**Physics of Renewable Energy Systems**
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Lecture 45
X- Ray Diffraction Method

Welcome back to the course on physics of renewable energy systems. In the previous lecture, I gave you the brief introduction about the various experimental techniques which are present and are used to characterize the materials that were discussed in the course and also we had discussed about the basics of X-ray diffraction technique and how do we prepare the sample, how do we load it on the diffractometer.

And in today's lecture, we will try to take the knowledge a step further and we will try to understand how to actually obtain the data and once the data is obtained, how do we analyse the data.

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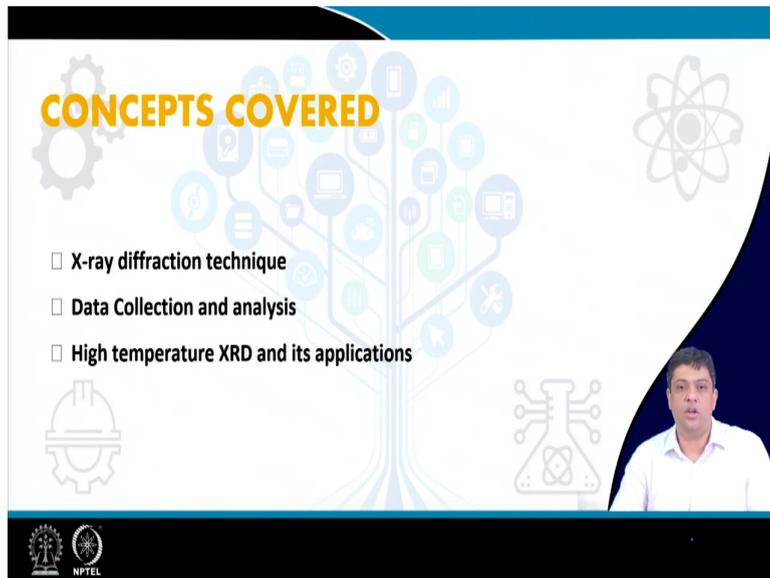
So, in today's lecture, we will be talking to you about the X-ray diffraction technique in detail. The data collection and the way you analyse the data and we will move towards a more advanced use of X-ray diffraction technique that it is not that you only have to use X-ray diffraction at room temperature or ambient temperature, you can also have low temperature X-ray diffraction as well as high temperature X-ray diffraction techniques.

And just to keep it concise I in this course, I will just introduce to you the high temperature X-ray diffraction technique and what are the application of high temperature X-ray diffraction technique that is going to be useful for our course.
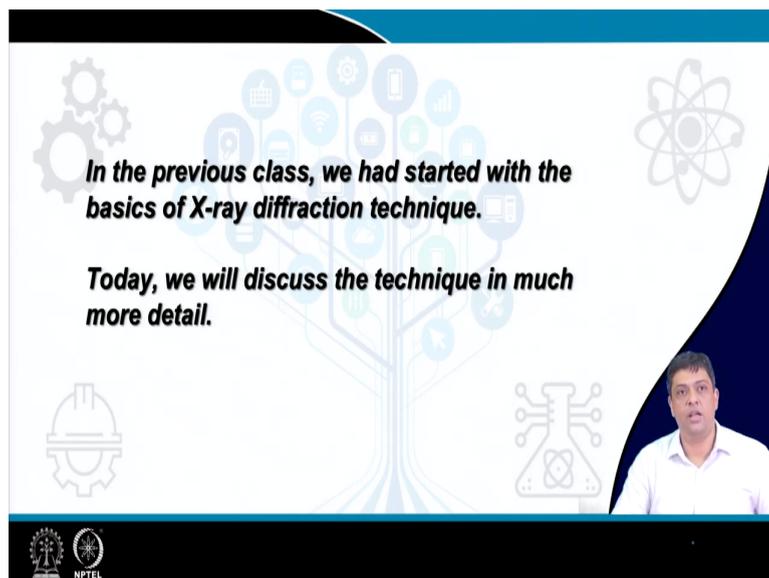
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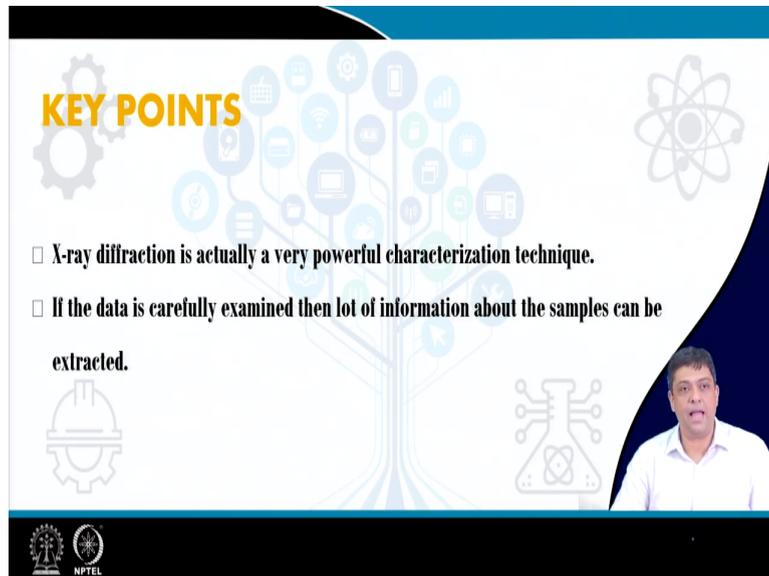
So, once again the key points which you will take back would be that X-ray is an extremely powerful technique and if the data is carefully examined, then a lot of information about the sample can be extracted which people generally ignore.
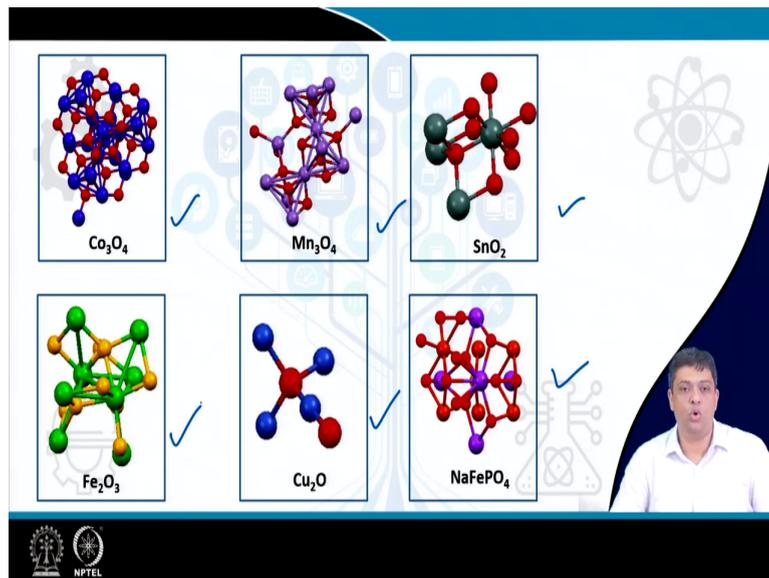
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So, as I said in the previous class, we had started with the basics of X-ray diffraction.

And let us start to discuss more in detail about the data which you get for different types of lattices that we discussed in the previous lecture and if you have different types of X-ray diffractogram or patterns, then how to analyse it.

We know the way the Bragg's law is obtained, if you have the incident beam, then if they are falling then there is a path difference which is obtained from the two beams which are actually coming in and if the rays interfere constructively you have the beams which give you high intensity otherwise you have low intensities and that is seen as the background in the diffraction pattern.

So, in the previous lecture, I gave you the steps of loading the sample in the diffractometer. Now, what happens, once I have a software then I have to define the range in which that diffraction data has to be collected. For example, let us say in this we have given a range of 5 to 80 or you can also give from 10 to 80. So, that gives you the diffraction angle in which the data would be collected.

So, that has to be defined in the initial step while you are writing the experimental protocol. So, once I have loaded the sample I have defined the range in which the data has to be collected at what steps you want to collect. Suppose I give you a diffraction pattern which is collected in 1 minute over a range of 80 degrees that means, I started let us say 10 degrees

and in 1 minute I move collect the data up to 90 degrees, that means the counter is moving at a very fast speed and if the counter is moving at a very fast speed what will happen you will not be able to collect enough radiation which is coming out after the diffraction from the sample and then the intensity is would be very weak.

So, to counter that what can be offered that, no, you please move to each subsequent step and then stay there and then collect for 1 second or 2 seconds or 10 seconds and then only move to the subsequent step. In that way what will happen the data which you were collecting in 1 minute or the range you were covering in 1 minute may actually be covered in let us say 5 hours.

So, then you will say okay, do not go to the next step and stay there move to the next step very slowly and so that you are able to collect the data and you keep on moving very slowly to the next step and that is what is going to define the various types of data collection. So, if you move from one step to the other and then stay there it is step scan and if you are moving continuously to cover the range and you are not stopping at a given point then it is called a continuous scan.

And if you are moving to the next step and you are waiting till the intensity reaches a particular value or the information has been obtained, so that the intensity is up to a given value and then only you will move to the next step then that is called fixed count. So, you have various types of data collection methods. So, let us see how to collect data.

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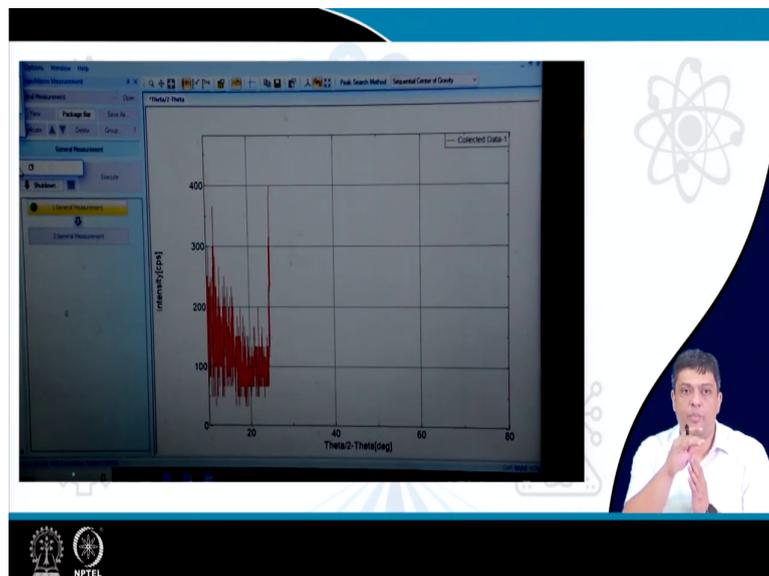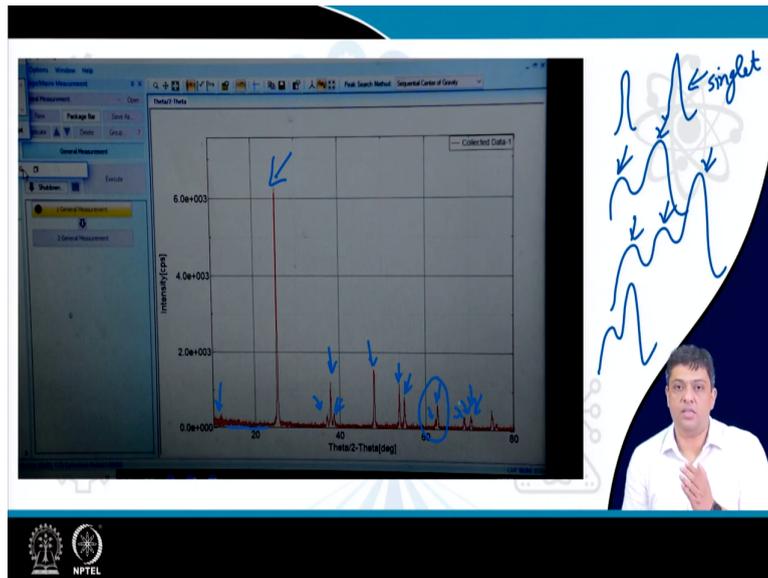
So, we have defined the range and in this range, we have defined the range from 5 to 80 degrees what you see is the background. So, X-ray generator, the source is now operational and the beam is now falling on the sample and you are trying to collect some information at the detector, what you see is typically the pattern which you get from a diffraction coming in from the effect of background.

And now you see that at suddenly let us say at approximately 24 degrees or so 2 theta value the diffraction condition was satisfied and the moment the diffraction condition was satisfied, you have a high intensity beam. Because you know diffraction condition 2d sin theta is equal to n lambda. So, what happens the moment this condition is satisfied the intensity shoots up.
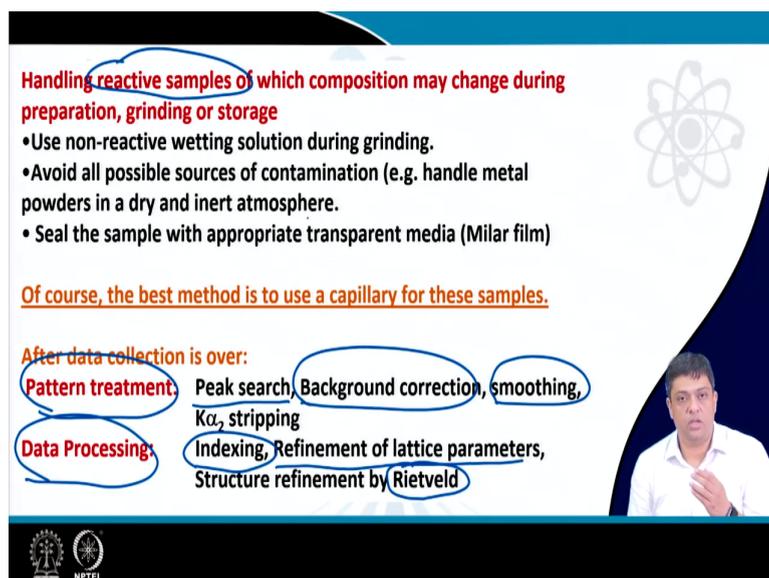
You can and you collect the data continuously up to 80 degrees and you will get different kinds of diffraction profiles. What do I mean by different kinds of diffraction profiles? Either you can have a singlet peak that means you have a singlet, you can have a doublet or you can have a triplet.

So, if I have let us say a singlet peak or doublet or you can also have triplet peaks. So, you can have different kind of peaks and why do they appear because of the diffraction conditions that are defined for each of the Bravais lattices and using the diffraction conditions. So, now for this particular sample you can clearly see that you have a small peak here also, which is rising over the background, this is the background which is rising over the background then you have a very sharp peak and you have if I if you see the peak here you can clearly see that it appears to be a doublet peak you have a small peak followed by a large peak.

Similarly, you can see this peak seems to be a triplet peak, you do not need to go to very detailed analysis, if you look into data carefully just by looking by eye you can see that okay this peak looks like a doublet peak, the other looks like a triplet peak and therefore, while I index the peaks that means I assign the Miller indices to these peaks, I should be able to assign them carefully. So, that the all these profiles are related to a particular Miller indices.

So, now, what we did in the earlier class, we had shown you the video where the sample was loaded. Now, after loading the sample in the diffractometer we had set up the program we had started the program, please note that while you are running the sample, we cannot show you the video of inside. Why? Because of the safety mechanisms that all the diffraction measurements are performed in a carefully and secured chamber which cannot be opened while the data is being collected, that means when the X-ray beam is switched on, because of safety concerns. So this is what you get as the data.

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Once I have the data you can understand by looking at the data what you can do, you can have you can look at the positions where the peaks are appearing as I said earlier, you have background and then the diffraction pattern, what is the nature which you of the background which is collected you can obtain and then perform the background correction so that the information which you then have is only related to the sample.

You can have the smoothing of the data, so that any erratic variations are removed and also because if I am talking about copper K alpha, then associated copper K alpha 1 you also have

copper K alpha 2 and then you will see two diffraction patterns which are superimposed. One is originating due to copper K alpha 1 and the other which is coming in because of copper K alpha 2. So, if I can remove copper K alpha 2 effect then I have to understand and analyse the data by only believing that the all the features which I get are because of one wavelength that is copper K alpha 1 that is 1.5406 angstrom.

After we have looked into the data treat had, carried out the treatment of the data, you can process the data. During the process, you can index the data, you can refine the lattice parameters and one of the most powerful techniques which are used in today's research for analysing an X-ray diffraction pattern is the Rietveld refinement of diffraction data.

Please note is the refined the term is not determination, it is a refinement. So, why it is refinement? Because you have to give up expected model right at the beginning around which the refinement will take place. If your hypothesis is correct, the data will be fitted from the fitted from the simulated profile, otherwise you will not be able to fit the data using this simulated profile. It does not determine the data you must have a basic information about the lattice and then only the refinements will take place.

And as we discussed earlier, we will we are talking about the materials which are useful for us in in devices that have been taught to you in this course, but, you must also know that there are other kinds of samples which are there and if they are reactive samples, then they have to be treated in a different manner.

And if you have samples which are going to react with air or with ambient conditions they have to be treated and then handled in a different manner and the data is has to be collected in different forms or using different kinds of sample holders and if you have a reactive samples, then they have to also be sealed in various kind of jars or sample holder which are transparent, so, that they it allow the beam to cross through them, fall on the sample and then exit the jar. So, it depends on the type of samples, but for the ones which we have discussed in the course, the sample holders that were shown to you in earlier lecture should be sufficient.
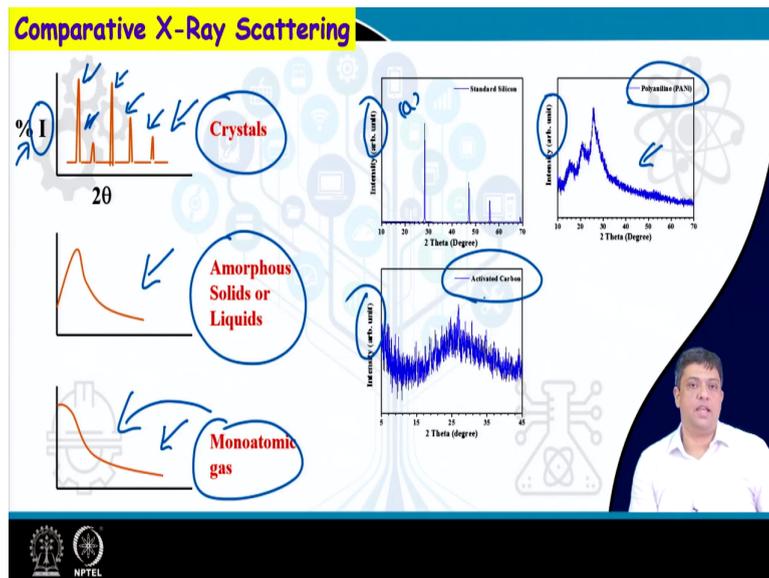
So, after having the data which is processed, you will get different kinds of patterns, you will have a pattern which may look like the ones where you have sharp peak, the ones where you have a broad hallow and you can also have a one where you see a continuously reducing intensities.

So, well the one where you see crystalline or well defined profiles those are associated with the crystal or polycrystalline sample. The one which you see indicating a broad hallow are associated with amorphous solids or liquids and this is a typical nature of monatomic gas. Please note intensity is given as arbitrary unit. Why? Because if I collect data from one diffractometer I can get let us say intensity 1000, if I go to another diffractometer the intensity may be slightly different.

Hence, it is important to know that it is the nature of the profiles and the relative intensities which are more useful and are used to indicate about the sample and not the intensities. So, when you plot you will if you see the data published in literature or any book you will always see intensity written as arbitrary unit. So, you cannot give exact values as we have indicated here. Graph a shows the diffraction pattern for standard silicon and standard silicon is the one which is used to calibrate the diffractometers.

As you saw that for an amorphous or a sample which has an amorphous nature, you get a broad hallow and for polyaniline which has certain order of short range ordering, you can see that this is the diffraction pattern and if you have a completely amorphous material or then

you have patterns like for activated carbons which we have shown here. So, this is the data which you obtain after analysing the sample.

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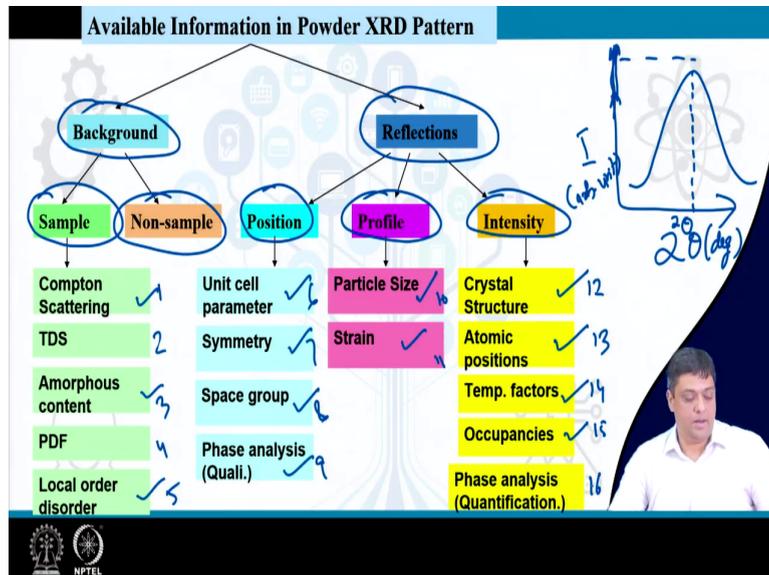
So what are the information that is available in an X-ray diffraction pattern? So, there are two things which I have been discussing you have a background and on top of it, you have the diffraction profiles which may appear. So, you have a background in the diffraction pattern and you also have the reflection, you cannot just ignore the background. Because if you analyse the background carefully, it also has a lot of information.

The background can appear because of two reasons one is the non sample because of extrinsic factors that if the background is associated with the sample then the background can be used to extract information like Compton scattering, local order disorder, the amorphous contents and so on so forth.

In comparison, now, we have the sharp peaks, if you have a sharp peak, let us say 2 theta in degrees and intensity I am drawing a zoom picture, which is not to scale and then just for explanation I am drawing this curve. Now, what do you see using this graph which I have drawn here? You see you have an associated 2 theta value that means, there is a position.

You see, this profile is not like a delta function, but it has some width it has some asymmetry, on the left side this profile is more symmetric than on the right hand side. So, you have the shape of the profile that is also clear and finally, you have the intensity which is there. So, for

a given profile, I can clearly see that there are three things which are associated with the profile.

So, if you analyse the position of the diffraction profiles, you can determine information regarding the unit cell parameters, the symmetry, the space group and the phase analysis, not quantification, but qualitative phase analysis. So, you can get a rough idea about what type of phase may be present not exactly value of phase and or if you have more than one phases, what is the contribution of one phase in comparison to the other.

So, you do have a qualitative information if you analyse the position, if you analyse the nature of the profile, you can get information about the particle size, the strain and finally, which generally people believe that it is only the intensity which you should analyse, yes, intensity should be analysed, because it gives you the information about the crystal structure, the atomic position, the temperature factors, the occupancies and it also can give you information about the phase and can lead to quantification of the phase.

So, if you just count the number of parameters or information that can be extracted using an X-ray diffractogram. Let us, see how many of them are there you have 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16 and this is only what is relevant to us. If you analyse even a step further more information can be obtained. So, just one X-ray diffraction pattern can lead to information of 16 parameters or properties associated with the material. So, do not take the X-ray diffraction pattern lightly, try to analyse the pattern to the best you can.

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So, you can have structural characterization or phase characterization as we just saw.

For example, if you want to determine the unit cell parameters, you will use the relation for 1 by d square and you can obtain the relation for determining the d values and the volume of the sample. This I think would be explained in any other course that is running on condensed matter or crystallography and I would ask you to please refer to it.

For example, if I want to use the data to extract information about the cubic systems, you will end up getting the relation that 1 by d hkl square is equal to lambda square divided by 4 into sin square theta hkl. That means, if this condition is satisfied, that is the place you will expect a sharp peak and all other places you will not get the sharp peaks.

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If I move from let us say I have a cubic structure and then I from there I moved to another structure this is what we are indicating and in this example, now, we are taking to tetragonal system then what happens you have for tetragonal system what is the condition that should be satisfied it is 1 by d hkl square is equal to h square plus k square upon a square plus l square by c square. Because in tetragonal a is equal to b not equal to c and alpha beta gamma is equal to 90 degrees. So, you can use these relations to obtain the unit cell parameters for a tetragonal system.

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And if you look into the web, the internet or if you have certain software repositories, then you will see then there are software's which are available to give you the information about the unit cell.

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And some of them are listed here. So, for example, you can use CELL, UNITCELL or any other software which is available to your library and you can extract the information about the sample.

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What are the factors which can lead to the change in the intensities? It is not only that you have coming, factors coming in directly only from the materials or any other surroundings,

there are intrinsic factors which can lead to the change in the intensity patterns. So, the first one is the structure factor which depends upon the position of the atoms you can have the polarization factors which depend on the intensity scattered by the electrons.

You can have Lorentz factors which is a geometric factor that varies as a function of theta, you can have multiplicities. This is a term let me just explain to you is slightly more in detail. So, if you have let us say a peak which is coming in from hkl. Now, at a distance you can have the second order which is associated with this hkl.

So, you have the second order coming in from this hkl. But at that position, you can also have the peak which is expected from h1, k1 but the counter does not know that this peak is coming in from two different profiles it will give you the intensity variations.

But the intensity is will look to be much more than what you expect from h1, k1, l1 and this kind of factors, if the intensities are there, you can have a rise in the intensity because of superposition of two profiles and those are generally explained in terms of multiplicities that is the number of overlapping reflections. You can have temperature factors and if you as the temperature increases mostly the intensity decreases. You can have preferred orientations you can have absorption factors or you can have the extinctions.

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Please note that the background in an X-ray pattern can come in because of the collisions between air molecules and the diffracted X-ray beam the white radiation the fluorescence from the sample the Compton scattering and this is mostly observed in low z elements you

can have crystal imperfections which can lead to the appearance of background or you can also have thermal diffuse scattering and you get various kind of changes in the background.

But mostly as the temperature increases the background increases is the observation which will be useful to remember as we move to the discussion on high temperature X-ray diffractometer.

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But, you should clearly remember that X-ray diffraction technique must be performed while you are ensuring proper safety protocols you should ensure that you must limit the time spent in the vicinity of the source also increase the distance from the source of radiation. So, that you limit the chances of radiation exposure and ensure proper shielding around this source so, that the possibility of radiation escaping from the source or from the diffractometer is reduced and does not lead to serious health hazards in the periphery of the refractometer. So, please be very, very clear that it is not to be performed in conditions which are not ensuring safety protocols otherwise you can have serious health issues.
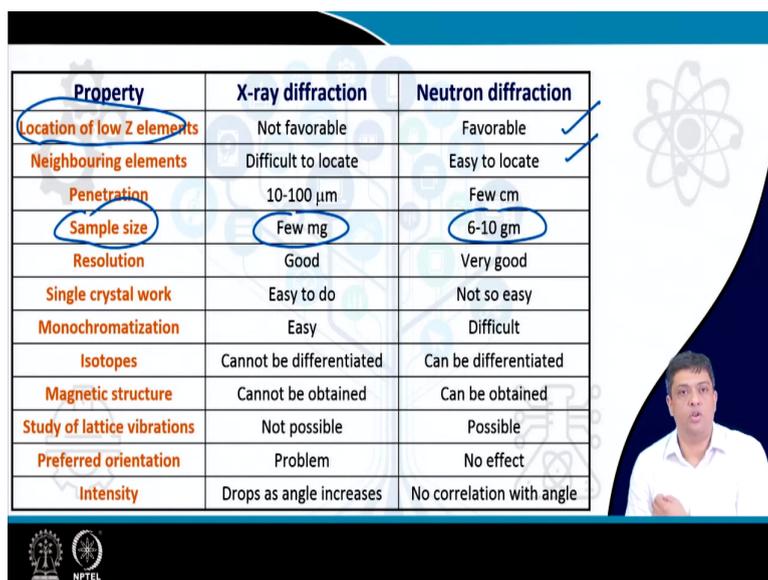
Property	X-ray diffraction	Neutron diffraction
Location of low Z elements	Not favorable	Favorable
Neighbouring elements	Difficult to locate	Easy to locate
Penetration	10-100 μm	Few cm
Sample size	Few mg	6-10 gm
Resolution	Good	Very good
Single crystal work	Easy to do	Not so easy
Monochromatization	Easy	Difficult
Isotopes	Cannot be differentiated	Can be differentiated
Magnetic structure	Cannot be obtained	Can be obtained
Study of lattice vibrations	Not possible	Possible
Preferred orientation	Problem	No effect
Intensity	Drops as angle increases	No correlation with angle

So, for diffraction techniques we had explained that there are various kinds of diffraction techniques you had you have X-ray diffraction, you have neutron diffraction, you have electron diffraction. And till now, I have spent most of the time on X-ray diffraction and the other technique which is there is neutron diffraction, so without going in detail about the neutron diffraction because that is beyond the scope of this course, let us, quickly compare.

See, each of these techniques are associated with certain advantages and limitations. For example, if you want to determine low z element and their position in the unit cell in a cell which is also having high or heavier elements, then that becomes difficult when you use X-rays.
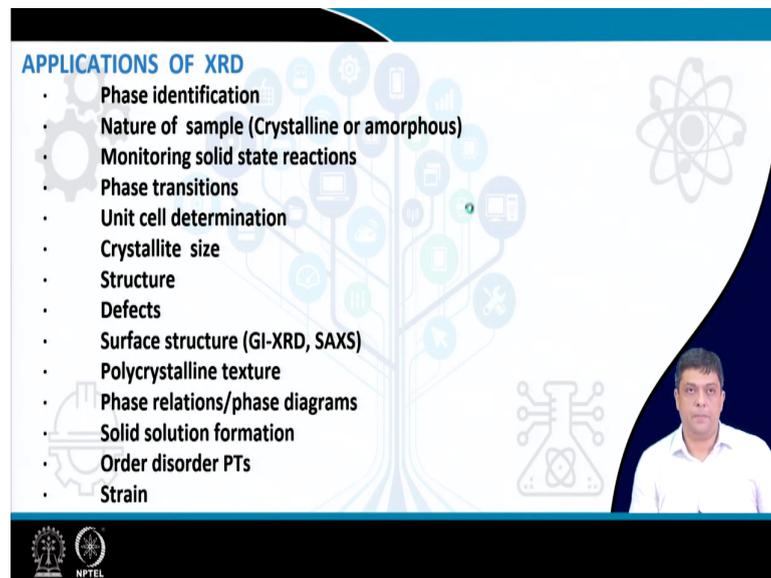
So, determination of low z elements in the unit cell with precise or with precision is more obtained using neutron diffraction data. Similarly, if you have very nearing or neighbouring elements in the periodic table which are used to synthesize an element or molecule or a material, then determining the contribution or the location of neighbouring elements is difficult using X-ray diffraction, but it is easy using neutron diffraction.

The reason comes in because of the difference in the interaction of beam with the sample. What happens in X-rays? The X-rays interact with the electron cloud of the element or the atom whereas neutron interacts with the nucleus which is taken as a point charge. So, the very basis are different and that leads to different kinds of results which you obtain.

But, if you look into the amount of samples which are which is required to obtain a good quality data for example, in X-rays you can work with few milligrams, but with a normal neutron diffraction experimental setup which we have in our country, the amount of sample you require is 6 to 10 grams, which is not always easy to obtain at the laboratory level.

So, certain have advantages associated with X-ray diffraction, while there are advantages which are also associated with neutron diffraction. So, depending upon the requirement you can choose whether you want to perform X-ray diffraction or neutron diffraction studies.

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And these are the typical applications of X-ray diffraction which we have already mentioned earlier and they are just written in words.

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So, for example, the last point which I wrote was determination of strain. So, let us see how we can talk about it, we know that the particle size given by the Scherrer equation is t is equal to 0.9 lambda by D cos theta, also please remember we Scherrer equation what is the basic limitation of Scherrer equation that you are always believing that the nature or the shape of the particle which you are considering is spherical.

So, that is the limitation in Scherrer equation which is here. So, you have t is the crystallite size, lambda is the wavelength, D is the line broadening and theta is the Bragg's angle at which you are obtaining the profile that is being considered. Let us see, how do we write the broadening due to strain. So, we will see how to determine this.

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In both the mechanisms you will see that the broadening in one case you are saying is appearing because of the change in the crystallite size and in other concept you are saying that the broadening is appearing because of this strain in the lattice. So, you have in one case t is equal to 0.9 lambda by Dp cos theta where then you can write Dp is equal to 0.9 lambda by t cos theta.

Now, I know that because of this strain you have the D value that is equal to 4 epsilon tan theta. Therefore, the total broadening becomes a summation of the two terms Dt is equal to Dp by Ds the broadening because of crystallite size and this strain. So, you write them together you get an equation which can be given as the form of Dt cos theta is equal to 0.9 lambda by T plus 4 epsilon sin theta.

What you will get? Plot a curve of Dt cos theta as a function of sin theta and you will get a straight line and if I get a straight line you extrapolate the slope will give the value of 4 epsilon; whereas, the intercept will give you 0.9 lambda by t and from there you can extract the information about the strain.

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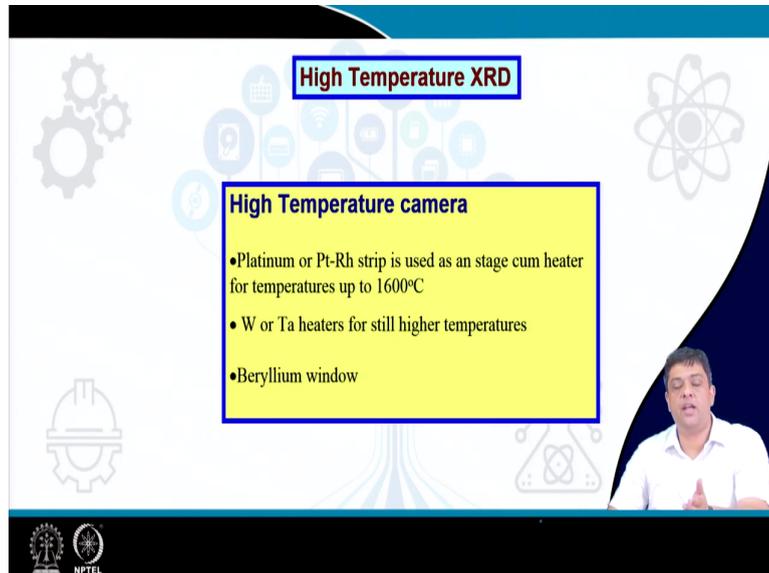
So, before I wrap up let me just give you another high end application of the technique of X-ray diffraction. You can use high temperature XRD to obtain a large number of information about the sample.

So, a typical high temperature camera if you have, then you have platinum rhodium strips, which are used as stage cum heater for temperatures up to 1600, you have tungsten heaters

for obtaining these high temperatures and the sample is covered using a beryllium window so that they do not allow the heat to dissipate outside but they ensure that X-rays can penetrate through them interact with the samples which are at the high temperature and then the X-rays can exit.

And using X-ray diffraction technique and the high temperature data, which you obtain that means, you are heating the sample continuously, and you are performing the diffraction experiment. You can again, obtain a large number of information. You can obtain information about phase transitions, order disorder phenomena's, thermal expansions, point defects, you can this is very important, you can draw phase diagrams using the data obtained from X-ray diffraction being perform at high temperatures.

You can talk about the terminal solubility of the guest ion host lattice you can talk about another very important concept, like kinetics of solid state reactions, you can talk about agglomeration studies or talk about the variation of strain as a function of temperature and many more other information can be extracted. So, you have experiments which are performed at higher temperatures, and then used to extract different information.

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So, I hope that I have given you an overview about the use of X-ray diffraction technique in characterizing the materials which are useful to us. What is the strength of this technique? What are the limitation of this technique? Why you should be very careful when you perform this experiment? You should ensure safety (mechanism); safety and proper shielding is there when you perform this experiment and the details about the, this technique have been taken from the references mentioned in this slide.

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And I hope after hearing these two lectures on X-ray diffraction you would agree with me that X-ray diffraction technique is an extremely powerful characterization tools. Generally,

the full scope of the data is not exploited by most of us and the importance of the technique is sometimes underestimated.

And with this, we finish the discussion on the first characterization technique that was X-ray diffraction and we will move on to the next characterization technique that is useful to us from the next lecture. So, I thank you for attending today's lecture and have a nice day.