Chemical Crystallography
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Lecture - 54
Powder X-Ray Diffractometer –Theory

Welcome back to the course of Chemical Crystallography. Today we would like to discuss about the basics and applications of Powder X-Ray Diffraction using a presentation. And then in a later stage we will take you to the Powdered X-Ray Diffractometer room and show how the sample is prepared, and how the diffractometer is used and the data is recorded.

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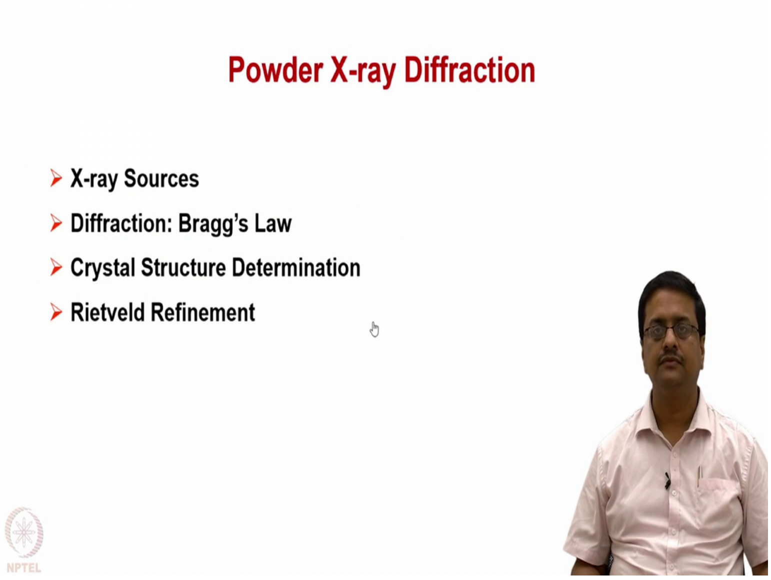

Powder X-ray Diffraction

- X-ray Sources
- Diffraction: Bragg's Law
- Crystal Structure Determination
- Rietveld Refinement

So, for our clear understanding I would again like to go back to something which I discussed in the very beginning that is; the sources for powdered X-Ray diffraction, little bit of Bragg's Law, which you already know, the Crystal Structure Determination using the powder X-Ray diffraction data. And I will introduce you to rietveld refinement, but I will not go in much details of refinement in this course.

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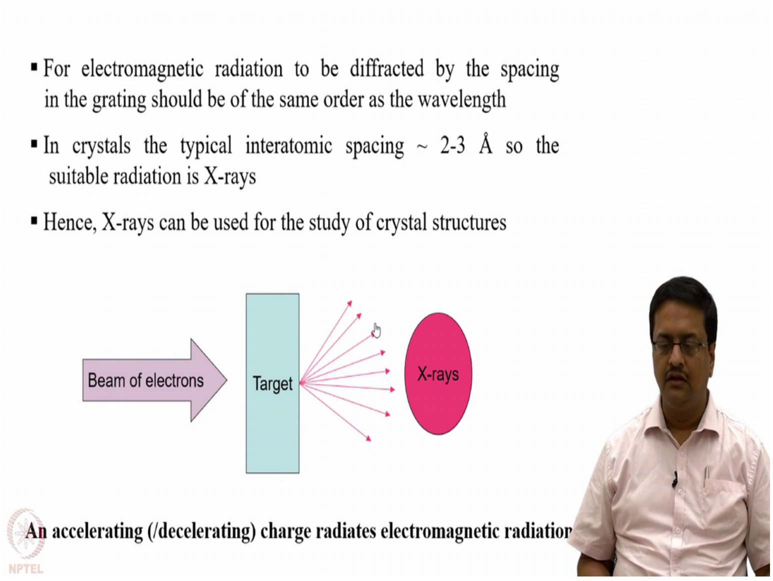

- For electromagnetic radiation to be diffracted by the spacing in the grating should be of the same order as the wavelength
- In crystals the typical interatomic spacing ~ 2-3 Å so the suitable radiation is X-rays
- Hence, X-rays can be used for the study of crystal structures

An accelerating (/decelerating) charge radiates electromagnetic radiation

So, as you know that electromagnetic radiation to be diffracted by the spacing in the grating should be of the same order of the wavelength. So, that is why we use X-Rays of very small wavelength 1 to 2, 2 to 3 angstrom is suitable for X-Ray diffraction. So, here X-Ray can be used to study the structures because inter atomic distances are inter planar distances are in the range of 1 to 2, 2 to 3 angstroms.

So, what happens as you know that the beam of electron falls on a target and is diffracted in all possible directions and it is the X-Ray that are generated. So, an accelerating source of electrons are allowed to impinge on a metal target so immediately it removes one electron from the innermost orbital. And the next level electron jumps down and emits a particular characteristic radiation.

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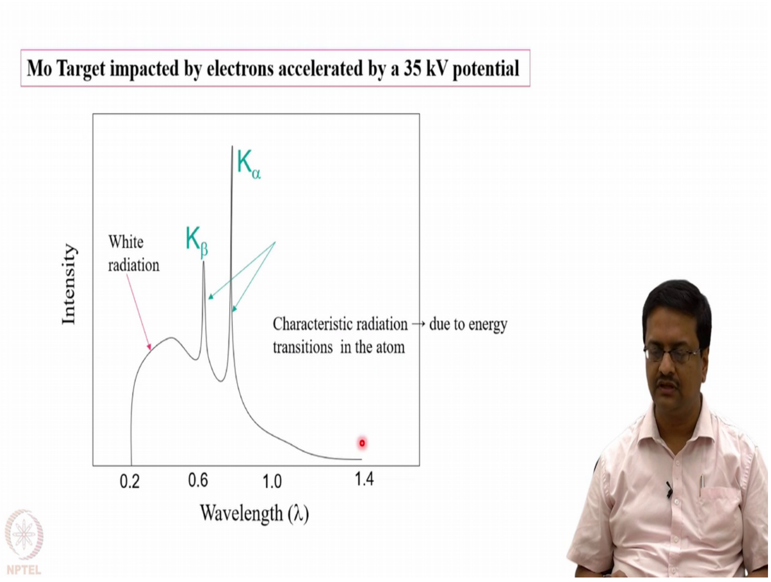
Mo Target impacted by electrons accelerated by a 35 kV potential

Characteristic radiation → due to energy transitions in the atom

So, when the electron jumps from the next higher cell it emits K alpha and when it jumps from the even higher next higher cell; second higher cell it is recall the K beta. In general for all X-Ray diffraction purposes, we use this K alpha radiation for any the X-Ray diffraction applications.

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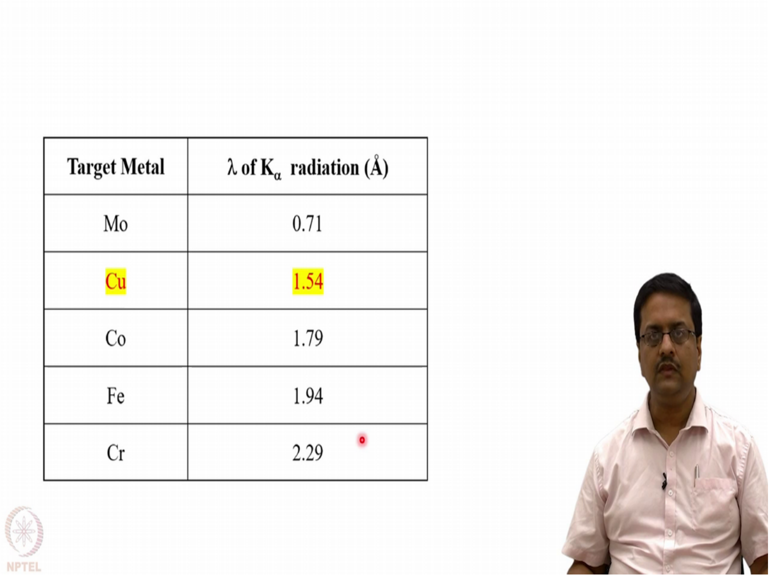

Target Metal	λ of K_α radiation (Å)
Mo	0.71
Cu	1.54
Co	1.79
Fe	1.94
Cr	2.29

As you already know there are different metal based sources that are use for X-Ray diffraction. Molybdenum, copper, cobalt, iron, chromium; these are different metals. Nowadays we have silver based sources as well and you can see the wavelengths are rading from 0.71 angstrom to 2.29 angstrom. The most widely used radiation is molybdenum and it is used for single pixel X-Ray diffraction which you already know. Copper X-Ray it is used mostly for powder X-Ray diffraction purpose because of it's larger wavelength.

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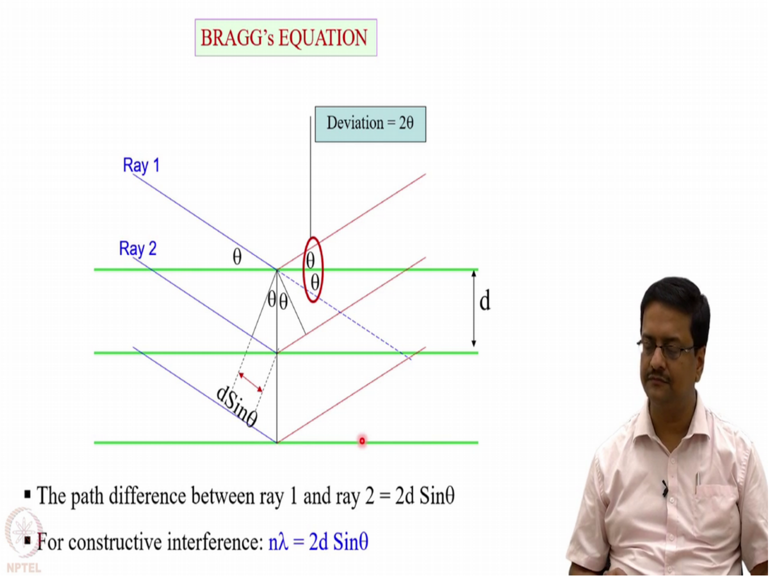

BRAGG's EQUATION

- The path difference between ray 1 and ray 2 = 2d Sinθ
- For constructive interference: nλ = 2d Sinθ

So, as you know in the from Bragg's Law that we have the Bragg's Law as an lambda equal to 2 d sin theta. So, we have X-Ray falling on the sample and getting diffracted from the bulk of the sample. And the constructive interference only happens when this path difference is equal to d integral multiple of the wavelength.

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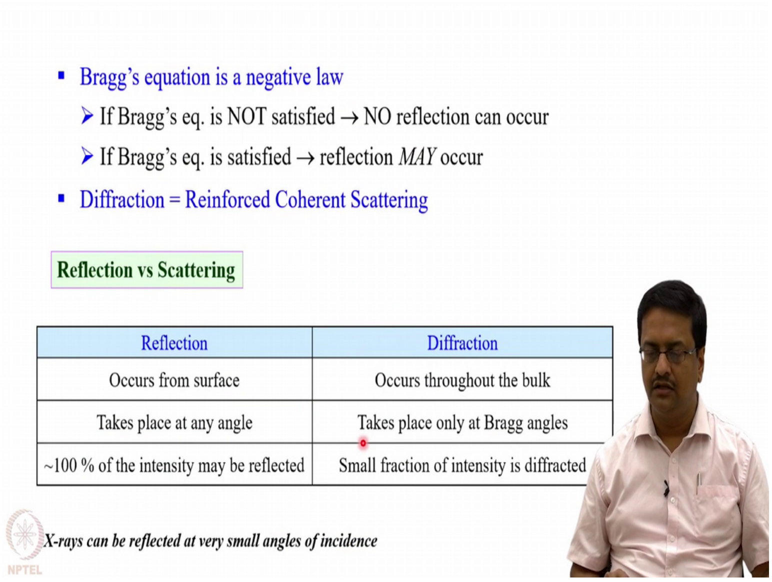

- Bragg’s equation is a negative law
  - If Bragg’s eq. is NOT satisfied → NO reflection can occur
  - If Bragg’s eq. is satisfied → reflection *MAY* occur
- Diffraction = Reinforced Coherent Scattering

Reflection vs Scattering

Reflection	Diffraction
Occurs from surface	Occurs throughout the bulk
Takes place at any angle	Takes place only at Bragg angles
~100 % of the intensity may be reflected	Small fraction of intensity is diffracted

X-rays can be reflected at very small angles of incidence

So, what we say is Bragg’s equation is a negative law; that means, if Bragg’s equation is not satisfied then no reflection occurs but if Bragg’s equation if we satisfied a reflection may occur. Why? Because you already have seen there are conditions where there is a systemic absence. So, if a particular plane follows or if a plane becomes systematically absent; that means, the diffraction is not happening in if a plane matches the systemic absence conditions which means that the constructive interference does not take place for that particular plane and then we do not see the diffraction from that plane. So, diffraction is a reinforced coherent scattering and it is different from reflection.

As you know the reflection occurs from surface whereas, diffraction occurs throughout the bulk. Reflection occurs at any angle when you shine light on a surface at any angle reflection occurs diffraction takes place only at Bragg angles. Generally 100 percent of the intensity may be reflected during a reflection process, but only a small fraction of intensity is diffracted during a diffraction process. So, X-Ray can be reflected at very small angle of incidence that is a different region of X-Ray which X-Ray crystallography.

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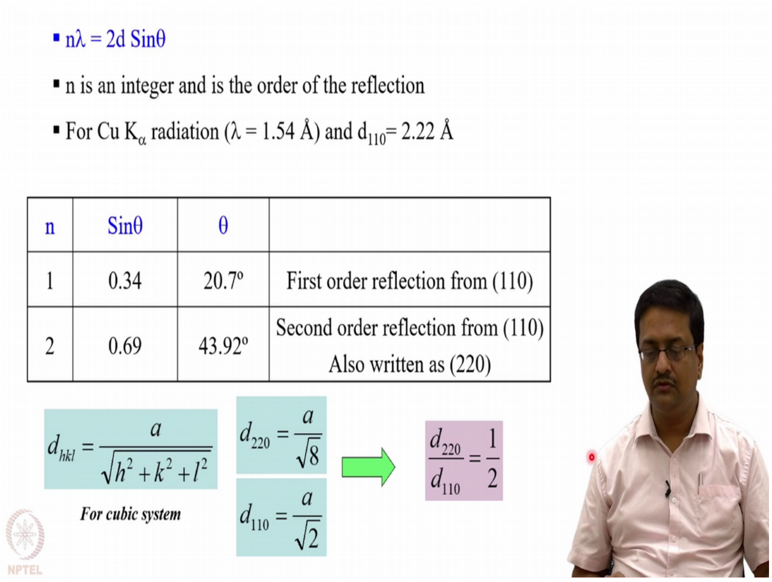

- $n\lambda = 2d \sin\theta$
- n is an integer and is the order of the reflection
- For Cu K_α radiation (λ = 1.54 Å) and d_{110}= 2.22 Å

n	Sinθ	θ	
1	0.34	20.7°	First order reflection from (110)
2	0.69	43.92°	Second order reflection from (110) Also written as (220)

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

For cubic system

$$d_{220} = \frac{a}{\sqrt{8}}$$

$$d_{110} = \frac{a}{\sqrt{2}}$$

$$\frac{d_{220}}{d_{110}} = \frac{1}{2}$$

So, as you know will not spend too much of time on these; that we have Bragg’s Law, n lambda equal to 2 d sin theta, n is an integer and it is order of reflection. For copper K alpha radiation we use and suppose the d 110 for a particular lattice is 2.2 we can calculate the corresponding lattice parameters and all that using this formula, which is d hkl is equal to a by square root of h square plus k square plus l square for cubic systems and so on.

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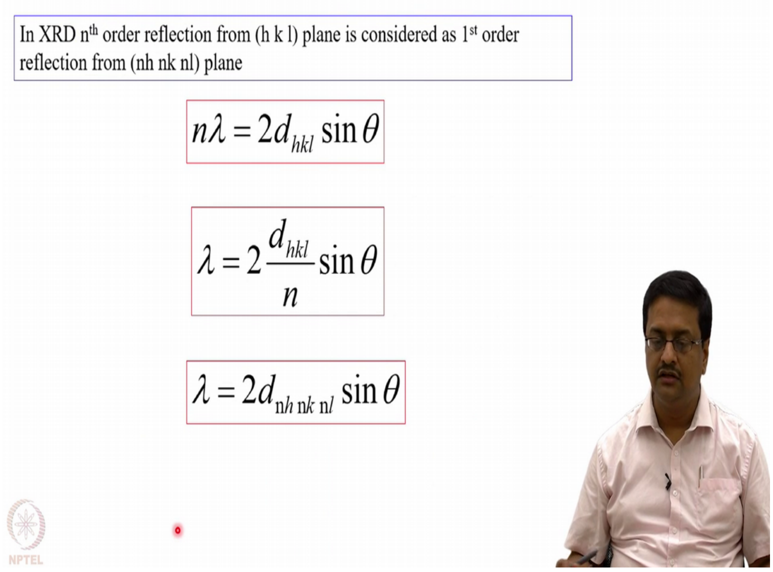

In XRD n^{th} order reflection from (h k l) plane is considered as 1^{st} order reflection from (nh nk nl) plane

$$n\lambda = 2d_{hkl} \sin\theta$$

$$\lambda = 2\frac{d_{hkl}}{n} \sin\theta$$

$$\lambda = 2d_{nh\,nk\,nl} \sin\theta$$

What we need to know here is in powder X-Ray diffraction or in X-Ray diffraction nth order reflection from hkl plane is considered as first order reflection from n h n k n l set of planes. So, we can write n lambda equal to 2 d sin theta, in another way that lambda equal to 2 d by d hkl by n sin theta which is nothing, but lambda equal to 2 d nh nk nl sin theta. So, this is a common setup of the powder X-Ray diffractometer of the instrument.

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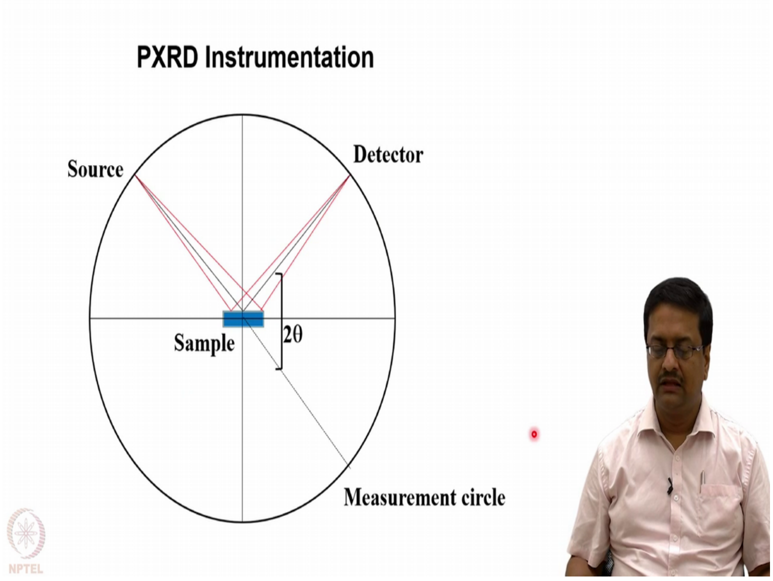

PXRD Instrumentation

What we have is a measuring circle like this, as I have drawn here. At the center of the circle we have a plate which holds the sample; at one end of the circumference of the circle we have the source; that is the X-Ray tube. And on the other side of the circle at the circumference of this measurement circle we have the detector.

And the angle between this direct beam and the diffracted beam is called d2 theta as you already know. So, in this X-Ray diffractometer we have three parts source sample holder and detector. This sample holder is shown in such a way that it works on the reflection geometry which is called the Bragg Brentano geometry, we will come to this soon.

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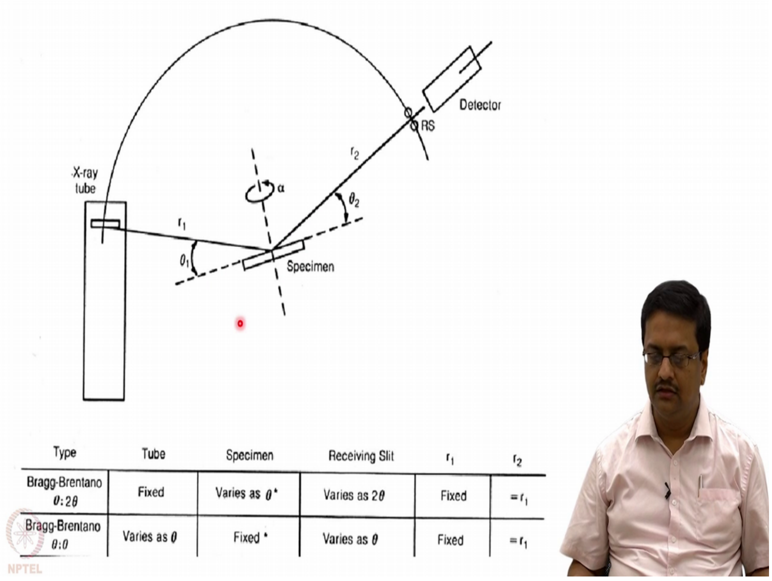

Type	Tube	Specimen	Receiving Slit	r_1	r_2
Bragg-Brentano $\theta:2\theta$	Fixed	Varies as θ *	Varies as 2θ	Fixed	$=r_1$
Bragg-Brentano $\theta:\theta$	Varies as θ	Fixed *	Varies as θ	Fixed	$=r_1$

This is again a schematic diagram of the diffraction experiment. Here you can see that the X-Ray tube is mounted in a vertical fashion and the X-Ray beam is coming from left to right as I am showing here. And then this I have a specimen holder that is the sample holder and it gets deflected and recorded there. So, now, it is possible that this specimen is rotated about its own axis as is shown here as the alpha.

So, this rotation of sample in presence in front of the beam is done to remove any special orientation effect. This angle of incidence theta angle of deflection is also theta and the difference between the direct beam and the diffracted beam is nothing, but 2 theta. So, now this reflection geometry which is called the Bragg Brentano geometry can be used in two different ways. In one case the X-Ray tube is fixed, both specimen and the receiving slit of the detector moves simultaneously.

So, suppose if this is the sample this is the detector the sample and detector both moved like that keeping the X-Ray source fixed at one place. So, that is called a theta 2 theta geometry because specimen rotates by angle theta when the detector rotates by an angle 2 theta. On the other hand the Bragg Brentano theta geometry is something where you have the X-Ray tube and the detector rotating moving together keeping the sample fixed in the middle.

So, if the source is giving the beam like that; you have the sample in the middle, and the detector is like this. So, then when this theta geometry use is used both detector and the source goes continuously up. This is the corresponding theta geometry which we also have in our diffractometer, where both the source and the detector goes up during the data collection process.

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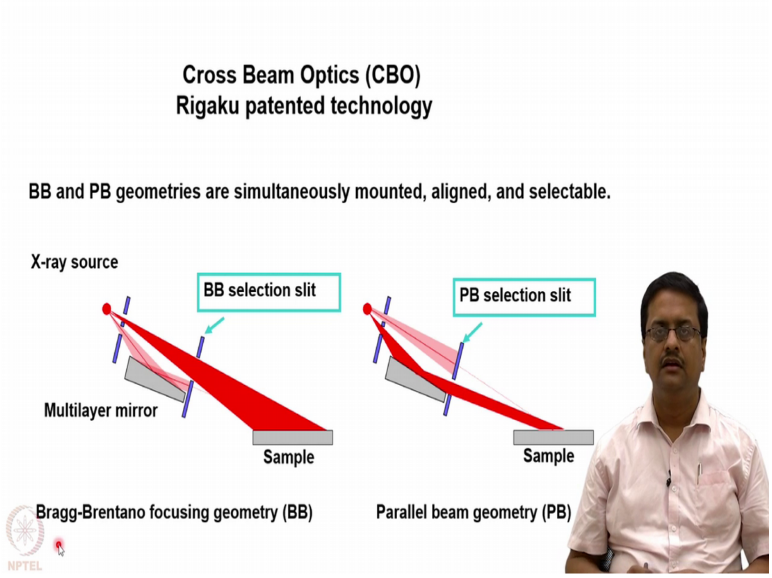

Cross Beam Optics (CBO)
Rigaku patented technology

BB and PB geometries are simultaneously mounted, aligned, and selectable.

Bragg-Brentano focusing geometry (BB)

Parallel beam geometry (PB)

This slide is going to describe the optics optical alignment of this powder X-Ray diffractometer X-Ray beam. See for a powder diffraction we do not use a circular focus beam, we use a line focus beam where the line is falling on the sample. So, now this line can be a divergent beam or can be a parallel beam. So, there are two different ways one can use that beam for the experiment.

So, this schematic diagram shows the cross beam optics which is a patented technology by Rigaku Corporation. Now it is Rigaku for diffraction the BB is Bragg Farentino. And PB means parallel beam geometries are simultaneously mounted and aligned and they are selectable by a change of slit. So, if you have a source and the source has two openings, here in the shutter and both the beams come.

So, once you pass through the first shutter then you have a Bragg Brentano slit; which allows the divergent beam to fall on the sample and cover the larger area as much as possible of the sample and go back and get diffracted. Whereas, in case of parallel beam geometry a parallel beam slit is used the top beam which was open here is now blocked. And the bottom beam which comes through the lower part of this slit gets reflected from this multi layer mirror.

And the divergent beam after getting reflected from this becomes a parallel beam which falls only on a portion of that particular sample and gets diffracted. So, this parallel beam geometry is actually useful when you have a very small amount of sample and the rest of the sample plate is empty. So, you do not want the sample plate also to diffract. So, if you want the beam only to fall on your sample we just localized the sample in the middle and do this experiment.

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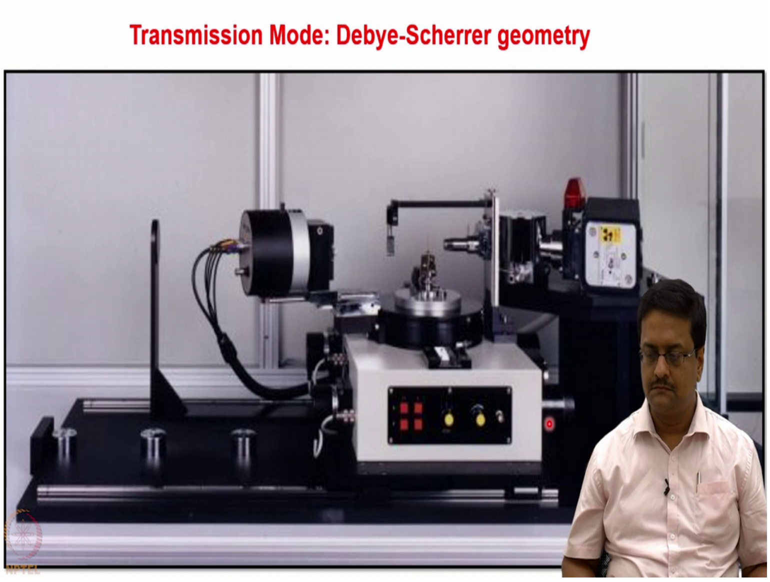

Transmission Mode: Debye-Scherrer geometry

This is a diffractometer the photographer a diffractometer of a very old fashion where the goniometer used to be mounted on the horizontal base. On the right hand side here we have the X-Ray tube the X-Ray beam comes like that in the horizontal direction. In front we have a beam stop which stops the direct beam and on the other hand. And we have a detector which in those days used to be where this detector or position sensitive detectors.

So, here what happens is the sample is placed in a capillary and the capillary can be rotated about its axis by about 300 RMP or 100 RMP or whatever depending on what you want. And then the diffracted beam is actually passing through the sample. So, it is called a device or a geometry not a reflection geometry it is a transmission geometry. So, you have one capillary mounted you have X-Ray beam coming from this side. It is getting transmitted through the sample and getting diffracted on the back and the detector is recording the diffraction pattern.

So, this transmission mode geometry is particularly useful for samples which are less absorbing less absorbing in X-Ray. And is also useful when we mount the sample in a capillary you see many samples can be moisture sensitive air sensitive or whatever. So, those samples they need to be closed or enclosed in a glass capillary. A special Lindeman glass capillary and then those capillaries are mounted on this type of rotating capillary rotating stage. And then you do the X-Ray diffraction experiment.

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Applications of PXRD

- Detection of the nature of the solid: Crystalline or Amorphous
- Bravais lattice identification
- Lattice parameter determination
- Identification of known/previously reported materials or phases
- Identification of different phases: Polymorphs, solvates etc.
- Detection of impurity
- Structure solution
- Rietveld refinement

So, what are different applications of powder X-Ray diffraction? The applications range from the detection of how the material is whether it is a solid or amorphous material. So, we want to know the crystallinity of a substance. One can use it for Bravais lattice identification only you can finally, use it for Lattice parameter determination, Identification of known or previously reported materials or phases, Identification of different phases or polymorphs or solvates, Detection of impurity, Structure solution, and Rietveld refinement as. We will try to see one of these points one by one.

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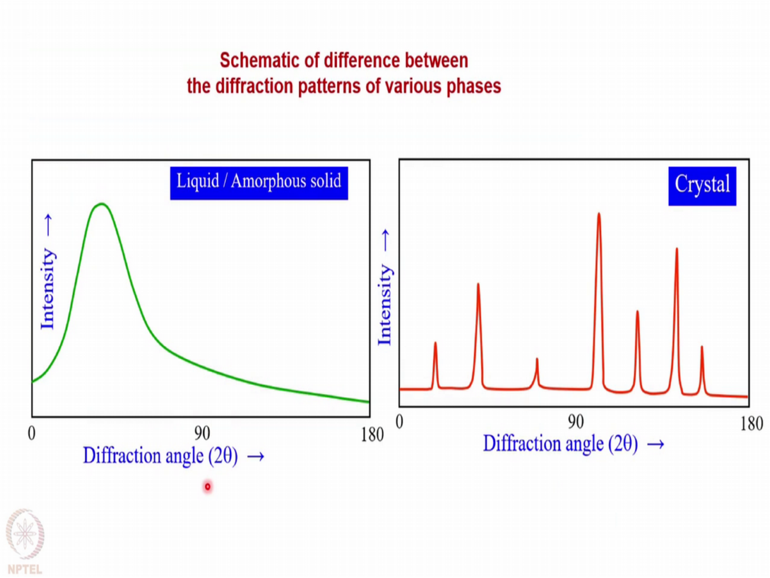

Schematic of difference between the diffraction patterns of various phases

So, as you know that the outer the amorphous materials do not diffract X-Ray, in any way that crystal. As you know that the amorphous samples diffract X-Ray and shows a peak like that which is a very broad hump and the crystalline materials the materials diffract X-Ray following Bragg's Law and gives individual peaks.

So, that indicates that the material will be crystalline if it go gives you a set of peaks following Bragg's Law. And if it simply gives a hump one or multiple humps it means that it is a liquid or an amorphous sample.

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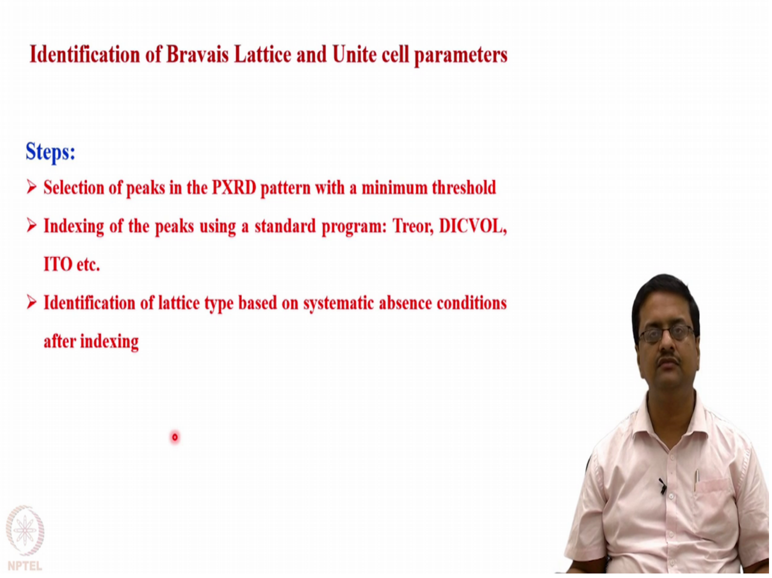

Identification of Bravais Lattice and Unite cell parameters

Steps:

- Selection of peaks in the PXRD pattern with a minimum threshold
- Indexing of the peaks using a standard program: Treor, DICVOL, ITO etc.
- Identification of lattice type based on systematic absence conditions after indexing

So, when we try to identify the Bravais lattice and unit cell parameters from a given powder X-Ray diffraction data. We need to follow a few guidelines or steps we first select, the peaks in the PXRD pattern with minimum threshold. So, we do not want to eliminate any very small peak that may be present in the powder X-Ray diffraction pattern.

Then we trying to index these peaks using some standard programs computer programs Treor, DICVOL, ITO and all that. Nowadays we have dash as well for some indexing PDXL also does the indexing path of powder diffraction data. So, then based on that one can identify the lattice type and based on systematic absence. Ad after indexing one can try to get the space group as well, but that is very different very difficult

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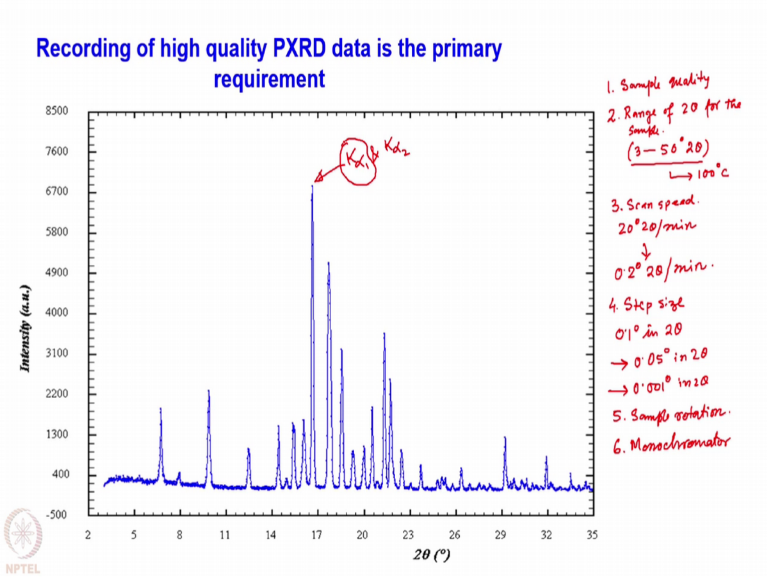

Recording of high quality PXRD data is the primary requirement

1. Sample quality
2. Range of 2θ for the sample.
$(3 - 50° 2\theta)$
↳ 100°C
3. Scan speed.
20° 2θ/min
↓
0.2° 2θ/min.
4. Step size
0.1° in 2θ
→ 0.05° in 2θ
→ 0.001° in 2θ
5. Sample rotation.
6. Monochromator

The first thing is that we one has to record a very high quality PXRD data using the instrument available. So, to measure the powder X-Ray diffraction data we need to remember a few things. Number 1 the sample quality; for a powder diffraction data measurement the sample must be finely powdered. It should not be with moisture we have a weight or moisture sensitive or it should not contain any moisture in it so that it should be free flowing powder.

Number 2, we need to know the range of 2 theta for the sample. so, at priori we will not know this number so what we can do is mount the sample collected data very quickly like; about 10 degree per minute or whatever from 3 to 70 degree, 2 theta and see what is the range of peaks that we are getting for this particular sample depending on what range we get we should choose a specific region. Say for example, we have only peaks from 3 to 50 degree in general for organic or organometallic samples this range is 3 to 50 degree 2 theta.

This is a general common range for organic and organometallic samples, but for different inorganic materials we may want to go to about 100 degree in 2 theta because that will be peaks at much higher angle as well. Then we decide the scan speed; depending on the need of this data what will be the application for of these data one has to choose this scan speed. The scan speed can be as fast as 20 degree 2 theta per minute, to as slow as 0.2 degree in 2 theta per minute.

You can emerging that for recording from 3 degree to 50 degree with 20 degree per minute it takes only about 3 minutes. When it is 0.2 degree per minute it will take about three hundred minutes which means about 5 hours. So, what we are going to do with the data becomes important while choosing this scan speed. What happens when we use a small lower scan lower scan speed we can use these step size. So, the fourth point is the step size what is the interval of two theta at which we want that data to have a one point.

So, normally this step size is about 0.1 degree in 2 theta this can be reduced to 0.05 degree in 2 theta, depending on the need. It can be as low as 0.001 degree in 2 theta. Provided the sample is highly diffracting and we would like to use this sample or we would like to use this data for structure solution and refinement purposes or for rietveld refinement and so on we need to choose the step size accordingly. The step size and scan speeds are to be chosen in such a way that it is not too fast or it is not too slow. So, suppose if we do a scan speed of 1degree per minute with a step size of 0.001 degree per minute the for 0.001 degree in 2 theta; that means, it is extremely fast for every data point.

Whereas, if we do the reverse if we do it like 0.05 degree per minute and 20 degree per minute scan speed, then also it is extremely fast. So, depending on the need and requirement we should choose this scan speed and step size accordingly. So, that a sufficient amount of time is given for every step to record the diffraction data. This will help us in resolving the peaks which are very close in d value in case of different samples.

The point number four that one has to remember is sample rotation. A powdered sample is a is an assembly of a large number of micro crystalline particles. And it may be possible that a large fraction of those micro crystalline particles when spread on a sample plate gets aligned in one particular direction due to the mechanical the force with applied during the spreading process. So, if that happens then some of those peaks some of the peaks which are coming from those pre aligned crystalline particles will have unusually higher intensity compared to the other peaks, which is called the preferred orientation effect.

So, to avoid that special orientation effect one has to rotate the sample about its axis during the data collection. Normally it is done at about 100 to 120RMP speed. In general these powder X-Ray diffractometers are not equipped with a monochromator. So, these peaks that we see are combination of K alpha 1 and K alpha 2, but if you want you can use a monochromator as well. To get only K alpha one, but in that case the intensity of K alpha one reduces drastically. So, these are the points one has to remember during a data collection.

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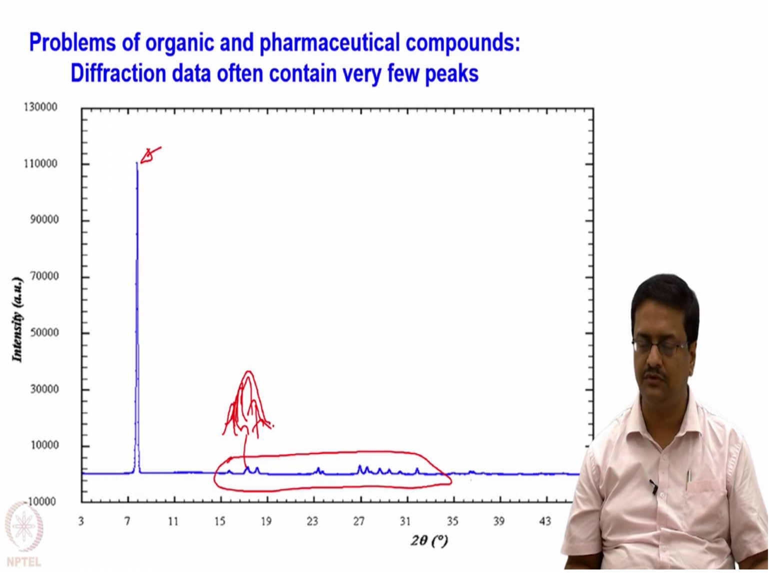

Problems of organic and pharmaceutical compounds:
Diffraction data often contain very few peaks

Often what we see is for organic and pharmaceutical samples diffraction data often contain very few peaks. See here we have one large peak, but other peaks are extremely small and they are very broad. If you try to enlarge them you will probably see this peak when enlarged looks like that. This indicates that a large number of d values are highly in between here and there. It may be a combination of several such peaks so this becomes a difficult process to get indexing done on this type of samples.

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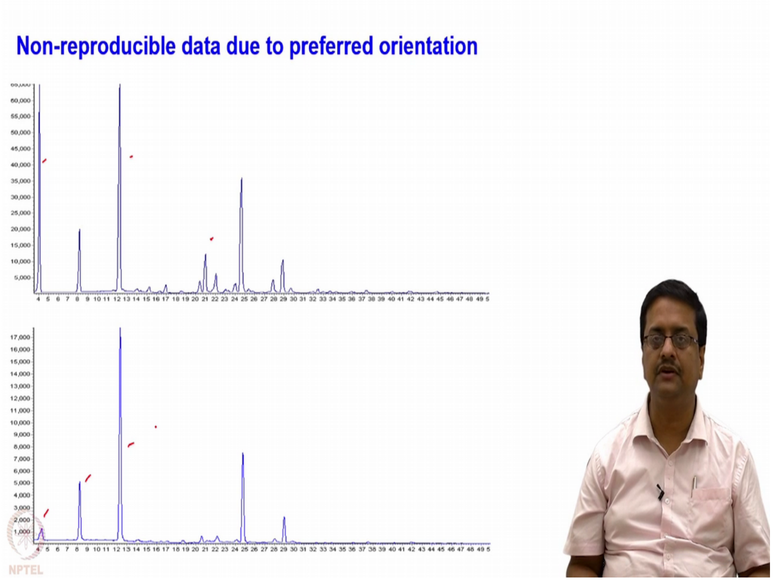

Non-reproducible data due to preferred orientation

It may this the case where it is non reproducible data due to preferred orientation effect. Once we have recorded a data we get this type of in density statistics as shown here. In a different experiment on the same sample we get different intensity statistics. You see the peak positions are same, but the intensity statistics and intensity ratios are different. So, this different intensity ratios indicate that there is some problem in sample preparation or the sample rotation was not done. As a result these preferred orientation effects have come up so strict significantly.

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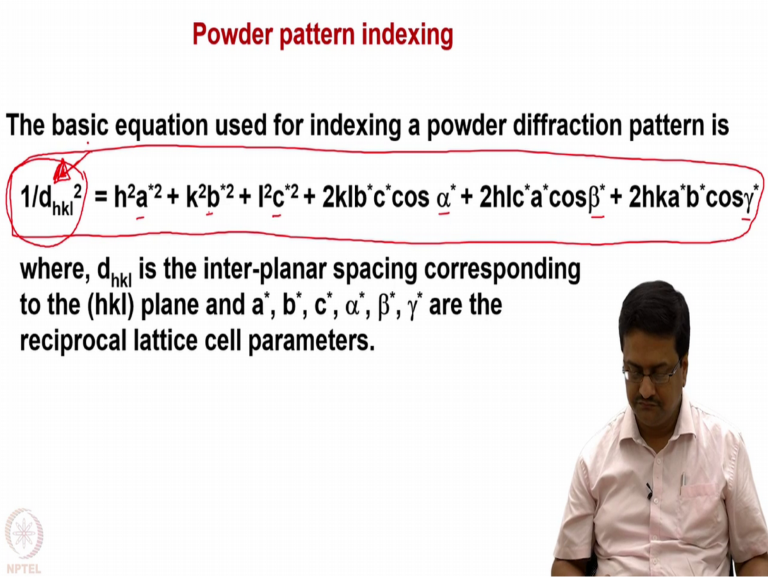

Powder pattern indexing

The basic equation used for indexing a powder diffraction pattern is

$$1/d_{hkl}^2 = h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2klb^*c^*\cos\alpha^* + 2hlc^*a^*\cos\beta^* + 2hka^*b^*\cos\gamma^*$$

where, d_{hkl} is the inter-planar spacing corresponding to the (hkl) plane and a^*, b^*, c^*, α^*, β^*, γ^* are the reciprocal lattice cell parameters.

So, during the process of indexing and once again we use the condition of Bragg's Law in reciprocal space. And all of us now know this particular relation between the 1 by d hkl with the hkl and the reciprocal lattice parameters a star, b star, c star. And alpha star, beta star, and gamma star. You see this equation is a compulsive equation when it is for triclinic and that is why we need a computer program to solve this equation for a large number of h k and l with a b and c as unknowns. What we have knowns are the corresponding d values and d two theta values where it is appearing.

So, here we have unknowns like abc, hkl, alpha beta gamma so we have 9 unknown quantities. So, we need a large number of d values to be able to solve this simultaneous equation to get the values for a b c. And then identify each and every peak in the powder diffractogram with the corresponding miller indices h k and l. This becomes easier when we use any cubic sample which I think have been discussed in one of the lectures where we try to index a powder pattern for a cubic system using a diversion or method.

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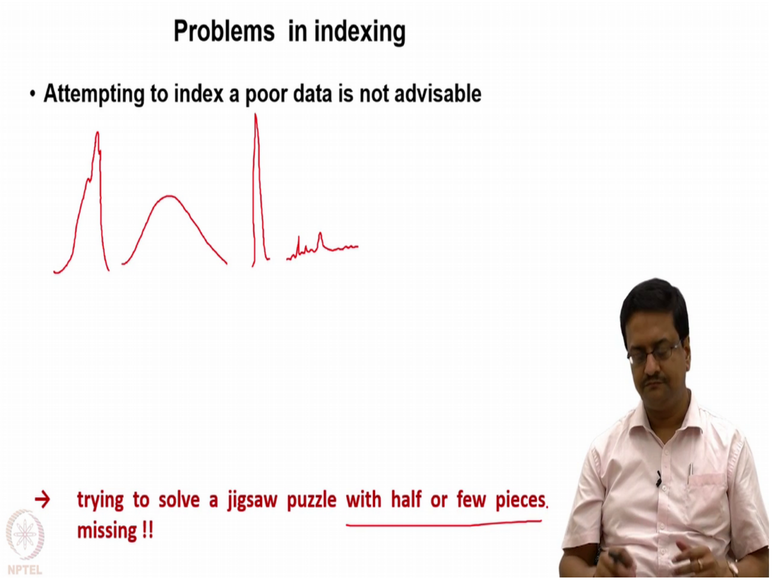

Problems in indexing

- Attempting to index a poor data is not advisable

→ trying to solve a jigsaw puzzle with half or few pieces missing !!

So, as you know for indexing you need large number of well defined peaks, attempting to index a poor data is not advisable. What do we mean by a poor data is nothing, but if you have data containing large number of this kind of peaks or the peaks are very broad or you have one peak very large and the other peaks are extremely small and disappearing in the background if you have some such kind of powder data.

There is no point in trying to index those diffraction patterns. It is like trying to solve a jigsaw puzzle with half or some pieces missing because you see you need to solve this simultaneous equation which contains total 9 unknown quantities and only observed parameters are a set of d h k. So, until and unless you have a large number of well defined d values the computer program will not be able to solve these equations and give you correct numbers for a b c alpha beta gamma and then hkl will also.

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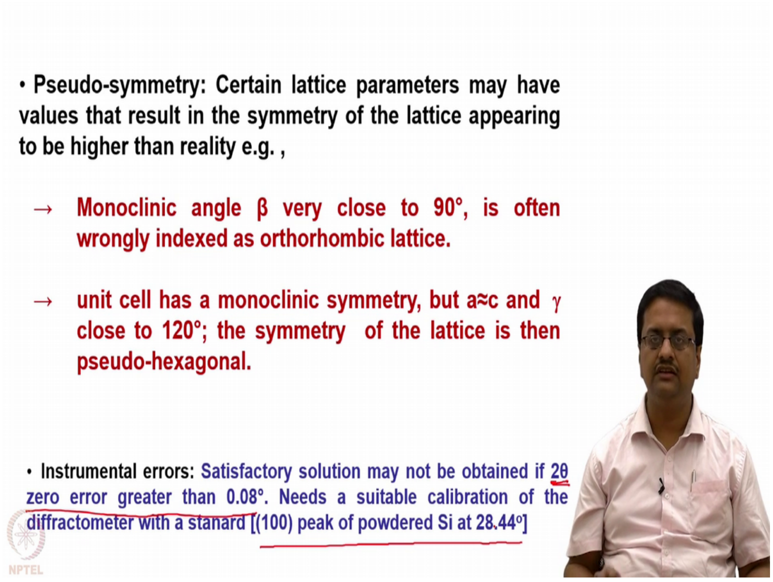

- Pseudo-symmetry: Certain lattice parameters may have values that result in the symmetry of the lattice appearing to be higher than reality e.g. ,

  → Monoclinic angle β very close to 90°, is often wrongly indexed as orthorhombic lattice.

  → unit cell has a monoclinic symmetry, but a≈c and γ close to 120°; the symmetry of the lattice is then pseudo-hexagonal.

- Instrumental errors: Satisfactory solution may not be obtained if 2θ zero error greater than 0.08°. Needs a suitable calibration of the diffractometer with a stanard [(100) peak of powdered Si at 28.44°]

Even in case of some pseudo symmetry for example, certain lattice parameters may have values that may result in the symmetry of the lattice appearing to be higher symmetry. For example, monoclinic b monoclinic system with beta angle very close to 90 degree often wrongly indexed as orthorhombic. Unit cell parameters with the monoclinic symmetry, but having a equal to c and gamma equal to 120 degree, may also lead to sorry beta equal to may 120 degree may also lead to hexagonal lattice. So, this things can give wrong information in your indexing para software.

There may be instrumental errors as well so a satisfactory solution may not be obtained if there is a 2 theta 0 error greater than about 0.08 degree. So, if there is any instrumental error in the system and every peak is deviated by above 0.1 degree, then the indexing software would help would, would fail. So, for every experiment of powder X-Ray diffracts one should look at this particular peak before measuring the sample. One should use powder silicon and measure its first peak which is call which corresponds to 1 0 0 reflection. That appears are 28.44 degree in 2 theta so by measuring the standard reflection we make sure that the diffractometer is well aligned and it is 0 when it goes to 0.

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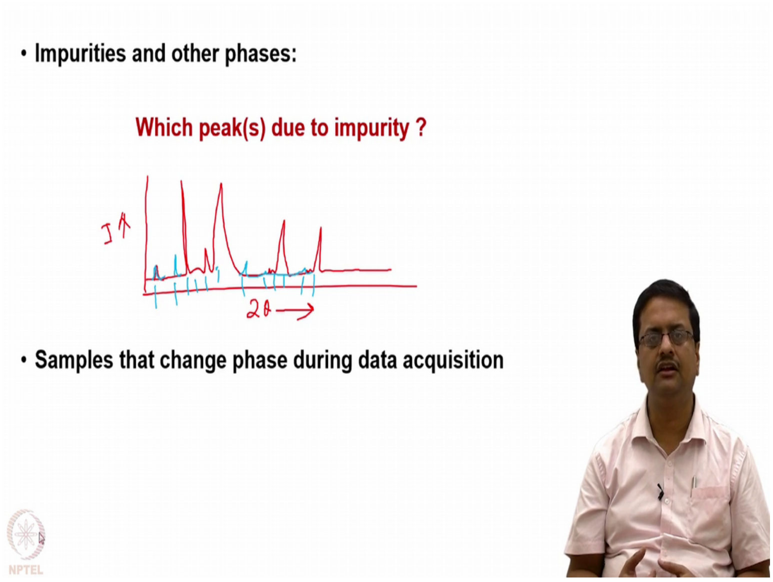

- Impurities and other phases:

Which peak(s) due to impurity ?

- Samples that change phase during data acquisition

A powder diffraction pattern may also show that there are presents of impurities. But when we get a sample when we try to measure powder X-Ray diffraction data on a sample we do not know whether the sample contains an impurity or not. So, in addition to the regular peaks which may be sharp and when spaced like a real structure. There may be some peaks which have might appear from some other impurity present in the sample. So, at the beginning we will not know that this sample is not pure. So, in that case what we would do is we would try to pick up all those peaks that have appeared.

And then throw them in a computer program to solve those simultaneous equations, but you see if the peaks are not from same compound although they are following Bragg's Law or reflection, but the unit cell parameters are not same. So, the d values will not match and as a result the indexing program will completely fail it will not be able to identify these peaks not be able to solve the a b c alpha beta gamma. The another case can be such that during the data recording, the sample might change the phase during the data collection itself; which can happen for samples which are sensitive to moisture.

During the X-Ray diffraction which may take anytime between 10 to 10 minutes to 1 hour. During this process if it absorbs moisture and changes phase, the beginning part of the data will have the patterns from one particular crystal. And the later part of the data will have the hydratent or acquated sample diffraction data. So, those peaks we will not be able to identify physically because we do not know that the change has happened. So, once we throw those peaks to the power structure solids, throw those peaks to be indexing programs like Treor, DICVOL; they will fail and will not be able to give us any indexing.

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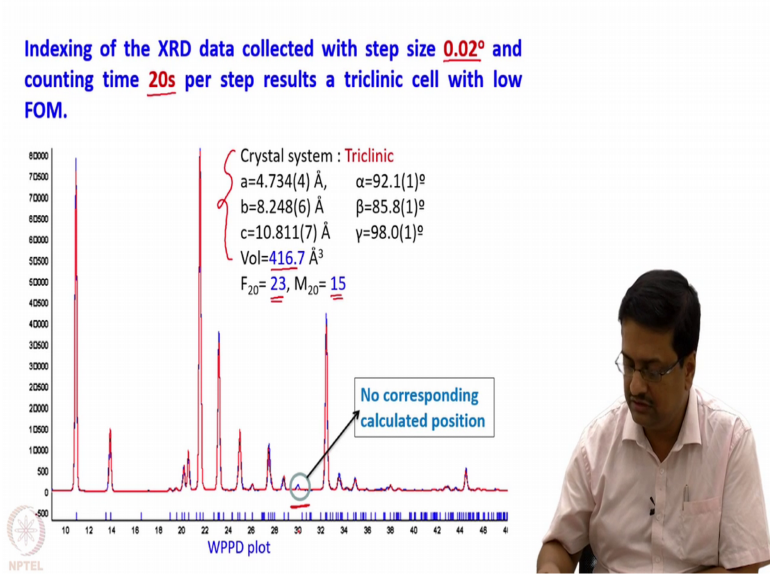

Indexing of the XRD data collected with step size 0.02° and counting time 20s per step results a triclinic cell with low FOM.

Crystal system : Triclinic
a=4.734(4) Å, α=92.1(1)º
b=8.248(6) Å β=85.8(1)º
c=10.811(7) Å γ=98.0(1)º
Vol=416.7 Å^3
F_{20}= 23, M_{20}= 15

No corresponding calculated position

WPPD plot

Here is one classic example of if the use of better step size than normal. So, when this data was recorded with a step size of 0.02 degree and the counting time of 20 seconds per step. All the peaks that were we have selected gave us one triclinic lattice like this with volume 416 cubic angstrom. But we saw that the figure of merit values are very small.

And what we identified is that for one particular peak there was no corresponding calculated position. So, there is option that you can calculate the peaks based on the indexing as well. So, one particular peak did not have the calculated position or rather the calculated peak position; there was a peak, but there was no real peak in red in that.

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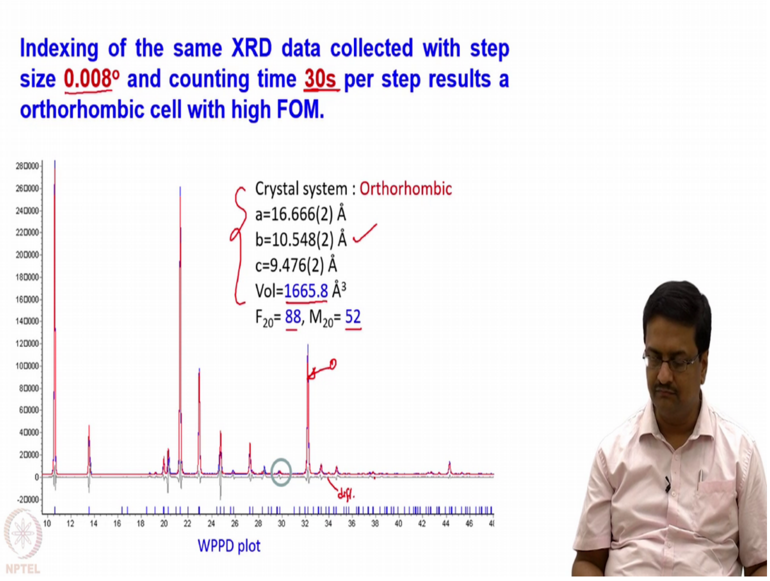

Indexing of the same XRD data collected with step size 0.008° and counting time 30s per step results a orthorhombic cell with high FOM.

Crystal system : Orthorhombic
a=16.666(2) Å
b=10.548(2) Å
c=9.476(2) Å
Vol=1665.8 Å^3
F_{20}= 88, M_{20}= 52

WPPD plot

But then when the same data was recorded with much smaller step size of 0.008 degree in 2 theta with a longer data relation times in, 30 seconds per step. What we see is that the figure of merit serving into improve they lot these are the parameters that come as outcome of that software data indexing software. And it gives an orthorhombic unit cell of 4 times volume.

And all the peaks that are originally there in red are calculated in blue and the difference is here. So, for that tiny peak which was not getting not there in the original peak is now showing up here. So, that peak means that that I had indexing means not be unit cell that we are getting is right. Because it then calculates all the peaks that are present and the lattice and it does not calculate any additional peak.

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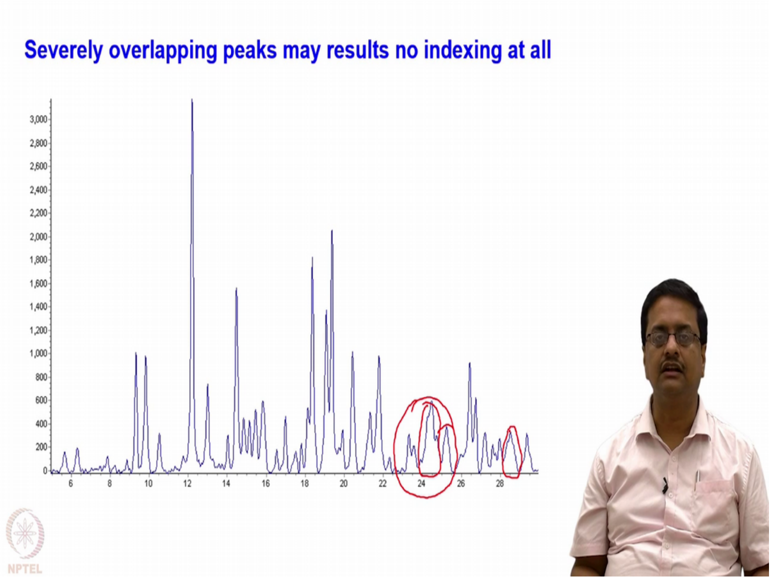

Severely overlapping peaks may results no indexing at all

Severely overlapping peaks also may result in no indexing at all; which means if the d values are very close for one particular sample then also the peak will the indexing software will fail. If you concentrate on this region you can see that the peaks around here, peaks around there, and also peaks around there are merging on one on top of the other; and hence the indexing software cannot do justice to this particular pattern.

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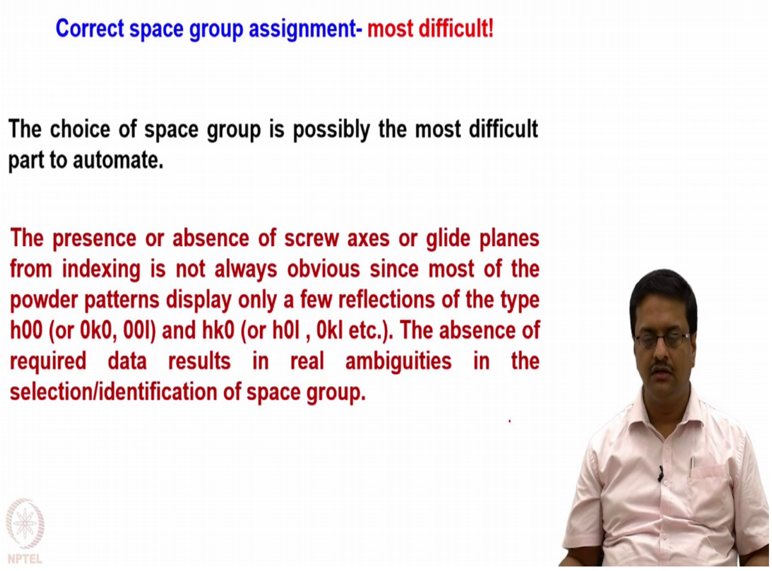

Correct space group assignment- most difficult!

The choice of space group is possibly the most difficult part to automate.

The presence or absence of screw axes or glide planes from indexing is not always obvious since most of the powder patterns display only a few reflections of the type h00 (or 0k0, 00l) and hk0 (or h0l , 0kl etc.). The absence of required data results in real ambiguities in the selection/identification of space group.

Correct space group determination is the most difficult job here because as you know the choice of space group is based on systematic absence conditions. In case of a routine X-

Ray data single crystal X-Ray data you have a large number of h k l's. For example, you may have some 1,000, 2,000, 3,000 reflections. So, once we will go through all those reflections it becomes easy to identify these systematic absence conditions.

But here the total number of peaks may be 100, at best 150, but then among those 150 we need to look for special reflections like 800 or 0 k 000 l or h 0 l. h k 0 are whatever. All those special reflections which suffer due to systematic absence are very less in number. And then it becomes very difficult to determine the space group from this powder X-Ray diffraction data. What one can do is that you can identify the index data using ICSD; Inorganic Crystal Structure Database is maintained by international center for diffraction data.

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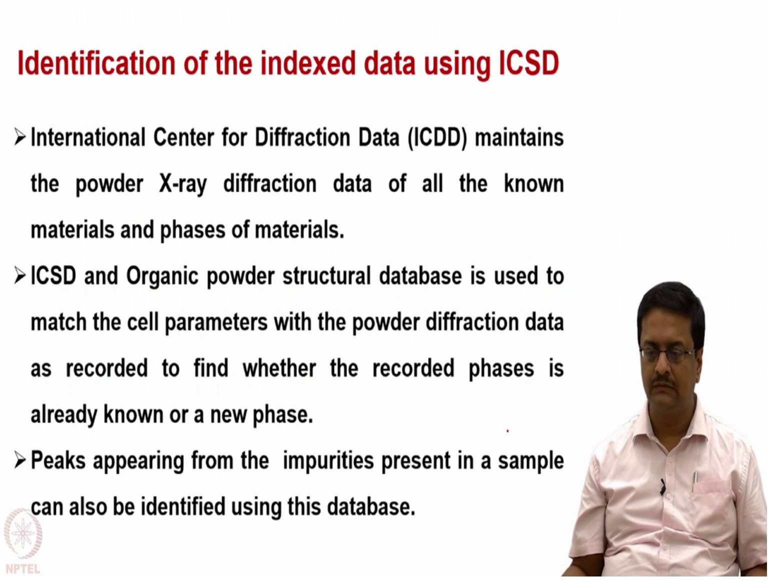

Identification of the indexed data using ICSD

- International Center for Diffraction Data (ICDD) maintains the powder X-ray diffraction data of all the known materials and phases of materials.
- ICSD and Organic powder structural database is used to match the cell parameters with the powder diffraction data as recorded to find whether the recorded phases is already known or a new phase.
- Peaks appearing from the impurities present in a sample can also be identified using this database.

So, it actually an out maintains both inorganic and organic powder X-Ray diffraction data. So, if one has access to this ICSD and organic powder structural database you can use the database compared the powder pattern that one has generated with the already reported powder X-Ray diffraction data. And then one can conclude that; ok, I have generated a previously known phase or I have generated a new phase of that same material.

If we know the history of a sample; how the sample was made then one can identify what kind of impurities that may be present using these databases as well. So, for example, if we have done a solid state reaction by reacting two different oxides at very high temperature and tried to make a new material. If the new material contains some of the starting material some of the starting oxides, tiny peaks of those starting materials would appearing the final powder pattern. And one can then identify by comparing the observed pattern with the reported pattern for starting materials the peaks that are from starting material.

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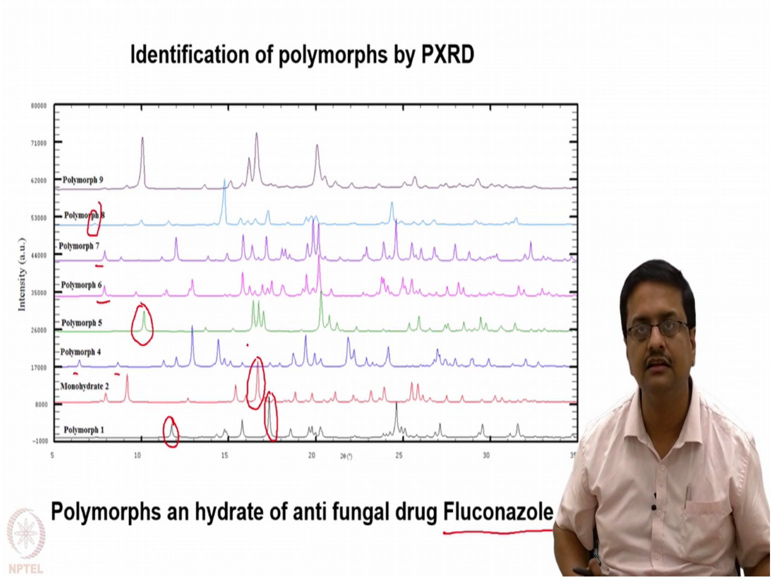

Identification of polymorphs by PXRD

Polymorphs an hydrate of anti fungal drug Fluconazole

So, here I am showing one example of identification of polymorphs by powdered X-Ray diffraction data. As you might know that polymorphs are structural variations of a given compound which was probably crystallized using different solvents, different temperatures, or maybe even different methodologies, like solvent evaporation solvent drop grinding and so on.

Even polymorphs can be generated from same beaker in the same solvent at, but have two different structures. So, polymorphs are structural variation of is single compound that we can think of. So, here you can see that a particular compound Fluconazole we used this for our experiments in the lab. There are nine different polymorphs of this compound known where the more polymorph 1 2, where this is a monohydrate polymorphs 4 5 6 7 8 and 9. If you look at their powder diffraction data you can see the peak positions are all different; polymorphs 1 has the first peak somewhere here.

But polymorphs 4 has peaks there, polymorphs 5 has a first peak here, polymorphs 6 has here, 7 here and all that; and then we maximize up at all different places. So, this indicates that a powder X-Ray diffraction pattern is very useful in identifying generation of different polymorphs. One can simply compare the powder patterns placed one on top of the other and identify whether they are the same crystalline phase of different.

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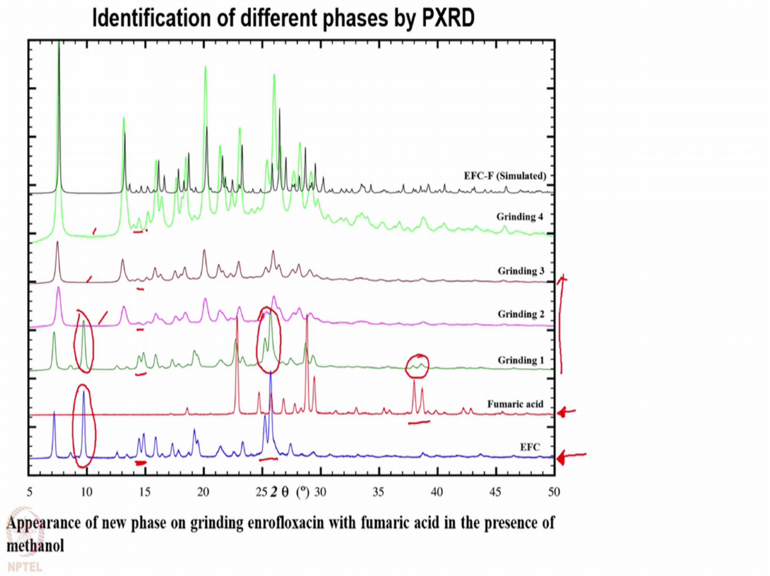

Identification of different phases by PXRD

Appearance of new phase on grinding enrofloxacin with fumaric acid in the presence of methanol

Powder X-Ray diffraction patterns can be used to identify different phases. So, here what I am trying to show is the following follow up of one experiment the lowest most one is a pure drug called enrofloxacin. The second one that we have is a coke list of former organic acid, fumaric acid. And we try to mix them in one is to one ratio and trying to grind them using some solvent; thinking that they will react and for may solve. So, after first grinding what we see is that the peaks of both drug and co farmer are simultaneously present.

See these peaks are from drug these peaks are formed sorry these peaks are from co foreman these peaks are from drug. And when we are doing this grinding experiment a few times what we see that slowly the peaks of the drug is disappearing. See this is a peak of the drug that peak has totally disappeared here, there, there, and that’s it. See these peaks were there it was slightly there is still little bit there and then new peaks appear here. So, this following up of a particular grinding and crystallization experiment is done using a powder diffraction method.

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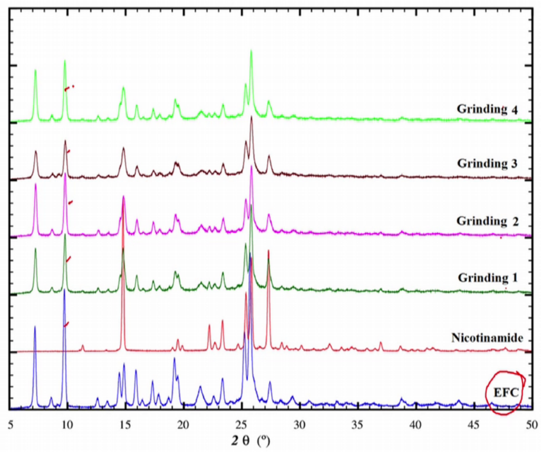
Identification of different phases by PXRD



Grinding of enrofloxacin with nicotinamide in the presence of methanol did not generate new phase

So, even the same kind of experiment that was done on a different sample and what we see here is that this experiment is not going. So, even during grinding 1 to 2 to 3 to 4 the peaks of the drug enrofloxacin is not disappearing this peak remains as it is after several rounds of grinding. So, this indicates that the reaction is not going. So, one can use powder X-Ray diffraction to see whether a reaction is going or not.

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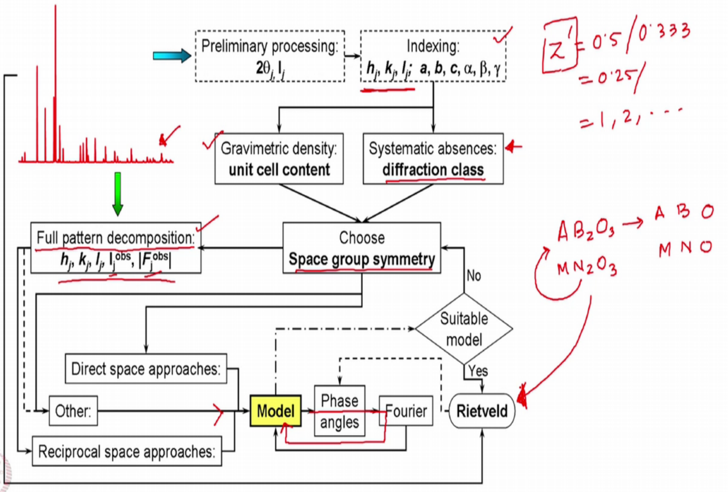
Steps in structure determination from powder data


Preliminary processing: $2\theta_i, I_i$

Indexing: h_i, k_i, l_i; $a, b, c, \alpha, \beta, \gamma$

Gravimetric density: **unit cell content**

Systematic absences: **diffraction class**

Choose **Space group symmetry**

Full pattern decomposition: $h_j, k_j, l_j, I_j^{obs}, |F_j^{obs}|$

Direct space approaches:

Other:

Reciprocal space approaches:

Model

Phase angles

Fourier

Suitable model

No

Yes

Rietveld

$\boxed{Z'} = 0.5/0.333$

$= 0.25/$

$= 1, 2, \ldots$

$AB_2O_3 \rightarrow A\ B\ O$

MN_2O_3 $\quad M\ N\ O$

Now, in this busy slide I will explain the steps in determination of structure from powder X-Ray diffraction; which I must say that is one of the most difficult tasks to do in X-Ray crystallography. But there are research groups who work on this for various samples where one cannot generate the single crystals or some phases only exist in order form and it changes its form when recrystallized and so on. So, what is done is that in case of structure solution from powder X-Ray diffraction. The first of most important point, is to get a very high quality powder X-Ray diffraction data.

So, normally this powder X-Ray diffraction data is recorded at a synchrotron source with a very high intensity X-Ray energy. And as a result the data that you get is highly resolved the peaks that you get are very sharp, not no merging of peaks, so one can identify all the peaks uniquely and then index those peaks. So, here the schematic diagram shows the entire process of powder such a solution from powder X-Ray diffracts.

So, the first point is the preliminary processing, that is; to extract the 2 theta values and intensities of all the peaks that are there in the pattern. In this case we try to collect the data as much as possible, sometimes from 3 degree to 100 degree in 2 theta in an for organic samples. And then we throw all these 2 theta values that is d values to a suitable indexing problem. And identify all the peaks with the corresponding miller indices hkl and calculate the lattice parameter a b and c with alpha beta gamma together.

We should have a reasonable idea about the density of the sample which then would allow us to identify how many such molecules are there in the unit cell to give us that particular density. This will identify whether we have z equal to half structure, z equal to 1, or z equal to z prime equal to 2. I mean to say that whether in the isometric unit. I have half molecule that is z prime equal to point 5, it can be dependent 0.333[noise]. If the molecule has a threefold axis z prime can be even 0.25 in the molecule is sitting on a 2 by m position. A special position half z prime can be equal to one two and any other higher number as well.

So, to know what is the value of z prime one has to have information about the density of the unit cell density of the compound so from that point m gets the unit cell contents. Using the large number of h k l's originating from the data; one has to gets the systematic absences get the systematic absences and try to determine the space group with the information of Bravai's lattice whether it is one of the primitive or centered lattice or whatever. So, once we know the mutual parameters and the space group.

The next step is to do a pattern decomposition, this pattern decomposition also is not very easy there are a few software that one can use to generate the I obs and get the F obs for a large number of reflections. Generated from a very limited number of reflection present in the powder X-Ray diffraction data. So, then if this pattern decomposition is successful there are only methods to do that. And then this pattern decomposition and maybe some other direct space approach you try to solve the structure. So, after getting in larger number of h k l's with the corresponding I observed and calculated structure factor that is F absorbed, one can solve using standard methods. And get a starting model that is the starting model of that particular structure.

So, then one can apply the phases you can do Fourier and go back and modify the model. So, this model to Phase, Phase to Fourier, Fourier to model this cycle continues repeatedly till again the r factor is lowered and so on and we reach a reasonable structure. There is another wave that is possible is that after getting the indexing done, if one can identify if this particular unit cell is matching with a known molecule. And if then known molecule has the same molecular formula with our compound then one can try to do a method which is called rietveld refinement.

And define the freshly collected powder data on our sample based on the data that is available on a different sample. So, suppose if one has a data on a compound AB2O3 for that we know the coordinates of AB and O. But then somebody has made a compound MNN2 ABO3 MN2O3 and finds that it has a same lattice parameter as that it has the same powder diffraction pattern as AB2O3. Then one can use the coordinates of AB and O for the coordinates of MN and O to start with.

And then group a refinement which is called the rietveld refinement of such a solution and use this method to illustrated structure of samples which are no not known, but is known in terms of structural class determined by somebody else. So, this rietveld refinement I am not going in much details because that is also a different area of research and involves a lot of mathematics and understanding of this refinement.

We will end our discussion on powder X-Ray diffraction today with this note that this is the most useful method for structural characterization. One can find out a large number of different physical point for parameters identifying polymorphs, identify impurities, and solve structures and do rietveld refinement. I must say that this structure solution from powder X-Ray diffraction is still very difficult even today.

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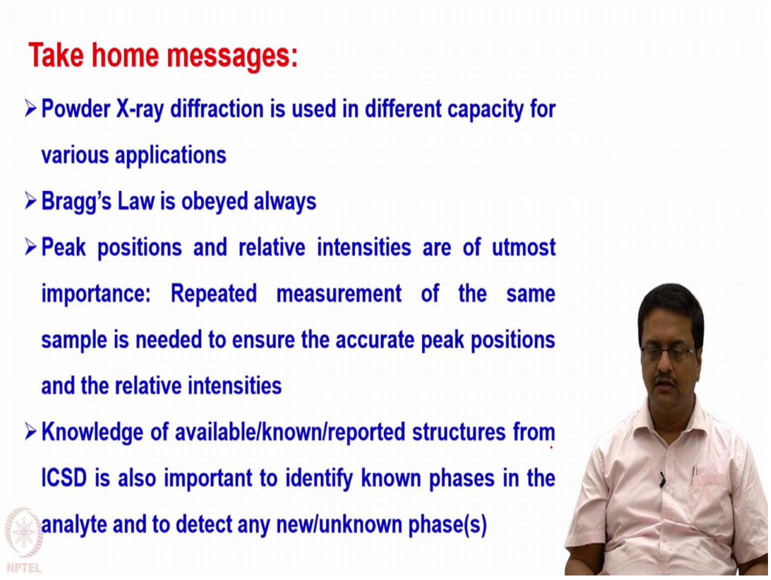

Take home messages:

- Powder X-ray diffraction is used in different capacity for various applications
- Bragg's Law is obeyed always
- Peak positions and relative intensities are of utmost importance: Repeated measurement of the same sample is needed to ensure the accurate peak positions and the relative intensities
- Knowledge of available/known/reported structures from ICSD is also important to identify known phases in the analyte and to detect any new/unknown phase(s)

So, the take home message is powder X-Ray diffraction is used in different capacity for various applications. Bragg's Law is always obeyed, Peak positions and relative intensities are of upmost importance. Repeated measurement of the same sample is needed to ensure the accurate peak positions and relative intensities. Knowledge of available or known or reported structure from ICSD is also very important to identify the known phases. In the analyte and to detect new are unknown phases. So, when we go to the powder diffractometer rule we will demonstrate, how a powder sample is prepared and a data is recorded and then interpreted.