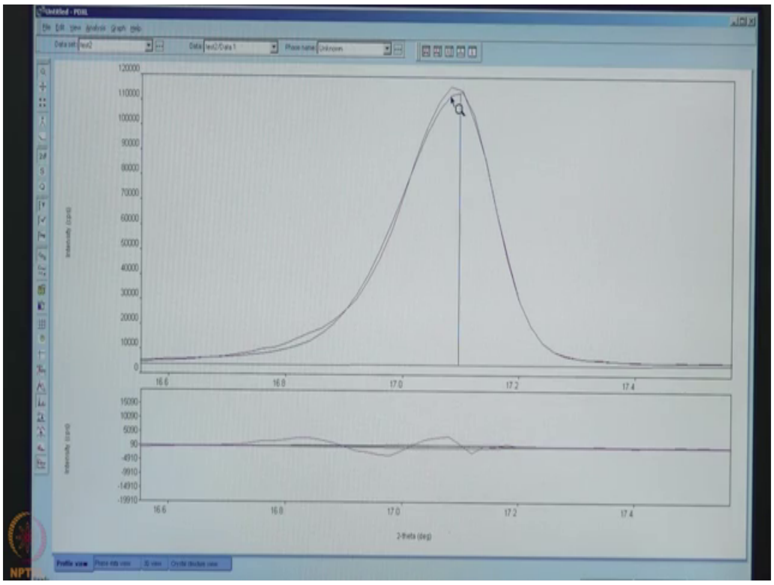

So, the red ones are absorbed and blue ones are calculated peaks in this pattern.

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And this particular software has already found out.

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The correct positions of those peaks and has put the software has already identified those peaks and marked them as blue sticks for indexing purpose. So, one can also do a powder pattern indexing using this software.

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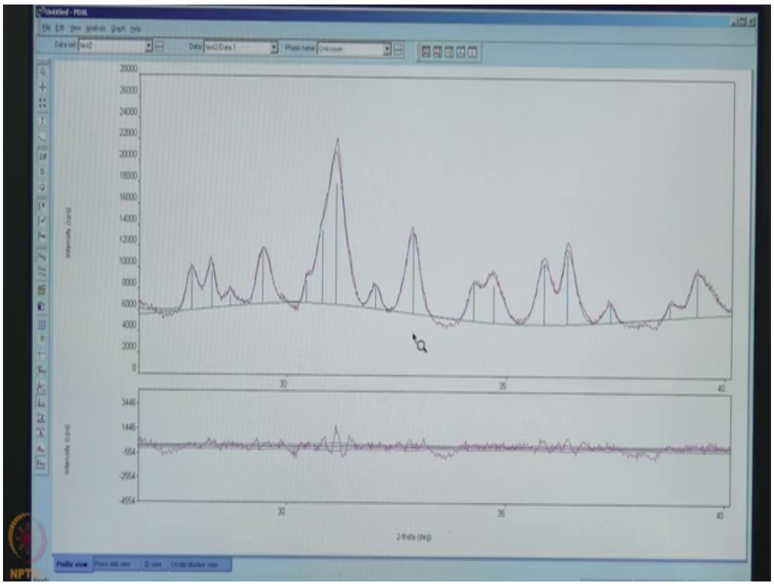

If we see the mid angle region what we see is that the peaks are very broad and they are not well resolved. So, this is the problem of a home based source which cannot resolve the pitch which are very close to each other. And that is why we sometimes try to record order X-ray diffraction pattern using synchrotron sources the advantage of synchrotron data that it will be highly resolved of with these peaks we will have very high intensity. And we should be able to solve and refine the structure from this powder X-ray diffraction data. Now, what we have done is that we have removed the background.

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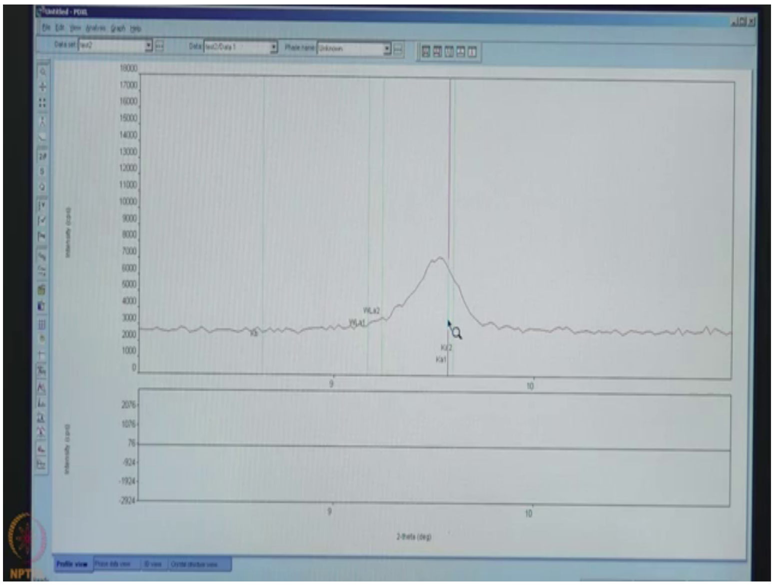

And what we are getting are the alpha 1 and alpha 2 peak positions that we can see. In this case if we fix that particular point as alpha 1, then the green line which is coming next to it is the peak for k alpha 2. So, this particular powder X-ray diffraction diffractometer does not use monochromatic radiation, but uses just copper k alpha 1 and alpha 2 as I come mixture. And hence, the peak finding software indicates the possible positions for k alpha 1 and k alpha 2 as well. This can be also seen at high angle peaks.

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So, the alpha 1 alpha 2 split is the wider at the high angles compared to the low angles. If you can see the red line, and the green line they are well separated at higher angles like 30 degree. If we go to a further high angle something like 48-49 degree.

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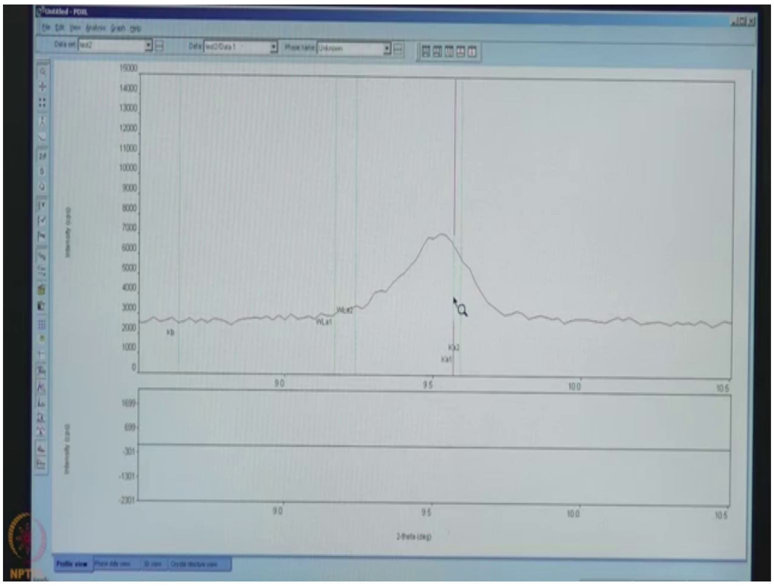

You can see that the alpha 1 alpha 2 split is much larger. But for this low angle peak they are extremely close. This is the characteristic feature of powdered X-ray diffraction when recorded using 2 different wavelength. So, if we had not put the k bit of inter we would have got another peak corresponding to k beta radiation and the pattern would become more messy

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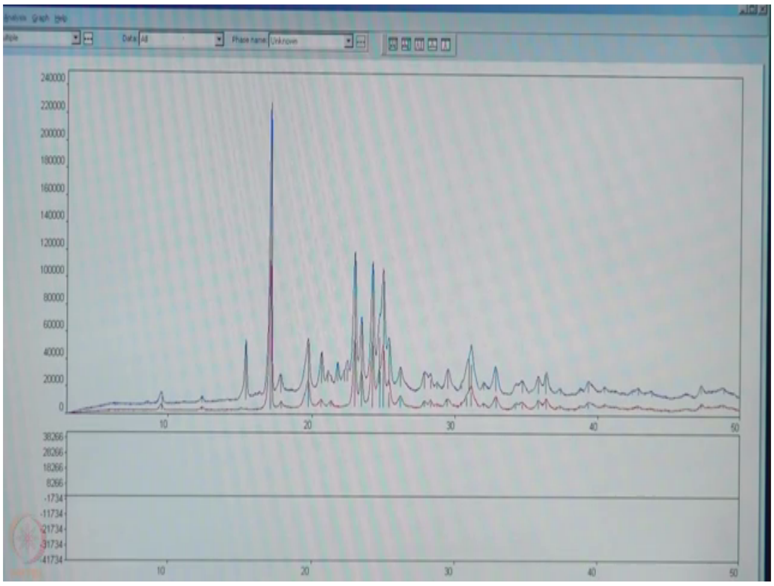

So, here in the screen what we are now seeing are two diffraction patterns. One is recorded in red, one is displayed as red; the other one is displayed as blue. The red one is with a nickel filter installed before the detector and the blue one is without the nickel filter placed in front of the diffracted beam. So, what we see in general in the blue pattern is that there are some additional peaks which are not there in the ray. That indicates the additional peaks that are coming are nickels of the presence of k beta radiation in the diffracted beam. That presence of k beta radiation is not very prominent for these weak diffraction peaks.

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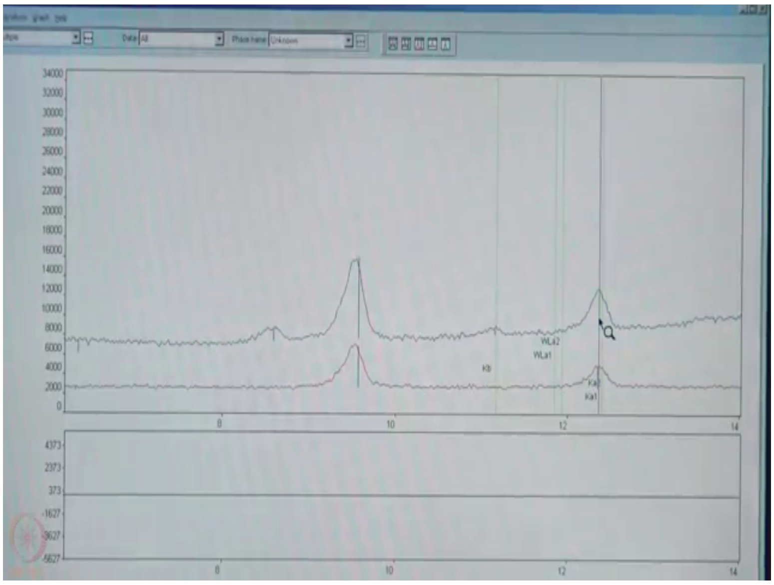

But still we can see that, if we place the k alpha 1 on this line. There is a k beta peak coming here which was not there in red. Similarly if we bring that line here on the right hand side this peak corresponds to the k alpha 1 and then k alpha 2 as well. But there is a very small peak which is appearing there which was not there here because it was a flat background, but here there is some indication of small peak; if we go and zoom near the highest intensity peak.

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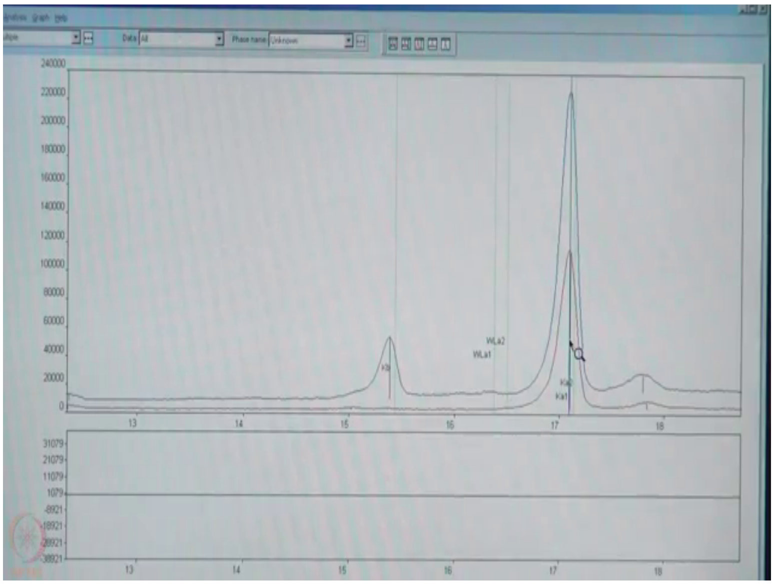

It becomes very much evident that if I make that peak as k alpha 1 and the alpha 2 is immediately next to it. This blue peak which has appeared in the blue pattern is the k beat peak which was missing when we used the filter. This case becomes more significant in the high angle region where we have lots of peaks.

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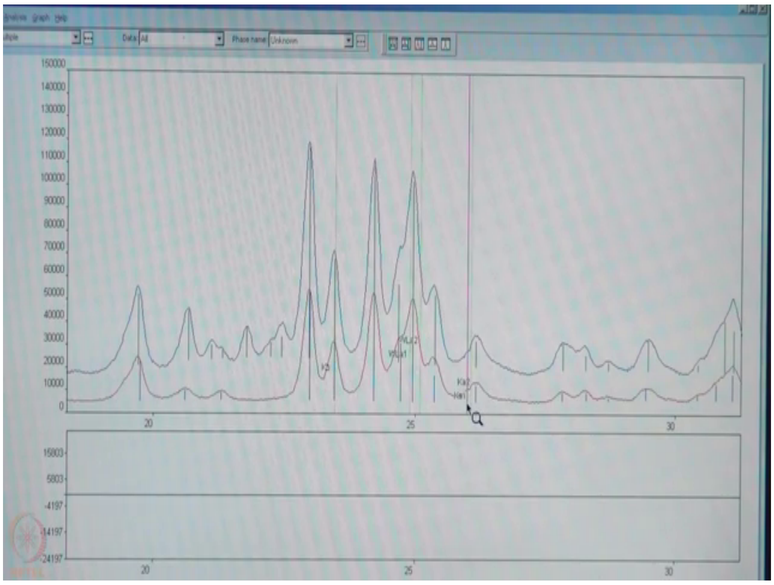

And some peaks which are actual peak from the sample peak for k alpha gets merged with the peak of k beta of another peak and makes the powdered X-ray diffraction pattern broad. So, if I try to look at this particular peak which is here and I then focus it as k alpha 1. The corresponding k beta appears here, but you see in the red also there is a peak. So, this original peak is now marged with k beta and become broad. The next peak that we have in the main pattern is now focused here.

So, this peak is the k alpha 1, but the corresponding k beta peak is here which was not there in the original pattern. The next larger peak which is somewhere here is the k alpha peak the corresponding k beta appears at much lower 2 theta value and as an independent peak which was marked there in the red. So, this actually this pattern comparison clearly shows that; if we have forgotten to put the k beta filter that is the nickel filter for copper radiation.

We will get additional peaks and then if we throw these peaks without knowing that they are from k beta any indexing software will fail to index this powder pattern. So, the presence of k beta a filter in all the diffractometer is essential. And we must not forget to put that the k beta peaks are both here shown for these 2 peaks which are here in about 25 degree into theta. And this red keeps on increasing at higher and higher angle if we try to see it at high angle.

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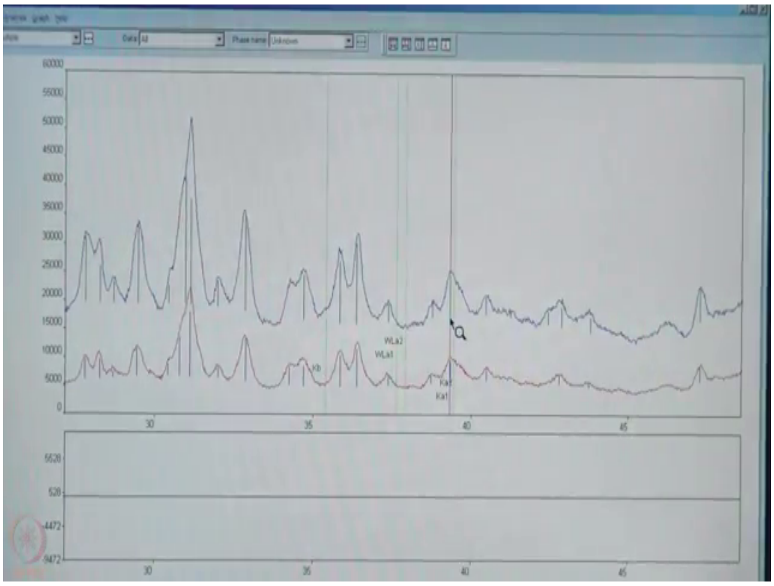

And in most of the cases then that this is the peak for k alpha that k beta peak appears somewhere there which is marged with one of those actual peaks and we do not get a different peak for that. See here again this case this peak is the k alpha peak the corresponding k beta is here as a result this peak intensity has increased. So, k beta is now hiding behind a genuine k alpha one peak. And since, we recorded this data only up to 50 degree to theta we have peaks up to about 46 47 degree. So, this particular peak also once again appear somewhere there as abroad which was not there in the red in the original.

So, this shows that the presence of k beta becomes more and more significant for all kinds of peaks small angle to high angle very weak reflections to strong reflection and hence it will then create problem in data indexing. So, always we must remove k beta either at the end of this holes that is before the diffraction occurs. Or before the diffracted beam meets the detector and generate signal the k beta filter has to be placed; k beta filter can be placed immediately after the optics before the X-ray falls on the sample. Or after the diffraction occurs from the sample and before the beam reaches the detector.

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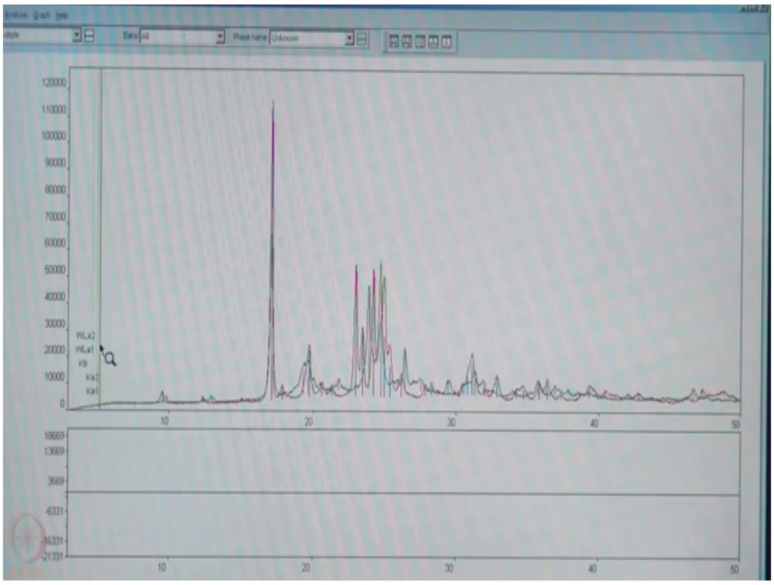

Here we are trying to compare the powder X-ray diffraction patterns of 2 polymers. As we have already discussed in the class polymers are different crystal structures of a particular compound.

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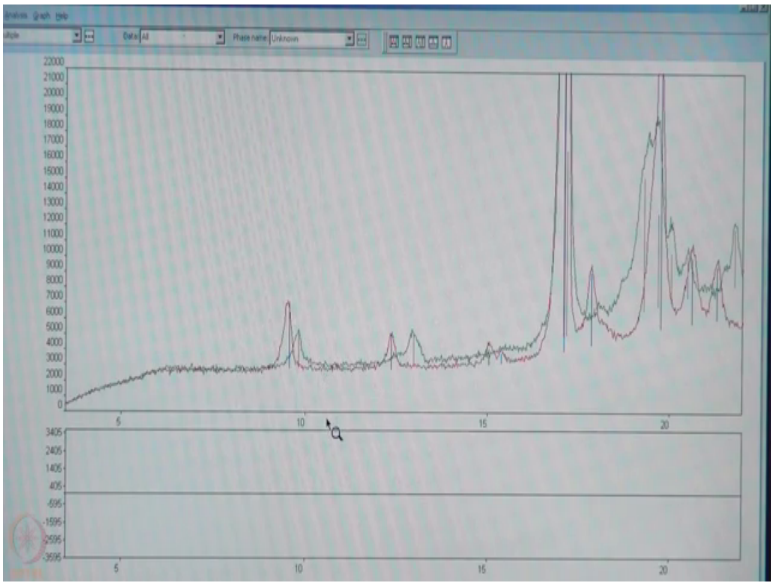

That means the internal structure in of the lattice is different as a result the unit cell dimensions could be different. And hence, the peak positions in powder X-ray diffraction data will be different for different polymers.

So, here what we can see is that there are 2 powder patterns red and green. These are recorded on two different polymers of same compound you see the peak positions are different.

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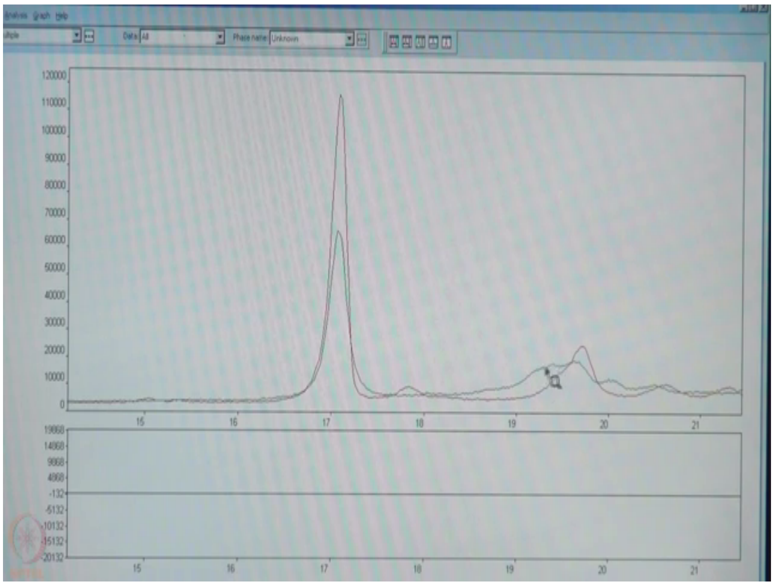

In some case the peak is shifted towards left.

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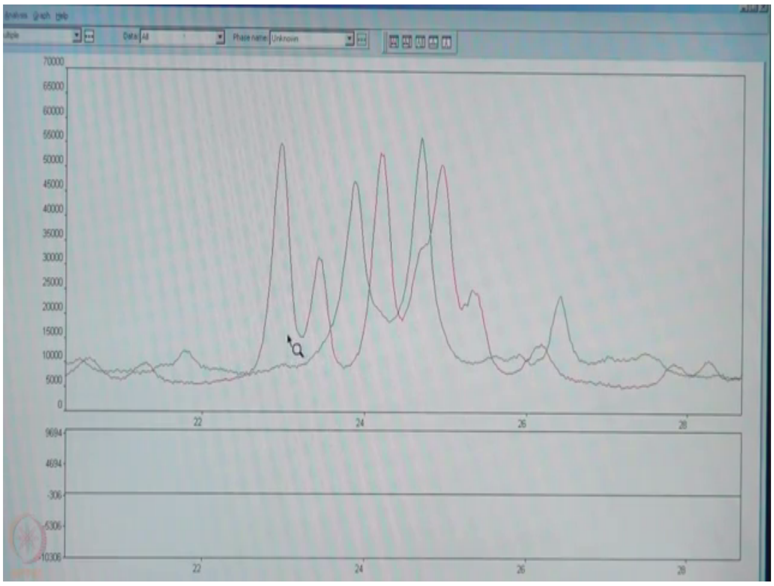

At this region the peaks are totally different because you had 1 2 3 4 and 5 peaks while you have only 1 and 2 green colored peaks. So, this type of difference in powder X-ray diffraction pattern clearly indicates the polymorphism present in this particular sample.

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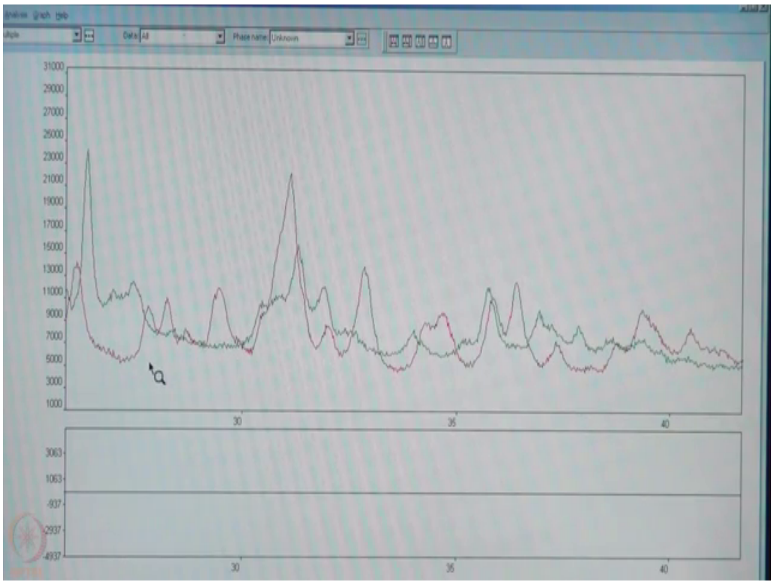

Of course, if the sample is completely different if the 2 patterns then the 2 patterns can be different they are not polymers. So, we need to have a prior information about the origin of the sample.

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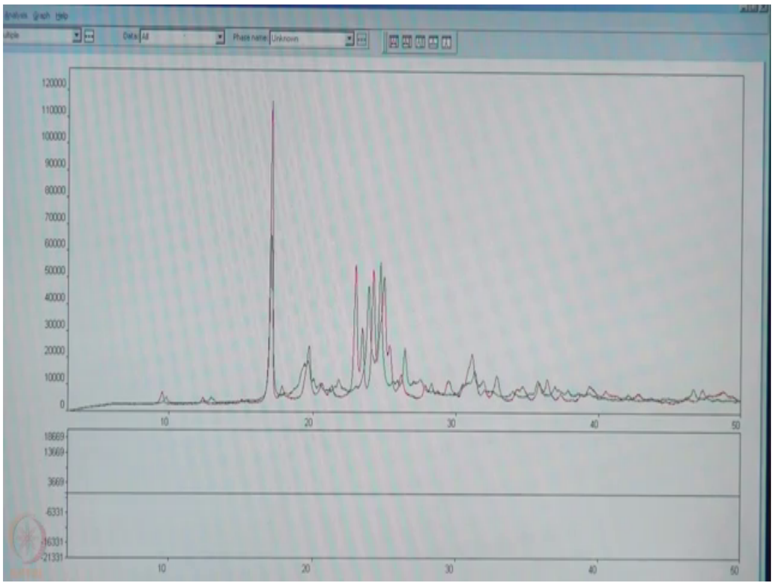

If we know that the sample is containing a particular compound and it was crystallized in 2 or more different methods from different solvents and so on. And we have resulted a powder material originating from the same compound 4 or 5 different crystallization method ending different early looking crystals. Then the powder X-ray diffraction pattern has to be recorded on all the samples all the powders and then compared like this by peak to peak matching to see whether the there is a difference in powder pattern as we are seeing here.

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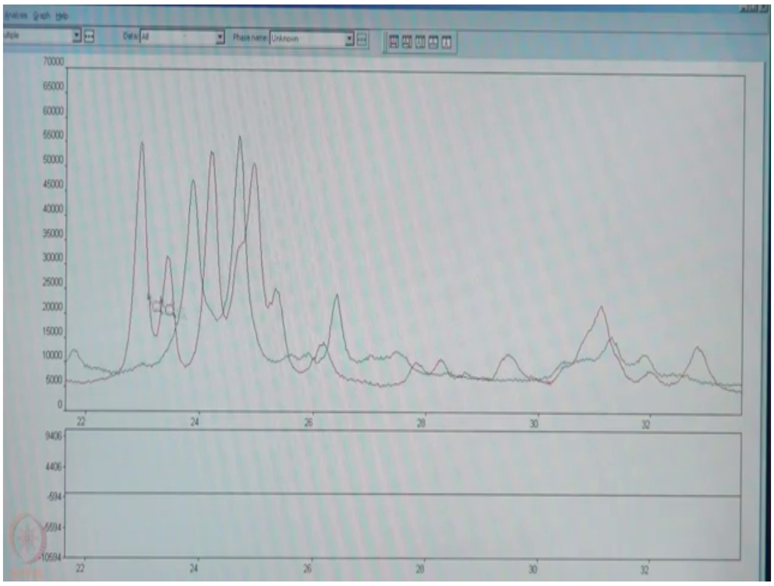

Data: All

Phase name: Unknown

This particular case where the sample we know has originated from one particular compound and is giving 2 different crystal structures with 2 different sets of peaks appearing at 2 different points. So, this is how one can identify polymers using powder X-ray diffraction data.