Physics of Renewable Energy Systems
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Lecture 44
Characterization Techniques for Solid Materials

Hello, so, we will start the final 2 modules of this course on physics of renewable energy systems. In these two modules, we will be talking extensively about the characterization techniques for solid materials and also the devices that have been discussed during this course.

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You will find that we will be talking to you about a large number of techniques, not only just 1 or 2 but I plan to discuss at least 8 to 10 techniques, which would be useful to you and we will also be giving you video lectures, recordings of the way the whole process or the protocols of completing a characterization technique or the experiment.

So, we will give you the video of the way you have to proceed and get the data from a technique. And in today's lecture, I will give you the introduction to various materials characterization techniques and we will also start with the basics of X-ray diffraction technique that is used for characterizing solid materials. We will specifically try to focus on solid materials because those are relevant to us and we will try to leave the discussion for some other course regarding the X-ray diffraction of liquid samples.

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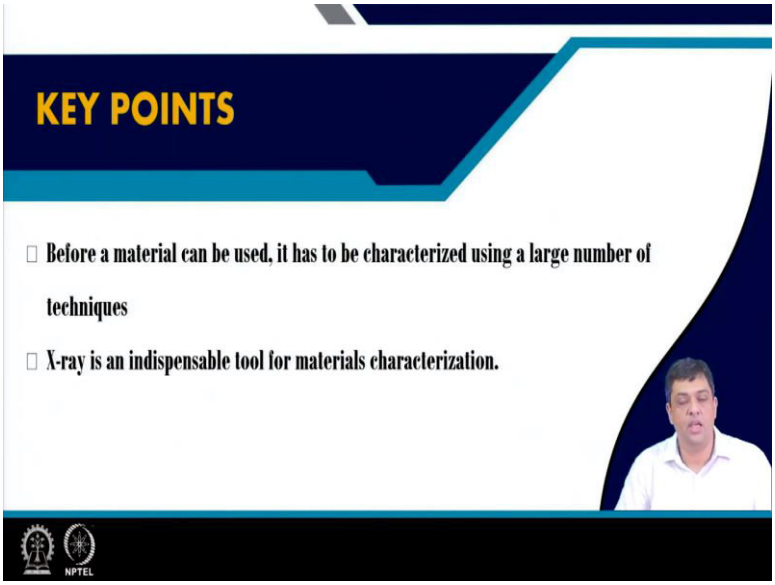

And hopefully, after you have gone through this lecture and you have revised some of the topics which I will recommend that you revise during this lecture, I will tell you that please revise certain topics. I hope after that you will clearly understand that before a material can be used in devices or for any other application it has to be characterized with a large number of techniques.

And X-ray diffraction technique is actually an indispensable tool for materials characterization. It is just not used for particle size calculation or unit cell parameter calculations, it actually gives you a large number of information, which if you are able to extract from data would be able to fully characterize a material.

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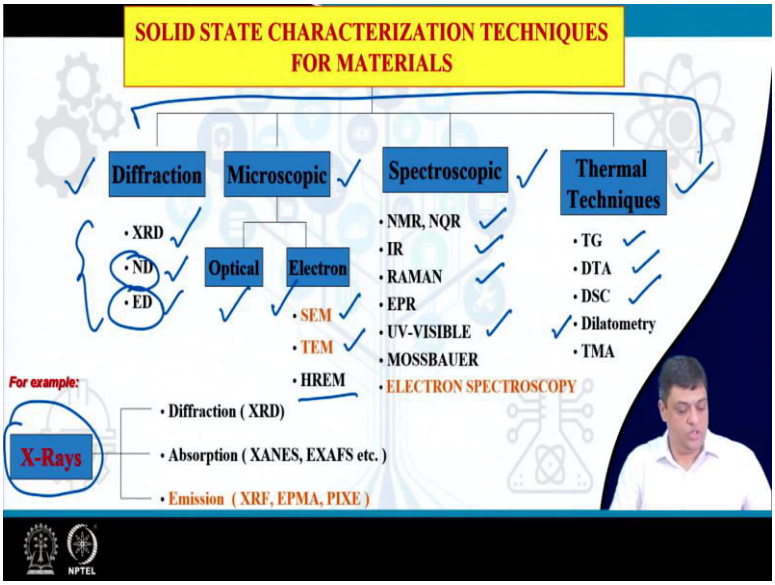

So, let us look into these characterization techniques. Broadly speaking, if you look into the techniques which we will be investigating or studying during the next 2 weeks, they can be classified under 4 broad headings. Those are the diffraction techniques, the microscopic techniques, the spectroscopic techniques and the thermal techniques.

The diffraction techniques actually encompasses 3 major techniques. Those are the X-ray diffraction, the neutron diffraction and electron diffraction and microscopic techniques can be sub classified under two headings as optical microscopy or electron microscopy. I will not discuss too much about optical microscopy, because that you have been studying probably from school days onwards

I will try to give you a brief overview on SEM, TEM, during the discussion on microscopic techniques. So, SEM stands for scanning electron microscope and TEM stands for transmission electron microscope or we can also have high resolution electron microscopy. Similarly, the spectroscopic techniques are NMR, IR, infrared spectroscopy or RAMAN spectroscopy, UV-VIS spectroscopy, MOSSBAUER spectroscopy or electrons microscopy and I plan to at least cover 3 to 4 topics of these spectroscopic techniques.

Similarly, you can have thermal techniques, those are thermo gravimetric techniques you have DTA differential thermal analyser, differential scanning calorimetry or dilatometry. So, we you can have various classifications of the characterization technique and if I look into let us say just for example, I have written X- rays, it is just not that you have one technique

based on X-rays, there are large number of techniques which use X-rays as the incident radiation and the consequences are analysed for determining various information's.

So, if you are talking about diffraction you have XRD, if you talk about the X-ray absorptions you have EXAFS or you have if you are talking about emission X-ray emission, then you have XRF, you have EPMA or PIXE. So, each of these incident radiation can be used for various characterization. In XRD, what is the incident radiation? It is the X-rays. In neutron diffraction, what is the incident radiation? It is the neutron beam. And similarly, what is the incident radiation or the beam? It comprises of electron in electron diffraction.

So, that is why you have a large number of experimental techniques and many a times people ask this question that you have a material, why do not you use a material quickly in a device and just bring out the device into the market and that is where as a physicist, as a scientist or as an engineer, we should clearly understand that before a material can be used in any of the devices which we have discussed or any other device, they must be thoroughly characterized using a large number of experimental techniques.

And if any one of these experimental results do not give you the desired output or the characteristic which you require from a material, the material will have to be resynthesized with different protocols. So, that you can get the desired performance and all the techniques actually corroborate the results from the other.

So, you an if you just can count from the slide which I have given here, you will see at least 15 techniques are mentioned. So, if a material has to be characterized using 15 techniques and you have to analyse the data and all the data should indicate toward a consistent picture, it will take a significant amount of time and therefore, taking the results from lab to market is a long drawn process and it requires lot of professional knowledge and expertise and that is why it takes significant amount of time to bring out a device and you should be able to justify this point if to anyone who asks you this question.

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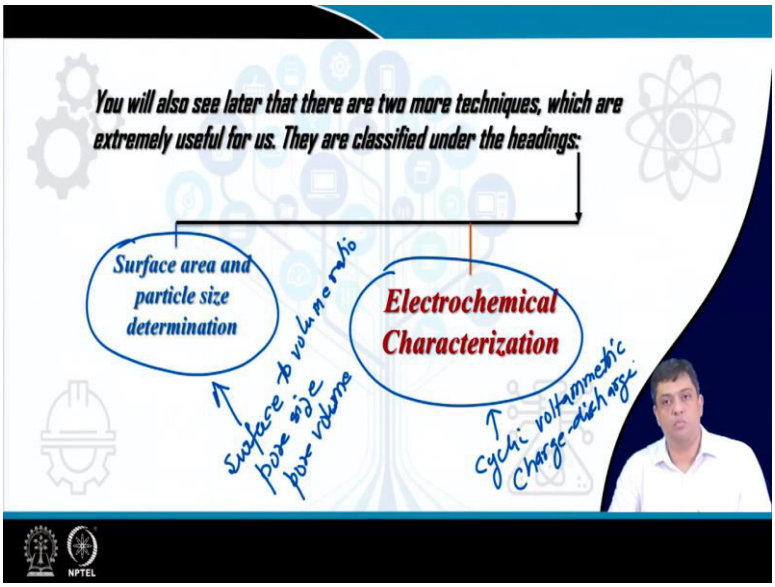

You will also see that there are two additional characterization techniques which are going to be extremely useful to us and they are routinely used in devices or for materials characterization that have been discussed during these previous 10 weeks. And those are the surface area and particle size determination techniques or the electrochemical characterization techniques and we will discuss in detail about these two techniques.

This technique for example, gives you the information about surface to volume ratio in nanoparticles, it can give you about the pore size, the pore volume, the nature of the pores. So, lot of information comes out from these techniques. And similarly, this technique can give you about information about the cyclic voltammetric response or they can give you about the charge, discharge studies or they can give other information, which we will discuss more in detail as we start discussing them bit later.

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So, let us start our discussion of today's class.

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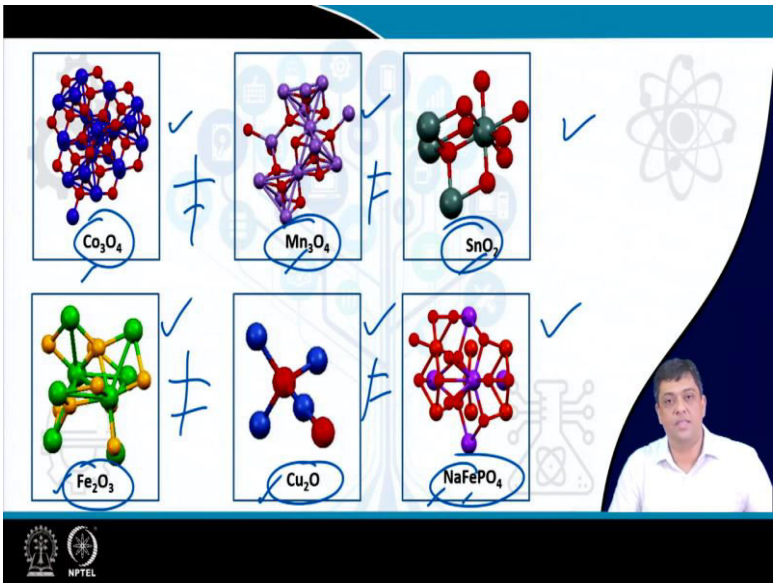

And we will start with X-ray diffraction. Why X-ray diffraction, that is the first thing what information can we extract from X-ray diffraction. These are the unit cells for various oxides which are routinely used in energy devices and what am I meaning from unit cell, these are the building blocks which lead to the appearance or the way which lead to the formation of lattice when they are repeated.

And you can clearly see in all of them, the unit cells are not similar, they are not similar that means, atoms are differently arranged. And if atoms are differently arranged then their lattice parameters are going to be different. And if you remember what we discussed during the free electron module, when we were talking about semiconductor materials, then depending upon the lattice parameters, your band structure changes, your energy bandgap changes, your conductivity changes, everything changes if you are changing the lattice parameters.

And clearly the lattice parameters in these materials are expected to be different as the atomic arrangements are different and along with that, you are using different types of atoms. So, here you are, let us say you are using tin you are using manganese or cobalt or iron or copper or sodium ion. So, therefore, it is very important that the first parameter which we are able to determine is the lattice parameter and also the type of lattice which is forming and the most important technique which is used to determine these information is the X-ray diffraction techniques.

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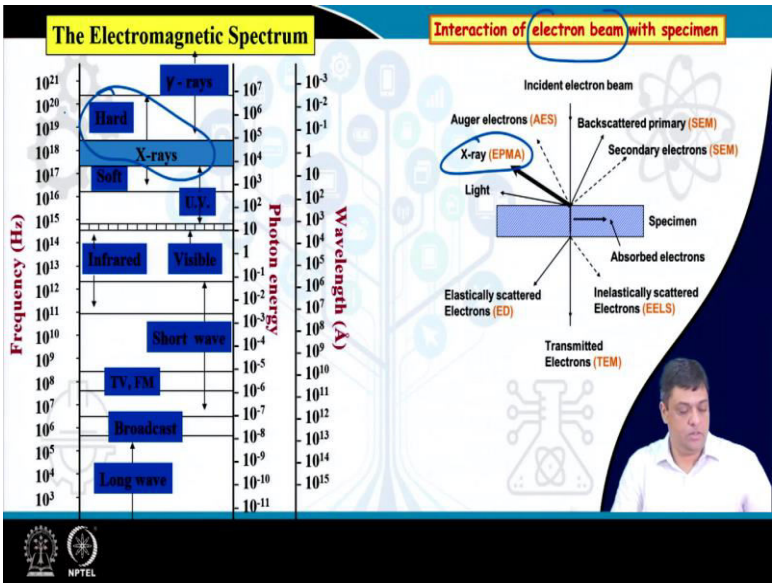

And as I mentioned earlier X-rays are the ones which can have various other sub classifications and different kinds of experimental techniques and similarly, you can also have using if you have an incident electron. So, you can have incident beam leading to X-ray generations or you can use directly the X-rays for characterization of materials and you as you have studied earlier maybe that the wavelengths of the beam should be comparable to the lattice parameter and then you will have the diffraction conditions being satisfied.

And electron are associated with the De Broglie wavelength. So, wave particle duality, therefore, you electron beam can also lead to the generation of X-rays and you have the associated De Broglie's wavelength and therefore, that wavelength if is interacting with the lattice you can have the diffraction conditions satisfied or you can expect diffraction as one of the consequences.

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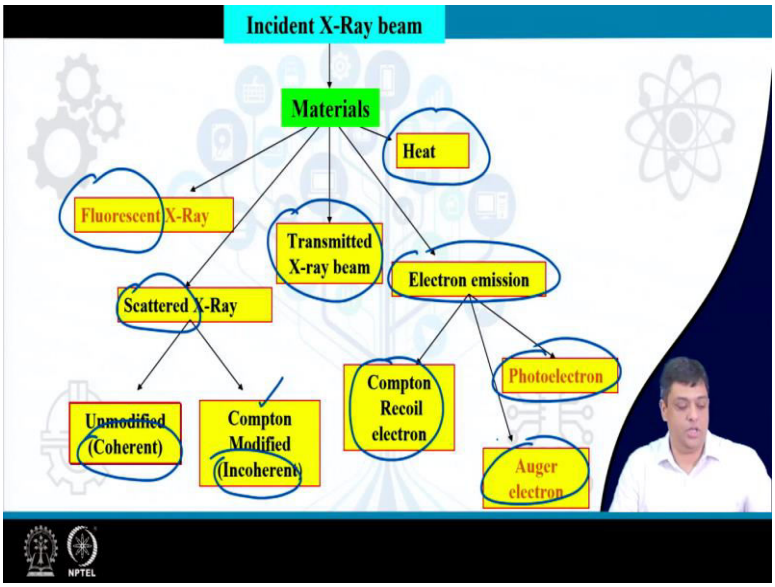

So, if we have an incident X-rays generally people talk that you have an incident X-rays and when there is diffraction and if the Bragg's law is satisfied you will get the diffraction pattern and that is where and then certain other calculations are possible and we ignore many more effects which the incident X-rays can actually lead to in appear in materials.

So, what can happen when there is an X-ray beam incident on materials? First of all, it can lead to the heating of the material and if you have very soft materials then they can actually get damaged by the incident X-rays. Because you are talking about hard X-rays in the techniques which we are using the source is giving out hard X-rays.

So, the first thing which can happen is appearance of heat and if you have very soft materials continuous incident beam on the sample can lead to the appearance of heat and that can damage the sample. If you ignore the appearance of heat and the impact of the increase in temperature because of the incident X- rays in the samples which we are talking about, then there are other consequences which become useful to analyse.

You can have fluorescence or you can get scattered electrons and the scattered electrons either can have coherently nature or they can have incoherent nature and that would give you the Compton modified scattered X-rays. Now, if you have X-ray beams and they are transmitted, then you can have the transmitted X-ray beams and you can obtain various other kind of information.

Similarly, if you have because you have an energize beam falling on the sample and if that is able to emit an electron, you can extract information about the Compton recoil electrons, the

photo electron or the auger electrons. So, it is not that X-rays are only resulting in the diffraction condition or the appearance of diffraction patterns that beam can lead to various other phenomena and if you analyse them carefully lot more can be obtained about the material.

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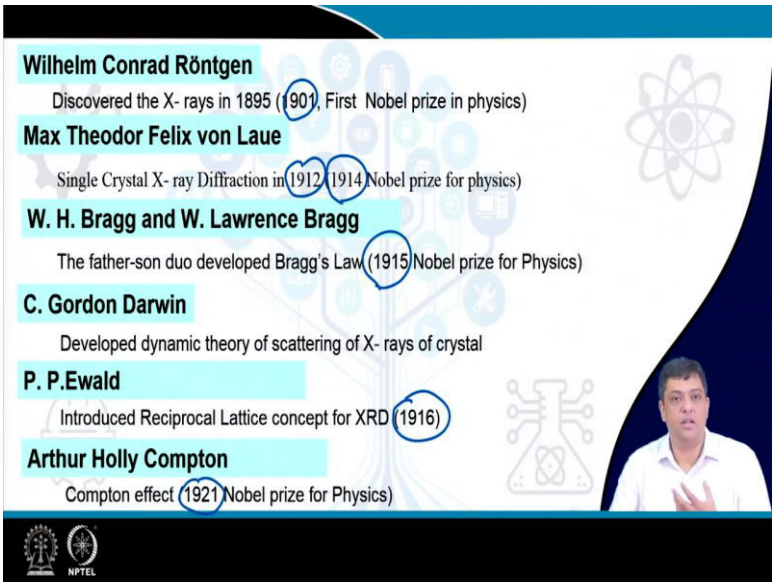

And as you have been studying from school days, Rontgen discovered X-rays in 1895 and was awarded the Nobel Prize in 1901. Then came the excellence studies by Von Laue and led to the characterization and determination of information about the single crystals and what you understand as Laue diffraction patterns and that study came out in 1912 and very soon in 2 years time, he was awarded the Nobel Prize.

Then the father-son duo of Bragg; Lawrence Bragg and W. H. Bragg came and gave you the Bragg's law condition and they were given the Nobel Prize in 1915. Subsequently, you had the dynamical theory of scattering of X-rays by Darwin, Ewald sphere and the concept of reciprocal lattice which can be used to explain the appearance of diffraction conditions by Ewald again Nobel Prize in 1916.

And then came the study of Arthur Compton, which is now understood as Compton Effect, again a Nobel Prize in 1921. So, if you see, if you talk about a particular technique and related physics which is associated with the data you obtained from that characterization techniques or a technique then probably XRD is the one which has obtained the maximum number of Nobel Prize in physics. So, that is the power of that characterization tool.

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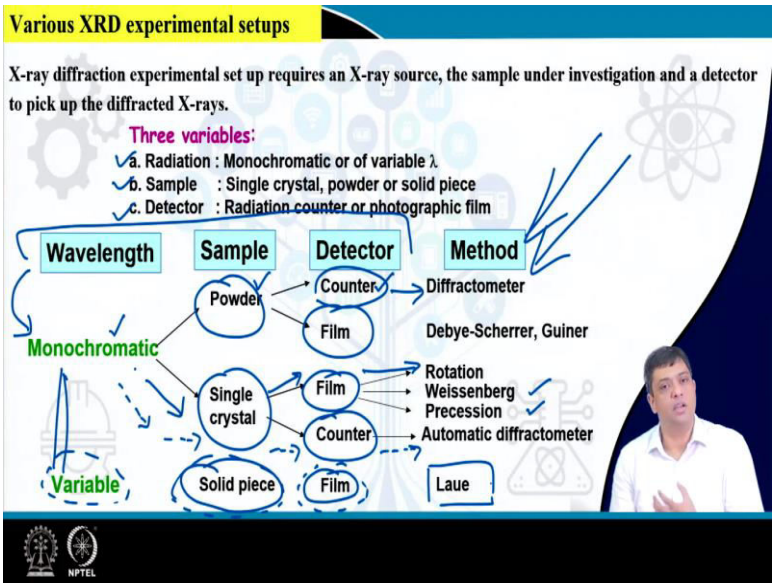

And if you look into today's laboratory level or industry level XRD arrangements or the setups or the instruments which are available then you can have various kinds of X-ray experimental setups and they are designed that different variables are measured. So, you can have three possible variables either you change the incident radiation or you change the type of sample or the third you change the type of detector.

Because the diffraction condition will remain the same, the physics will remain the same, it is only that you can change lambda or you can change D is what coming in from the D spacing of the samples. So, you can change the sample or by detector you can have different kind of patterns either at one go or in continuous theta 2 theta scans.

So, wavelengths either you can use a monochromatic wavelength or you can use a variable wavelength. Generally, for the materials which we have discussed in the course, as I mentioned earlier we will not focus on liquid samples; for the materials which we have discussed in the course, the samples are either in powder form or single crystal when we are analysing the X or collecting the XRD pattern and if you have variable beams then also you can have a solid piece of sample.

Now, when you are talking about a powder diffraction, then you can have detectors which are counter type or film. If you are talking about single crystal diffraction, then you can have again film or counter type detector. But if you are talking about a variable wavelength X-ray diffraction of a solid sample then mostly you use a film and based on these combinations, there are various methods of diffraction characterization tools, which have been designed and are routinely used.

So, if you have a monochromatic wavelength, you use a powder sample and you have a detector which is counter or film type then you have a diffractometer. Similarly, if you have a monochromatic beam, you have a single crystal, you use a film type detector then either you can have a rotation type method or Weissenberg type method or a precision method or if you have a monochromatic beam a single crystal, you have a counter type detector then that is called an automatic diffractometer.

In comparison, if you have a variable wavelength, you have a solid piece of sample you use a film type detector then what is the method you are getting, very good, you are going to get a Laue type method. So, depending upon the combinations you have different types of diffraction methods or experimental setups which have been designed and are used.

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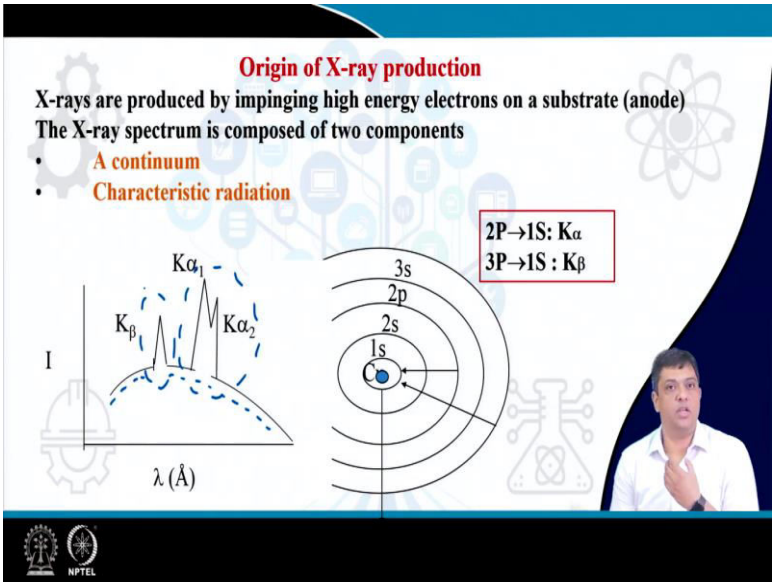

So, you know that X-rays are produced by impinging high energy electrons on a substrate that is called as anode and the X-rays which are obtained have two components a continuum and on top of it, you have the characteristics radiations. So, if I say copper K alpha 1 that is the characteristic radiation of copper which was used as anode and you had the high energy electron beams falling on the copper target and you had the corresponding wavelength being generated.

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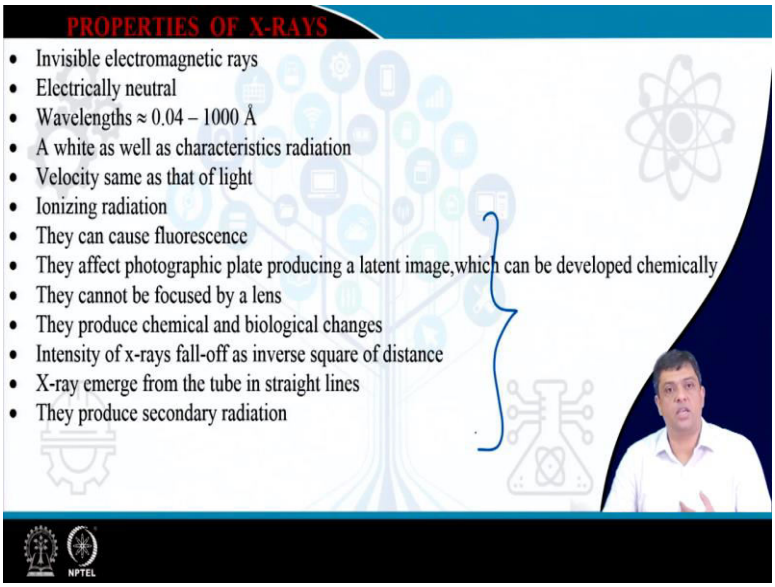

What are the properties of X-rays? A very quick revision, they are electromagnetic waves, electrically neutral, wavelengths are in the range of point 0.04 to 1000 angstrom. They can have as I just discussed you can have a white as well as characteristic radiations electromagnetic waves. So, the velocity are same as that of light, they can ionize the sample. So, they are ionizing radiation then we had discussed the various impacts which the X-rays can have on the material on which they fall and these are again mentioned here and I will not repeat them here. These informations were already discussed in the previous slide.

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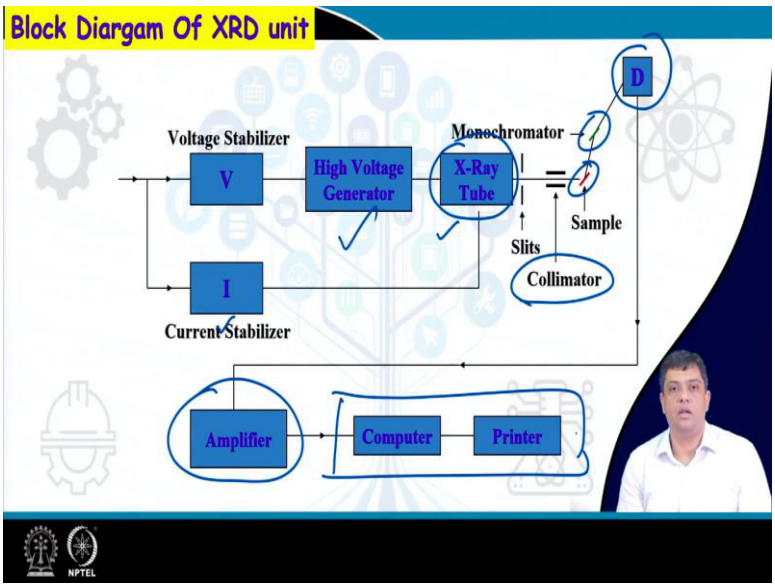

So, how does an X ray diffractometer actually looks like? So, you need to have generation of what, of electron beam which is high energy. So, you need a high voltage generator and

current source, you have an X-ray tube. So, in this tube you have a filament, if you have a thermionic emission, we are talking about a sealed tube once I have written a sealed tube here I am indicating towards the seal tube type X-ray generator instrument.

So, you have a tube where you have a filament and then you will have a thermionic emission and that will lead to the appearance of an electron. If you apply high voltage, then they will be moving towards the copper anode with high kinetic energy and they will fall on the anode and when the excitation takes place the radiation which is emitted are the X-rays.

So, you have an X-ray tube and then you have these slits. The role of the slits will become clear there are various types of slits but they are actually used for allowing a certain fraction of the emitted X-ray beam two moves toward the sample. Collimator as you know what is the role of collimator it sends out parallel beam of light or here we are talking about the electromagnetic radiation that is X-ray.

So, parallel beam which is falling on the sample and then you have a monochromator. So, that any other diffracted beams coming in from other sources are removed and then after the monochromator you have the detector. Once the detector gets the diffracted beam you can amplify the signal and then analyse the data which you have.

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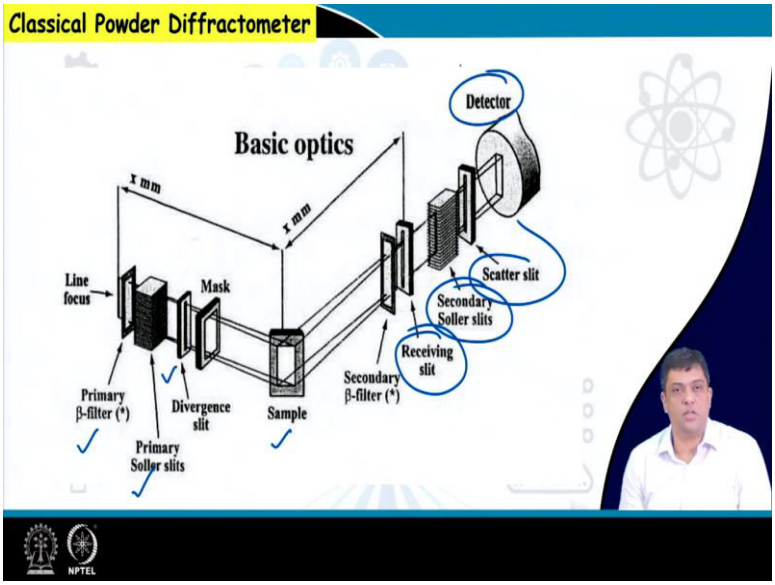

This is a typical and a classical powder diffractometer. So, you have the primary soller slits, the beta filters, the divergence slits, the sample, the receiving slits, the secondary soller slits, the scatter slits and the detector.

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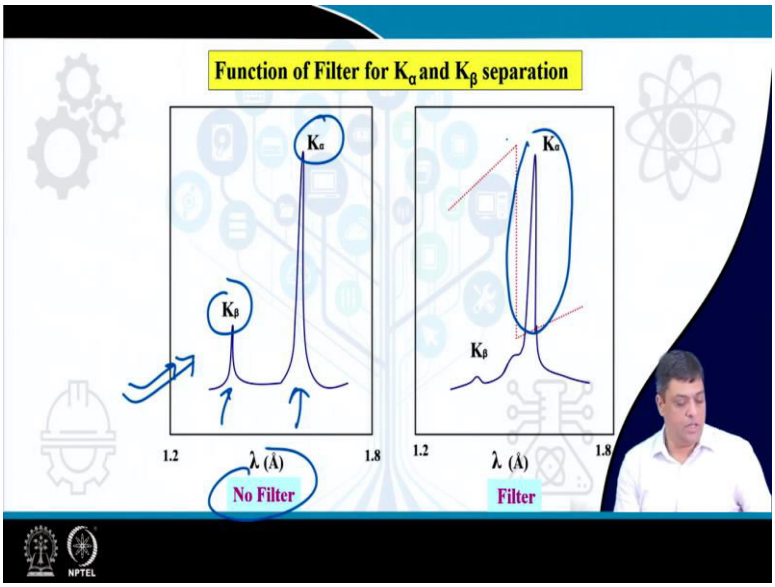

What is the role of the slit will become clear with this slide and also what are the filters doing? So, what happens if I do not use a filters, which I mentioned in the previous slide, then if there is no filter all the X-ray beams which are generated be it be K beta, be it be K alpha will be falling on the sample and there will be two beams which will be satisfying the Bragg's condition and then you will get a series of diffraction patterns which are superimposed on each other one coming in because of K alpha and the other which is coming from K beta.

Now, if you want to have a diffraction pattern, which is coming in from a single wavelength that is lambda is let us say K alpha, then you must make sure that only K alpha is incident on the sample and that is what the role of filters are obtained and the better is the quality of the filters that they are able to suppress the incident K beta then the beam what it if will be having predominant component from K alpha and what the pattern you will get will be originating from K alpha only and so, you will have ease in analysing the data.

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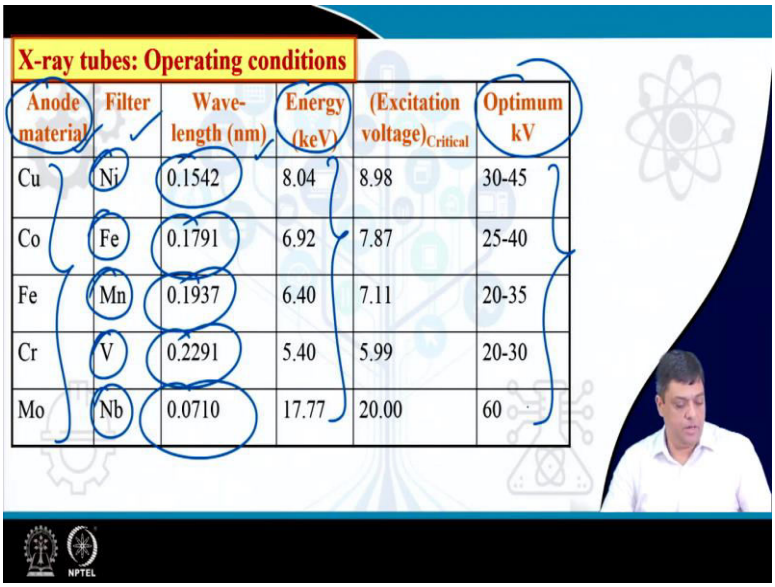

As I mentioned earlier you have a copper anode, but it is not so, that you can only have copper anode. You can have various type of anode materials, if you have different types of anode materials, what is the consequence the wavelengths which you get from them are of different nature.

So, the incident, wavelengths are different. So, you can analyse different order of lattices or lattice parameters using various types of incident radiation because their wavelength change. And you can see when you have different anode materials and the corresponding wavelengths which you obtain, which can have the different characteristic wavelengths associated you have to use different types of filters. So, that you ensure a condition that unwarranted wavelengths or any extra wavelengths which are being generated by the material are not incident on the sample.

So, you have to carefully choose the anode material, the filter and the wavelength which you will get will be the one which you are desiring and these are the typical energies which you obtain in different forms of anode materials. And, you can see that the optimum kilovolt or the voltage range in which these instruments are working are also quite different. Depending upon different voltage which you apply the kinetic energy of these electron beams which are emitted will be different and if you apply very high voltages the energies would be much higher.

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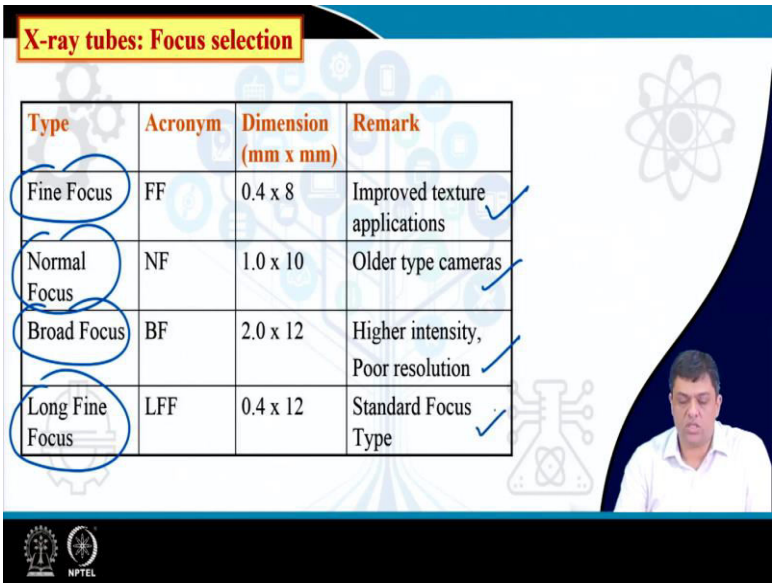

And if you are talking about X-ray tubes, then you can have fine focus, you can have normal focus, broad focus or long fine focus. These are the different kinds of X-ray tubes you have and if you are talking about fine focus then they generally lead to improve texture application purposes. Normal focus is based X-ray tubes are older using older type cameras, broad focuses focus type X-ray tubes do although have high intensity but poor resolution and long fine focus type tubes are the standards focus type tubes which we use.

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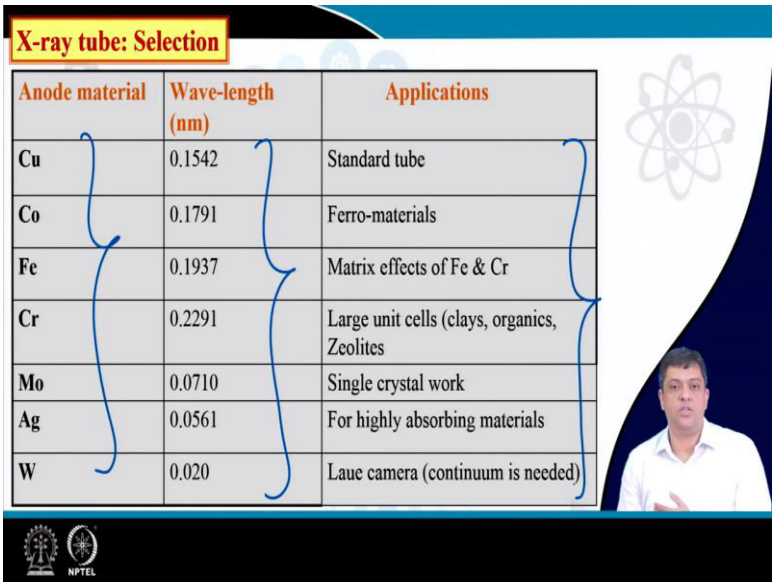

Once again as I said earlier, you have to choose the anode material carefully so, that the wavelengths which you obtain are the ones which can be applied for different applications. So, it is not so, that one wavelength, one setup will be used for all types of measurements. So,

you have to be very careful in choosing the type of instrument which you will be using to characterize your material.

And the type of materials which we have discussed in this course, we can generally use a copper based X-ray tubes or cobalt based X-ray tubes or iron base tubes they are reasonably okay and these are the ones which are used for characterizing the materials which have been discussed in this course.

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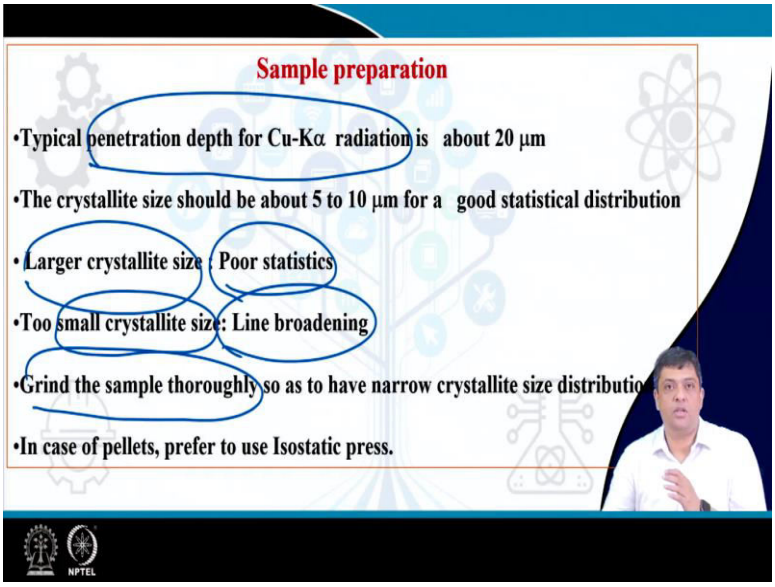

Now, as we are talking about the characterization technique, how do we measure this? Is it like you can have just go and start measuring? No. There is also a way in which you will have to proceed and prepare the samples. And can we have a very thick sample or a very thin sample? This is also very critical because the penetration depth of X-rays also vary.

Now, can I use samples which are very, very fine, let us say 1 angstrom the if you have the dimensions or the particle which are of 1 nanometre size or I can use materials which are of let us say 1 centimetre dimensions, what is the type of crystallite size you are talking about, that can be analysed easily using the X-ray techniques?

If you use a very large size crystallite size, then generally you get a poor statistics and if you have very small crystallite sizes that means you have nanomaterials and that to the ones which are tending towards let us say 10 nanometres, 5 nanometre dimensions and if they are confined in all the three dimensions then you are talking about three dimensionally confined nanomaterials that is quantum dots.

Then you have very serious line broadening effects and then getting the information is not a trivial exercise, it becomes a non-trivial exercise. How do you prepare the samples? Can you just go and paste it on the sample holder? No, if you have a powdered sample, then you have to be very careful. And how you make the samples?

While making the sample also you have to be careful in the way you slide the glass slide on top of the sample holder. So, that you do not induce any preferred orientation. Each of these steps will become in a video which I will just show in one of the slides. So, all these steps are very, very critical and must be carefully followed while you are collecting the data, do not rush through any one of these steps.

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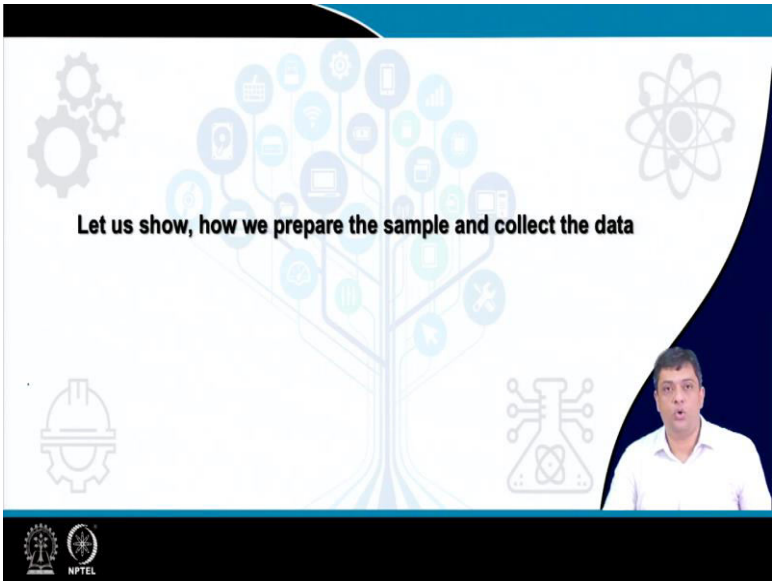

So, let us try to explain the things which I said in words and using a video and hopefully, things will become much clearer to you.

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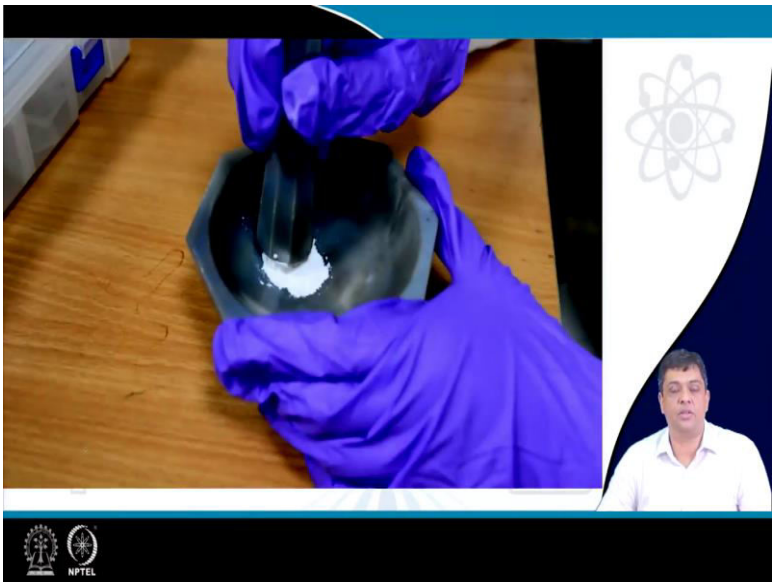


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So, let me play a video. So, we are talking about collecting X-ray diffraction data for a powdered sample. Now, if I look into this the way if you see the student, the one who is making the sample and crushing the sample is moving the mortar pestle in the form of 8, they are not moving it like is or in any preferred direction.

Why? Because when you move the sample, pestle in the form of 8, you actually cancel any preferred orientation which you can induce in the lattice. So, if you are applying a stress in this direction, then that gets cancelled by the reverse stress and therefore, you avoid any preferred orientation in the lattice which can lead to change in the intensity the peaks. These are the two types of sample holders which are routinely used what the one which you are seeing is the being cleaned by the student is that glass slide and the other one was the like the one which is used for steel or aluminium glass slides or the solid holders.

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NPTEL


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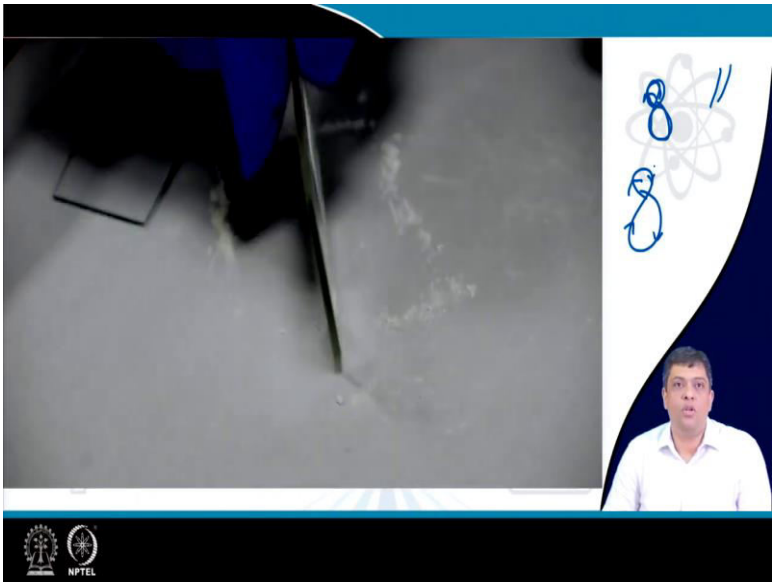
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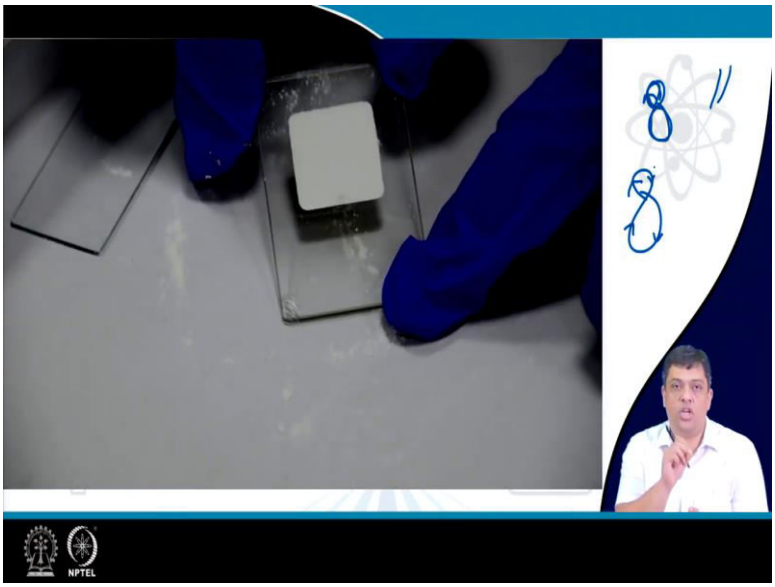
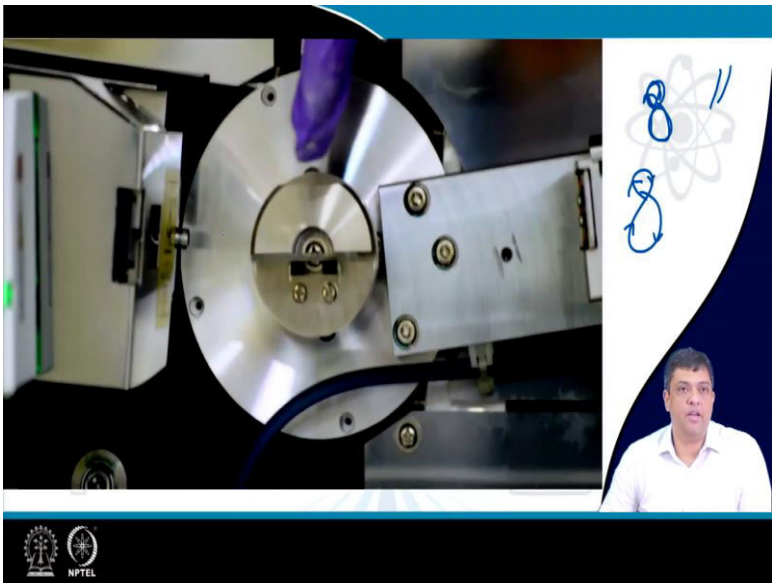
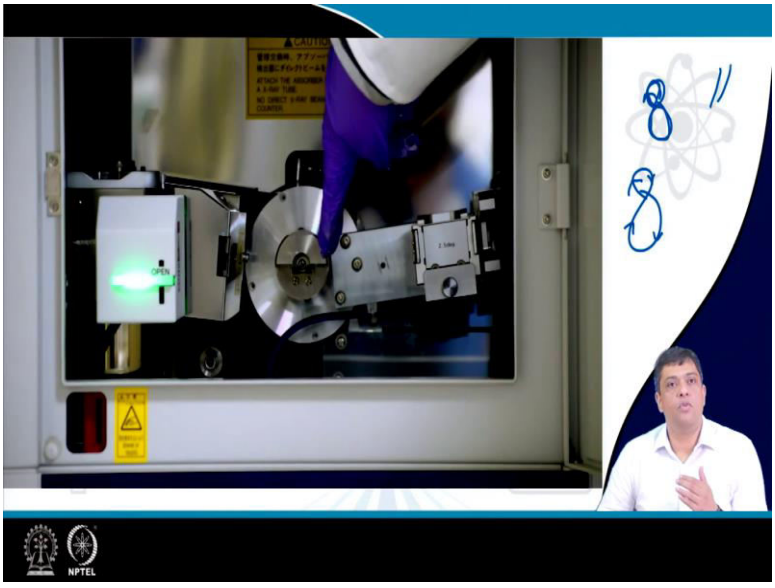



MiniFlex





Now, let us see how to prepare a sample. So, you sprinkle certain sample on the slide and then using a glass slide you try to smoothen the surface and ensure that the sample is now only in the groove region, the groove region inside the glass holder. You still see this is a typical example which people miss if you see that at the bottom too, we have two small areas which were not covered completely.

So, you must sprinkle some more powder, if you have that and then try to make a smooth completely covered slide of the sample you will see what the slide which has been prepared completely is looking like. Now, you should also be careful that you cannot take this slide and just put it in the in the diffractometer you see the student actually gave us a small jerk on the slide.

Because if you just put them in the diffractometer the sample may fall while you collect the data. This is a typical diffractometer table top Rigaku diffractometer, which we have at IIT Kharagpur mini flex type. So, this is how a X-ray diffractometer looks like. On the left side you will see that the one where you are seeing the green light is the one where which is the source of X-ray.

So, X-ray tube is on the left of the screen. From the left you see the beam is generated, it falls on the sample and then on the right you have the detector and this detector after the beam falls, we will move in the theta 2 theta circle and you will have the X-ray diffraction pattern. So, this is the way an X-ray diffraction data is collected.

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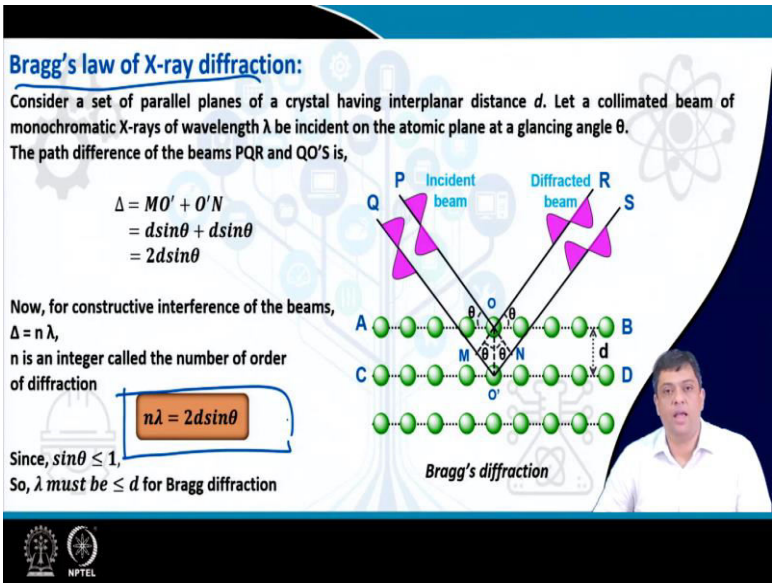

And once I have the data which is coming in because of the Bragg's law, you have the condition of 2D sin theta is equal to n lambda getting satisfied you will have the Bragg's law condition and if you have high intensities that means you have the constructive interference and if you have low intensities or you have the diffraction, where there is no sharp rise in the data that is coming in because of the background X-rays. So, you have a background on top of which you have the X-ray peaks or profiles, which will appear and those are coming in when the Bragg's law condition is satisfied.

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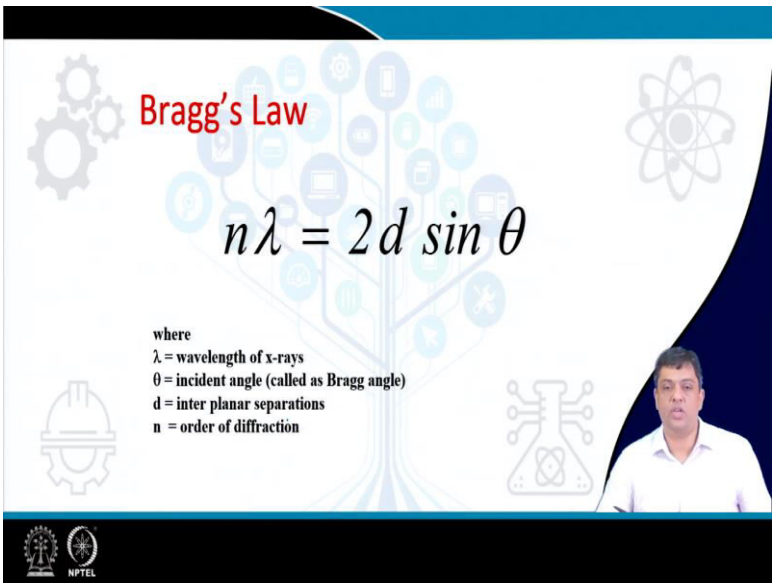

This is the condition which needs to be satisfied and in the subsequent lecture, you will see what data, you get for a polycrystalline sample or a powdered sample, which has crystalline.

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So, hopefully, in today's lecture, I have given you a brief introduction towards the large number of experimental techniques, which are used to characterize the materials and we have also been able to convince you with the fact that X-ray diffraction is one of the most important tool for characterization of materials. What type of materials? The materials which are useful in devices that are being discussed in this course.

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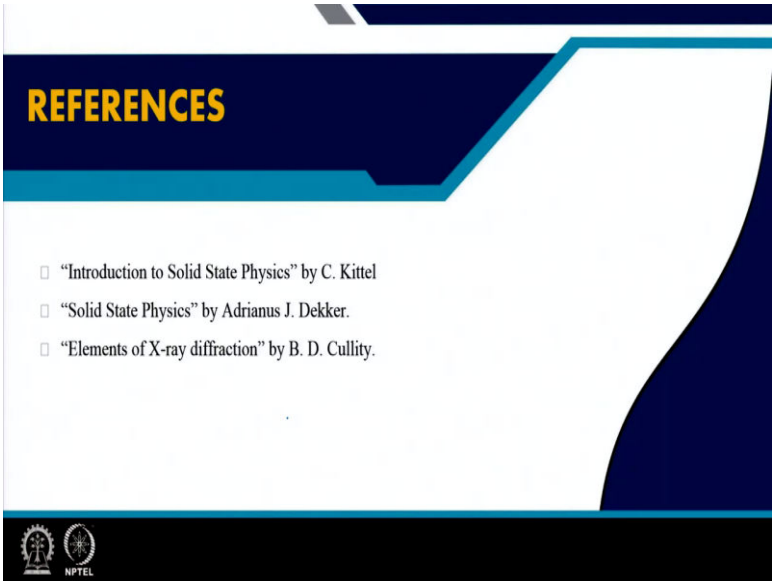

These are the references from which the data was obtained and I thank you for attending today's lecture and in next lecture we will discuss the X-ray diffraction technique much more in detail. Thank you very much.