Carbon Materials and Manufacturing
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Lecture - 52
X-Ray Diffraction Analysis of Carbon Materials

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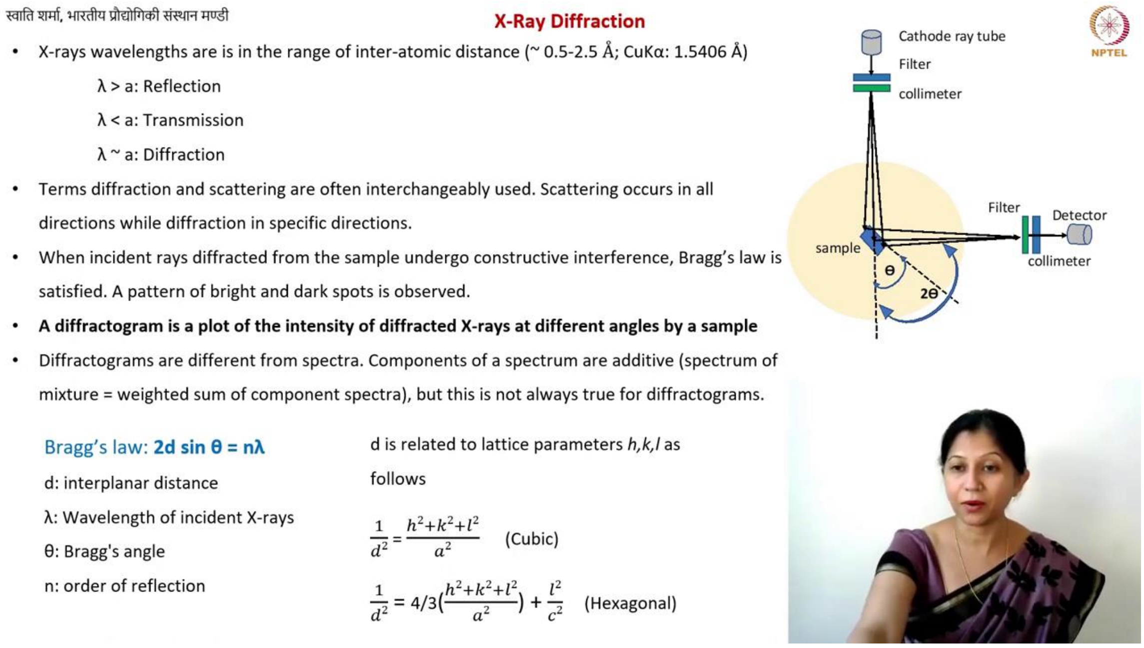

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X-Ray Diffraction

- X-rays wavelengths are is in the range of inter-atomic distance (~ 0.5-2.5 Å; CuKα: 1.5406 Å)
  - $\lambda > a$: Reflection
  - $\lambda < a$: Transmission
  - $\lambda \sim a$: Diffraction
- Terms diffraction and scattering are often interchangeably used. Scattering occurs in all directions while diffraction in specific directions.
- When incident rays diffracted from the sample undergo constructive interference, Bragg's law is satisfied. A pattern of bright and dark spots is observed.
- **A diffractogram is a plot of the intensity of diffracted X-rays at different angles by a sample**
- Diffractograms are different from spectra. Components of a spectrum are additive (spectrum of mixture = weighted sum of component spectra), but this is not always true for diffractograms.

Bragg's law: **$2d \sin \theta = n\lambda$**

d: interplanar distance

λ: Wavelength of incident X-rays

θ: Bragg's angle

n: order of reflection

d is related to lattice parameters *h,k,l* as follows

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} \quad \text{(Cubic)}$$

$$\frac{1}{d^2} = 4/3\left(\frac{h^2+k^2+l^2}{a^2}\right) + \frac{l^2}{c^2} \quad \text{(Hexagonal)}$$

Hello everyone.in the next couple of lectures, we are going to discuss some characterization techniques. Characterization basically means we want to understand what the microstructure of the material is, and accordingly what are the properties of the material.

Sometimes, we will measure a certain property to understand the microstructure; sometimes we will just see the microstructure under an electron microscope, and then accordingly we will try to understand the properties; often we will do both.

So, characterization techniques can be used for understanding a certain material. In the case of carbon, it becomes very important to characterize the material not just at its final stage, but also during the fabrication process. Because you know that all our carbon materials, at least the graphitic carbon materials, they all are very strongly dependent on the heat treatment temperature at which they were prepared.

If we want to understand the carbonization mechanism, pyrolysis mechanism or graphitization mechanisms, in all cases we need to characterize the material at different process temperatures. So, if I take a new polymer, I have no idea about it. And then I want to understand what kind of carbon I am going to get from it.

I can have some things, I can guess, but let’s say I do not know anything about the chemical structure of that polymer. Then what can I do? I can place it inside my furnace and heat it say up to 900 °C, and then I do certain analysis that tells me this is the size or fraction of the crystallites inside this material.

Then I further heat treat it at 1000 °C, 1100°C, 1200 °C and so on, same sample or different samples. The idea is that I can then plot all of these points and I can see what the effect of increase in process temperature on the crystallinity of the material is, because crystallinity can be important for various reasons because that will give me increased electrical conductivity and also Young’s modulus will increase. So, this is important for all carbon materials.

So, what are the common techniques that are used for understanding carbon materials? Well, the first one that we are going to talk about today is X-ray diffraction. So, X-ray diffraction technique is probably the most used technique as on date. And also in the past, it has been used. In fact, this technique is what helped us understand different types of carbon materials, even the discovery of non-graphitizing carbons.

Or at least when we understood what non-graphitizing carbons are; the study by Rosalind Franklin was also based on X-ray diffraction, and a lot of very fundamental studies about activated carbons even before what Rosalind Franklin did, were based on X-ray diffraction patterning. So, this is something which is very common, which is very important for anybody who is working in the field of carbon.

By the end of this lecture, so I will probably not go too much into the details of the fundamentals of X-ray diffraction, I will focus more on how this technique is used for carbon materials and how do you analyze the X-ray diffraction patterns for a graphitic carbon material.

So, towards the end of this lecture, you should be able to at least figure out that you know what the primary peaks for graphite and graphite like carbons are. And more importantly, you should be able to understand how the shape of these peaks do how changes when we have more disorder or more order in our carbon material.

Let us get started. As so we are not going to talk too much about the fundamental things, but I will very briefly I will let X-rays. What is their wavelength range? They are basically of the same order of the inter atomic distances. So, when you want to get the atomic resolution, what do you need?

Your characterization tool should also be of that range, of that order. Why? Because, if the lambda or the wave length of your whatever radiation is too much larger than the inter atomic distance I have mentioned it as here, if it is too much larger, then it will reflect.

If it is smaller than your inter atomic distance, let us say you have two atoms, your wavelength is so small that it will just pass through; it may just go through between two atoms. That is what we call as transmission. These principles are also used in different types of spectroscopic or microscopic techniques. But in this particular case what we want is diffraction. Diffraction takes place when your lambda is pretty much of the same order of the inter atomic distance.

What is diffraction by the way? When there is an incident ray, and then there is a particle which can change the direction of that particular ray or wave. So, we are now essentially talking about the wave like nature of the electromagnetic radiation that you are using.

So, that wave is bent and redirected into in a certain direction; that is what we call as diffraction, very much related phenomenon is also scattering, but there is a minor difference. In fact, you will often also hear the word the term scattering in the context of X-ray diffraction.

There is a minor difference though that scattering can take place in all directions while diffraction rather takes place in specific directions. What is important in the case of diffraction or for us to get the diffraction patterns is that there is a constructive interference between the waves.

What is constructive? What is destructive interference? That you can learn as I said I will also mention some references towards the end, some other NPTEL lectures from there you can learn. But this is something probably you also remember from slit experiments constructive and destructive interference patterns. So, we need to have the constructive interference in order to have the diffraction patterns.

And what is most important when it comes to X-ray diffraction, the entire studies or entire field is kind of based on what is known as the Bragg's law.

$$2d \sin\theta = n\lambda$$

d is the most important parameter for us that is your interplanar distance. Interplanar means the plans of the crystal 1 2 3. So, what is the distance between that them that is what is d.

Now, when we talk about graphite, we have a hexagonal crystal. And it is not hexagonal closed packed system that is something you need to remember, because this Bragg's law has certain different parameters when we talk about let us say a cubic system, cubic and hexagonal already have slightly different parameters.

In the case of graphite like carbons what is also very interesting is that we do not have crystallites like in the case of cubic systems. You will have certain crystalline regions, in certain amorphous regions or there will be certain cubic systems which at a certain temperature they convert from FCC to BCC.

In those cases, X-ray diffraction becomes very important, you try to understand. But you can very clearly see the change in the parameters of FCC and BCC using X-ray diffraction. In the case of carbon, we have arrangement of layers, but those layers have a lot of defects and they are probably turbostratically arranged. And with the increase in temperature, we want to have most of the defects annealed out. We want to get more and more order.

So, the ordering does take place, but it is very gradual.it does not so happen that at a givens temperature point, let us say 1200 °C, it will never happen that at 1200 °C you suddenly see a jump in the properties or completely changed crystal structure, you will not see big difference in your d spacing also.

This is gradual and that is why it becomes a little bit tricky to understand how does this increase take place, and also it becomes a little bit tricky to define the crystal structure because we know the crystal structure for graphite is well defined. But most of the carbons that we are dealing with, they are not graphite, they do not have a 3d arrangement.

So, for us to define the crystal parameters for them is also tricky, also given they contain a lot of defects. And we do not understand the nature of these defects as well. This is what we are going to discuss. And we will also talk about how we can come to a certain trade off, a certain set of parameters which gives us more or less accuracy information.

So, this is the Bragg's law. What are the other terms is θ, theta is your Bragg's angle. Basically, this is the angle of your incident ray. And from a very simple geometry, you can understand how does ray is incident, and how does it get diffracted, and what is the relationship between θ and 2θ. So, this is what I will quickly explain to you.

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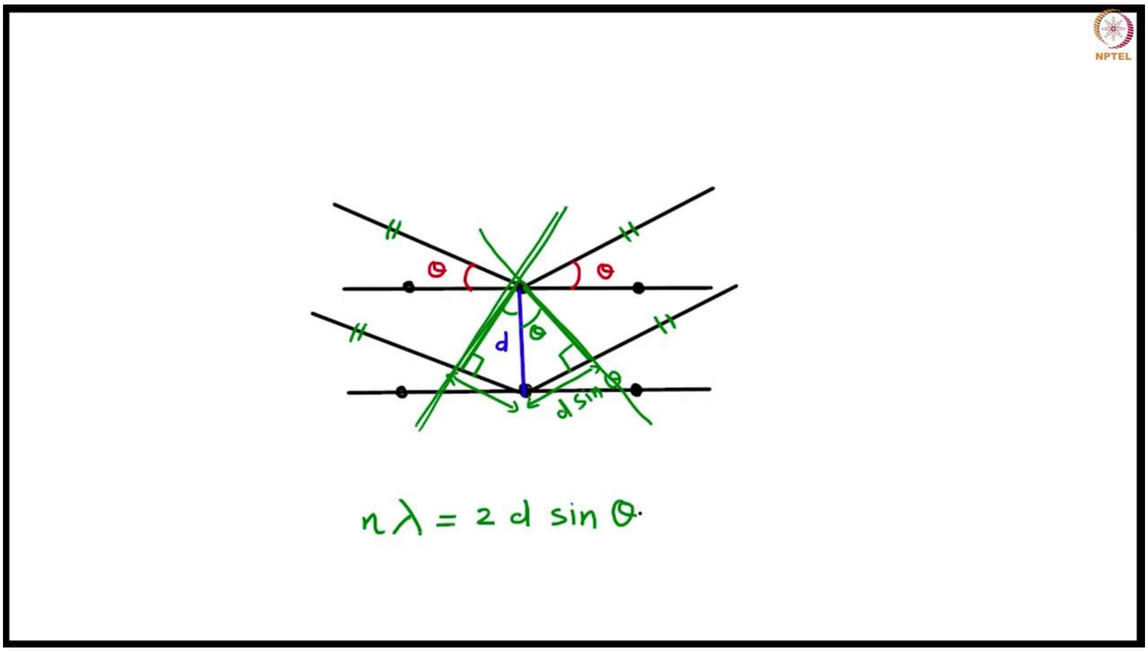

$n\lambda = 2 d \sin\theta.$

Now let us quickly derive Bragg’s law. Here I have drawn two planes of your crystal with the atoms. And this is your first incident X-ray and this is your diffracted X-ray. You can also use the term reflection. Here is the second one and that is also diffracted. Now, these angles here, this is the angle of your incident ray.so that is theta and this angle will also be equal to theta.

And now, we need to find out the relationship of d. This is your spacing between the two layers, this is what you need to find out. And for this purpose, we need some triangles to find out certain relationships between the angles.

So, let me draw one perpendicular on this line, and on both of these lines. So, when I say perpendicular, this means that this angle is 90, this angle is also 90. And this value here is my d. Now, if you will see from these two triangles, you can very easily calculate that this angle and this angle are also equal to theta.

Now, we need to find out the relationship of d with that of the wavelength. The Bragg’s law is valid only when there is constructive interference. And for the constructive interference, there is a condition that λ should have its integer multiples which means we should have something like nλ only then there will be constructive interference.

And what we need to find out something in terms of d n θ. So, this is now very simple. From these triangles, you can see that this value is equal to dsin(θ), and similarly this value here. And why do we care about these two values, because well till here both our beams — the first one and the second one, they both traveled equal distance right.

And also after this particular value here — this part and this part are also equal. The only additional part is this 2dsin(θ) that your second X-ray has traveled. So, that is basically

$$n\lambda = 2d\sin\theta$$

And this itself is your Bragg’s law’ it is as simple as that. So, another thing that is important for us here is what is the experimental value? What is the value that you receive from your experiments? that is the value of d, because d is the unknown in the Bragg’s equation. We know that θ is the value of the angle. So, we know always the incident angle and we also have a detector in our instruments. So, we know the value of 2θ that is what basically you will get.

So, you can calculate the θ. We always know the value of λ because that is the wavelength that we used.in most cases, the most commonly used wavelength is CuKα. And on top, I have already mentioned the value of it; it is 1.5406 Angstrom. So, this value you will always know.the only thing that is unknown is your d.

So, what are 00l planes? 002, half of it 004, 006. So, you have I just call them 00l, but 2, 4, 6 these are the reflections or the next order of the same type of planes.

So, what value you will see you will get a certain peak for 002 plane, and then after some time you might get a peak which is shorter than this one, that is known as the reflection and that is also known as the second-order peak for 00l plane. So, in that case, the value of n is 2, in the case of 006 it will be 3. For 002, it will be 1.in most cases, we are going to just use a value of n as 1.

Here I have also mentioned that d is related to h, k, l, and to 2a which is your crystal lattice parameter as well. So what are h, k, l? These are miller indices of any plane. Here I have mentioned these two relationships, one is for cubic crystal and the other one is for hexagonal crystal systems.

Often what happens is when you get the value of d from your experiment, then you can using these relationships. You can find out what are the possible values of h, k, l often you will because all three of them are unknown, you will probably often you will know some things about your material.

So, you will also guess like it can be 100, or it can be 111, and 002, whatever. So, you will guess certain values and you will find out what the values that you receive that satisfy this kind of equation. And then whatever different values from different peaks you get from a certain X-ray diffraction pattern — you will get different peaks in one pattern itself or one diffractogram itself — in that case, you will get some sets of values for your h, k, l and often there are some rules which will say the summation of h, k, l is; even in that case it could be FCC or it could be BCC or if the summation is odd, and then, in that case, this is the possible crystal structure.

So, basically based on those rules, then you will guess what your material is. Similarly, for hexagonal systems, the only difference is that now you also have a value of c. These are the exercises you will do if your crystal structures completely unknown to you, if you have no idea, let us say even if whether the material is FCC, BCC. You have no idea about it maybe you even do not know what kind of metal it is. In that case, you will start from here that you now guess your h, k, l values. And whether it is closer to FCC or closer to BCC or closer to a simple cubic system, accordingly you will guess what your material is. But in the case of carbon materials, especially graphitic carbon materials we already know what we are dealing with.

We know the crystal structure of graphite; we know that we have basal planes; basal planes are most important. So, when we have these graphite-like sheets stacked on top of each other, these planes are known as the basal planes, and these are denoted as 00L. Why 00L? Because, well, the first one is 002. If you remember the unit cell of graphite, we have A B A. So, one A, then B, and then an A layer again.

And this entire thing is your crystal parameter c. So, c basically also has one sandwiched B type layer. So, when you calculate the lattice parameters, again we have done it in the graphite crystal structure class, main you will find out that these are 002 planes. And these are kind of the most important planes because this is what actually defines all the properties. This plane and the organization of this plane are what define most of the properties.

So, the point is that we do not really need to go into these kinds of exercises where we need to guess the crystal parameters, but what we rather need to do is to see whether or not what is the location, and the width of the peak for 002, and some other peaks. Still, I am talking about the basics of X-ray diffraction.in the diffractogram pattern, you get all your peaks that is known as diffractogram, also people call it X-ray diffraction pattern.

It is not called spectrum by the way. Although it looks very similar. And certain things are also valid for both spectra and diffractogram. They are similar in some sense, but there are minor differences. So, one important difference is that, in the case of spectra, we are often measuring a property that is related to energy, but in the case of diffractogram, we are measuring just geometric calculation. So, that is one important thing.

Another thing is that in the case of spectra, if you have a spectrum of a mixture, then it is additive. So, properties of a plus properties of b, will give you the properties of a plus b, but that is not the case that is not necessarily the case when it comes to diffraction patterns. So, that is why they are slightly different. So, it is not correct to call this X-ray spectrum, that is why use we use the term diffractograms.

Here I have shown a very basic schematic of an instrument. You see that we have a cathode ray tube and cathode ray tube are used for the production of X-rays. You can also have any other method. You can go to a synchrotron also, and then you can have any source of X-ray as long as you have well-defined λ. And in some very specialized cases, you might also use a mixture of lambda; there the calculations are slightly different, we will not go into that.

For common X-ray diffraction analysis that is performed for chemical compounds or materials, in that case, we have often cathode ray tube and then you will have certain wavelength filters, and then you have your sample at a certain angle, and the X-rays are then incident upon the sample and then they are diffracted. And you can see the angles are θ and 2θ.

And then of course, you have a detector, and it is typically the detector that rotates and not the cathode ray tube. Although in some cases some instruments may also have the tube or the source of X-rays rotating. But in most of the common X-ray diffraction equipment, you have a detector that is rotating with a certain angular speed.

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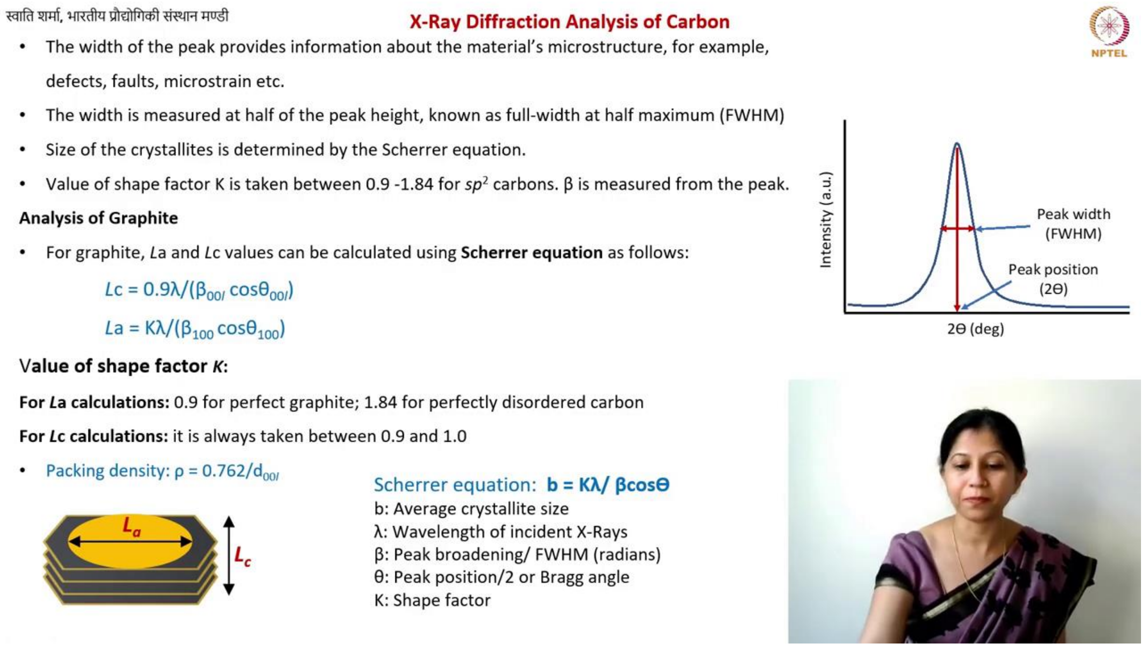

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X-Ray Diffraction Analysis of Carbon

- The width of the peak provides information about the material's microstructure, for example, defects, faults, microstrain etc.
- The width is measured at half of the peak height, known as full-width at half maximum (FWHM)
- Size of the crystallites is determined by the Scherrer equation.
- Value of shape factor K is taken between 0.9 -1.84 for *sp*^{2} carbons. β is measured from the peak.

Analysis of Graphite

- For graphite, *L*a and *L*c values can be calculated using **Scherrer equation** as follows:

$$Lc = 0.9\lambda/(\beta_{00l}\cos\theta_{00l})$$

$$La = K\lambda/(\beta_{100}\cos\theta_{100})$$

Value of shape factor *K*:

For *L*a calculations: 0.9 for perfect graphite; 1.84 for perfectly disordered carbon

For *L*c calculations: it is always taken between 0.9 and 1.0

- Packing density: $\rho = 0.762/d_{00l}$

Scherrer equation: $\mathbf{b = K\lambda/ \beta\cos\Theta}$

b: Average crystallite size
λ: Wavelength of incident X-Rays
β: Peak broadening/ FWHM (radians)
θ: Peak position/2 or Bragg angle
K: Shape factor

Now, let us come to the XRD analysis of carbon materials. So, we will start with graphite, because first of all, you need to understand what is graphite only then we will understand the materials that are not graphite or that we are comparing the graphite. So, you remember this little schematic La and Lc.

What is La? It is the crystalline diameter. And if you are looking from the top view, and this stack thickness is when you have a lot of these sheets stacked on top of each other, then how many sheets are stacked that is stack thickness. What would be the d interlayer spacing? That is between the spacing between two layers. So, within Lc if you let us say your Lc equals 5 times d. So, if you have 5 layers, so whatever is this space or 6th layer, so whatever is the spacing between them, that is the spacing which is known as d, which is your most important crystal parameter especially in the XRD. So that is one thing that I have already mentioned.

But the other thing is what is the width? Now, we know that we will get a certain peak if we have a graphite-like material. If you have pure graphite, you will get a sharp peak for a 002 planes. If you do not have pure graphite, then you will get a broader peak. But now how is this width of the peak related to your graphite or graphite-like materials? This is very important to us.

How do you measure the peak width? Let us say this is any standard given peak in your XRD pattern and the peak is not too short at the end, it broadens a little bit. There are two important parameters here. When you measure the width of your peak, you often measure it at the center or at half of its height, and that measurement is known as the full width at half maximum. So, that is what you call peak width. And the position of the peak is essentially your Bragg angle 2θ.

Now there is also another important equation that is used for the calculation of the parameters that is where you will get your Lc and La values. So, this equation is known as Scherrer equation. So, this is your Scherrer equation which basically relates the average crystallite size b to the rest of the crystal parameters λ and cos(θ) value.

θ here still is the same so you will get this from your diffraction patterns. You can get the value of 2θ, and you can calculate θ. What else we have? The other new things that we have here is β, it is basically nothing but your FWHM, so that is your inradius, you take your peak width. So, this is also something that you can experimentally obtain.

There is something known as a shape factor. So, you see it is like a constant in this equation that is not something that you will get experimentally; that K is important. And typically for most materials, the value of K is taken between 0.9 and 1.2, and actually many calculations it is just taken as 1. But in the case of different carbons, then this value of K will differ.

But the idea of Scherrer equation is that this is the equation that will give you the value of both La and Lc from different peaks from different sets of planes fine. Now, let us come to what is the value of K for graphitic or for carbon materials. So, I said that this is between 0.9 and 1.2 for most materials, but here we will go all the way to 1.84. Why? Because you see these 002 planes, they can be very far from each other as your material becomes more and more turbostratic.

If you look at even a TEM pattern image or you see an XRD pattern or anything about carbon materials, the minute you say see that the separation between the d — the interlayer separation, is more than 0.335 nanometer, then that this is not graphite. So, in the case of graphite, this is exactly 0.335 nanometer.

Now, what happens when this distance increases; when it increases up to 3.44, it is considered turbostratic carbon.above 3.44 although it is debated that 3.44 should be considered the limit or not, but at least traditionally up to 3.44 it was considered turbostratic carbon.

After that people though it is just totally disordered and the material was not even studied if the interlayer spacing was more than 3.44 because in that case it is supposed to have too many curves or too many defects.

But nowadays because we understand curved carbons. We understand non-graphitizing carbons contain fullerenes, and in that case even 3.44 is not considered as a limit. If it is let us say 3.5, we still call it just a turbostratic form of carbon. So, the idea is that if anything is above 3.354 Angstrom, in that case it is not perfect graphite crystalline.

If it is graphite, then we take the value of this shape factor K as 0.9. As it becomes more and more turbostratic, the value of K increases in the case of completely disordered carbons. What we would assume that if layer spacing is above 3.44, in that case, you will typically take the value of your K as 1.84 for the calculation of L a. But in the case of L c, you will still take the value between 0.9 and 1.

So, I have mentioned all of these here. These are the two important things. Which planes do you use for analyzing your La, and Lc? In the case of Lc, it is actually easier to calculate. Lc is the stack thickness because we are more concerned about the 002 planes which are also very easily visible. This is the strongest peak that you get between 26 and 27 points something like that.

And that is in fact, considered the signature of graphite-like carbon materials which is your 002 peak. So, this is an easy to calculate, you will typically have reasonable shapes of this peak. This does not mean that your material is graphite because in the case of perfect graphite you should have perfectly Lorentzian peak; very narrow peak. So, if you are not getting a perfect Lorentzian peak, then it’s not graphite. It is definitely not a perfect graphite crystal, still this is the signature peak of graphitic carbons.

So, Lc is easy to calculate, and here also your value of K is taken as 0.9. In the second one, the calculation of L a, I have just written Kλ, because this is where the value of K will change.

This is where it will be between 0.9 and 1.84 depending upon what is the degree of disorder in your material. So, if you have completely curved carbons, very high disorder; in that case, you will go all the way to 1.84. And in the case of Lc, as I mentioned this is always 0.9.

Another important parameter is the packing density. Packing density becomes more important when you have perfect graphite crystallites, but not in the case of non-graphitizing carbons so much. But if you want to see the packing density and even you can calculate the number of atoms in a certain sheet of graphite, but that relationship I have not mentioned here.

But packing density which is more commonly calculated is this ρ. And this is the formula for that

$$\rho = \frac{0.762}{d_{00l}}$$

Again 00l, here typically you will use the value 002 because that is your first order peak, and where n equals 1. But you can also potentially calculate it from 004 or 006 peaks.

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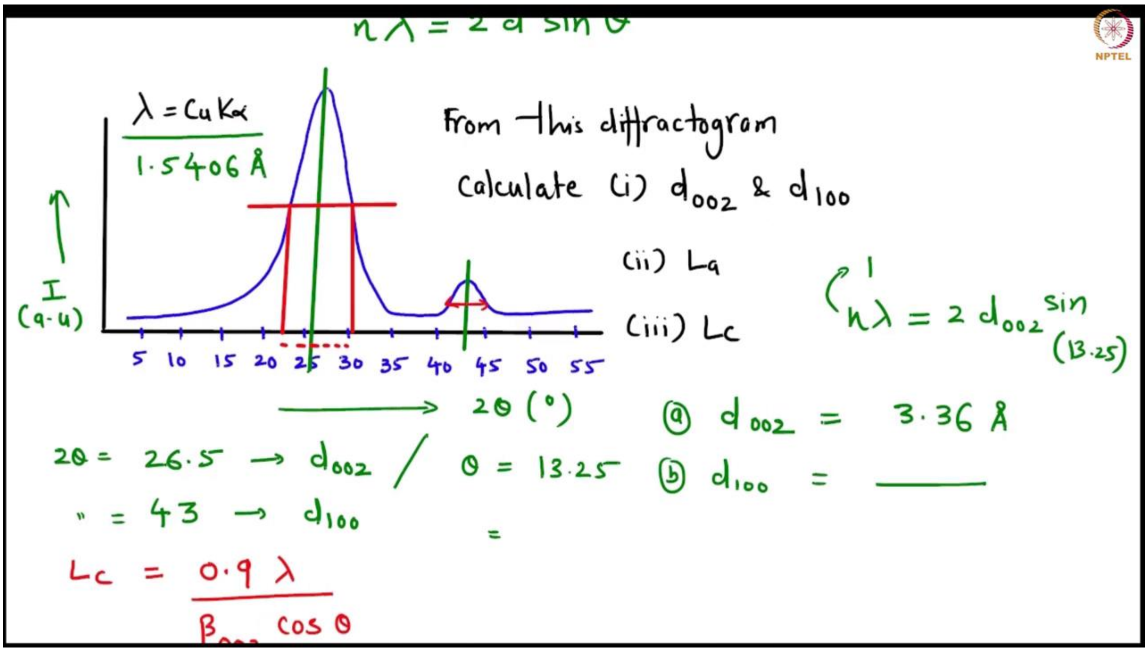

$n\lambda = 2d\sin\theta$

$\lambda = Cu\,K\alpha$

1.5406 Å

From this diffractogram

Calculate (i) d_{002} & d_{100}

(ii) La

(iii) Lc

$\overset{1}{n}\lambda = 2\, d_{002} \sin (13.25)$

ⓐ d_{002} = 3.36 Å

ⓑ d_{100} = ______

2θ = 26.5 → d_{002} / θ = 13.25

" = 43 → d_{100}

=

$L_c = \frac{0.9\,\lambda}{\beta_{002}\cos\theta}$

Now, let us solve a quick problem hopefully that will help you understand in case something was not clear from the slides. You are given this particular diffractograms, and there are a few things that are given to you. For example, this is the wavelength that you have used is CuKα. So, you already know what is the value of CuKα, wavelength — 1.5406 Angstrom. So, this is something that is given to you.

What is this? This is your 2θ in degree, and this is your relative intensity. This is in arbitrary units. So, this is the diffractograms that is given to you. Now, first of all you need to calculate the d spacing for 002 planes and also for 100 planes that is number 1. Number 2 is the crystalline diameter or La, and number 3 is the stack thickness.

Now let us get started. We have the first peak that we see, what is the position of this peak?let us draw a line here somewhere here. So, approximately let us say I have calculated it to be 26.5, and this one here let us say I found it out found out that this was 43.

So, our first peak position is 26.5 which is for d002 planes; and the second one is 43. So, this is for my d100 plane. So, these are the values of 2θ.

And we need theta values. So, in this case, it will be 13.25, and here also you can accordingly find out. So, this is number 1. From here itself we can calculate the d spacing. So, d002 basically can be calculated by simply by Bragg’s law.

$$n\lambda = 2d_{002}\sin 13.25$$

So, if you calculate this value, so the n here is 1 because it is a first order peak. If we were calculating it using 004 peak, in that case we will take it as 2. So, from here you can already calculate. I have already calculated it. You can do this simple calculation. But it comes out to be something, what is the value? It comes out to be somewhere around 3.36.

λ here by the way was our 1.5406 Angstrom and that is why the value that I will get here will also been Angstrom and not in nanometer. You can also take your λ in nanometer in that case, you get nanometer value. So, this is your already the first part that is solved, for the 002 planes. And accordingly you can also solve it for 100 planes whatever is the value. So, this is the first part.

Now, what else do we need to calculate? La and Lc. So, let us, let us first calculate the Lc value, because this is the easier one.in the case of Lc when we use the Scherrer equation, we take the shape factor as 0.9; in the case of stack thickness. So, what is your Scherrer equation?

Kλ/β is the width of your peak. So, here we are going to take it for the 002 planes. So, this is what we need to do for Lc. So, let us first find out what is your peak width. By the way, usually you will do it using some software. Often the XRD software will give you the peak width, and also you can take the data and find a fit in origin or any other software for that matter. But here let us see how do we calculate this? So, well this is my full width at half maximum. So, what is the half maximum let us say somewhere here for my peak.

And now, I draw two lines from here and here. And this value here is what I need to see, what is it? So, approximately its 8, but that is in degree and what I need this in radian.

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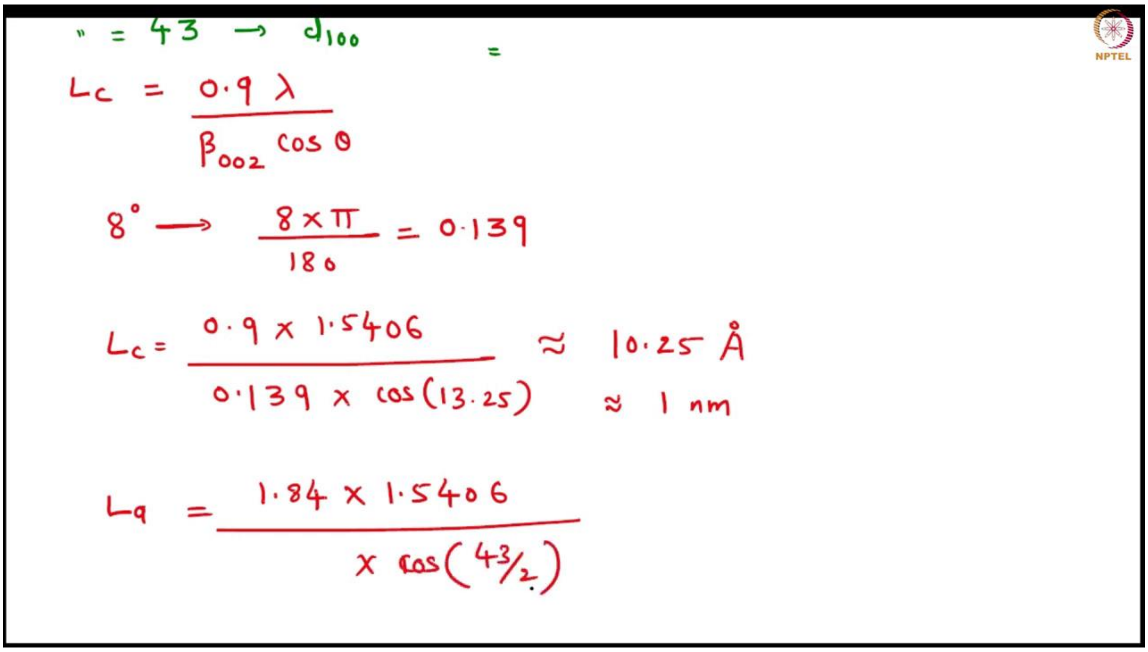

$$'' = 43 \rightarrow d_{100} \qquad =$$

$$L_c = \frac{0.9\,\lambda}{\beta_{002}\cos\theta}$$

$$8^\circ \longrightarrow \frac{8\times\pi}{180} = 0.139$$

$$L_c = \frac{0.9\times 1.5406}{0.139\times\cos(13.25)} \approx 10.25\,\text{Å} \approx 1\,\text{nm}$$

$$L_a = \frac{1.84\times 1.5406}{\times\cos(43/2)}$$

So, I just calculated to radian. How do I do that?

$$8^\circ \longrightarrow \frac{8\pi}{182}$$

So, it comes out to be something like the value I have calculated as 0.139, so that is my value in radiant. And now I can just calculate the rest of it. So, this is basically my Lc

$$Lc = \frac{0.9 \times 1.5406}{0.139 \times \cos 13.25}$$

So, again I have calculated this value; it comes out to be approximately 10.25 Angstrom. So, you can see that the value is approximately just 1 nanometer that is your crystallite thickness, this is your stack thickness. So, this is already kind of a disordered carbon.

Now, let us now come to La value here. So, for La you need to calculate the width or FWHM for the second peak, La is calculated using d_{100}. So, you have the same formula, but what you have here is number 1 and your shape factor is now 1.84.

Also because we see that the crystallites are so small and the peaks are broad, so we kind of have an idea, it looks like a turbostratic carbon. It looks like a disordered carbon rather than a perfect graphite because in that case you will get relatively sharper peaks. So, we take 1.84 as the value of K, so that is the major difference. Of course, the value of λ does not change.

Now, here some values, so the θ is the 43/2, so that is the value that will change. And of course, the peak width which you will calculate from again from this diagram. So, this value, peak width, this also will change. And now whatever is it is let us say x and then you can calculate it for yourself. So, this is how you will calculate different crystallite size and crystallite diameter from a given peak.

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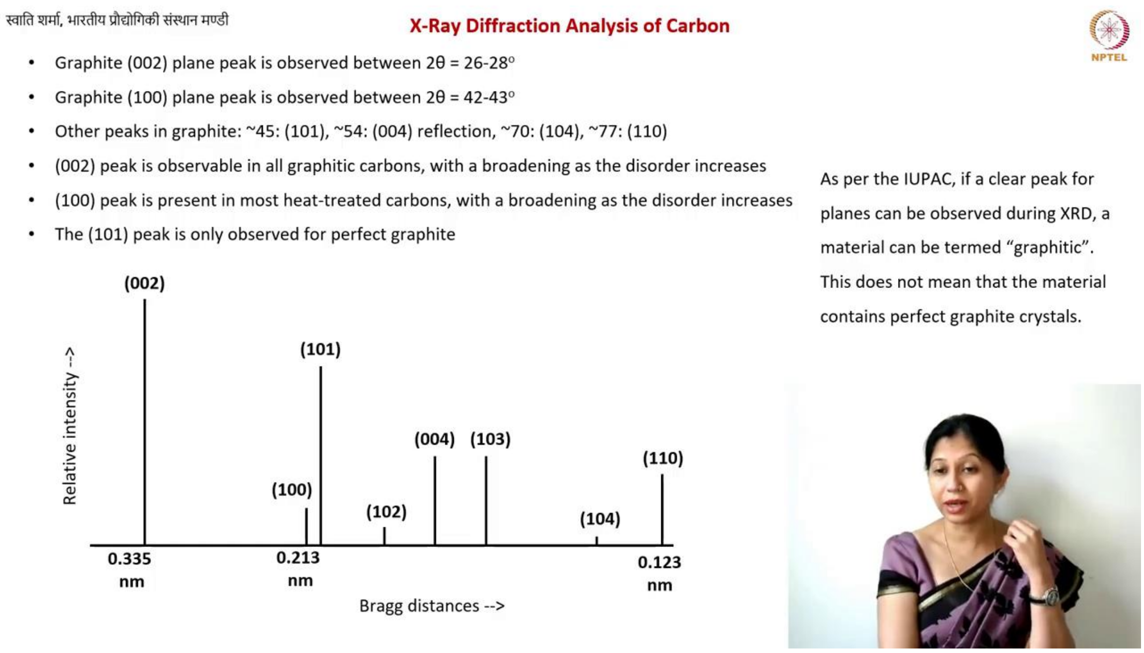

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X-Ray Diffraction Analysis of Carbon

- Graphite (002) plane peak is observed between 2θ = 26-28°
- Graphite (100) plane peak is observed between 2θ = 42-43°
- Other peaks in graphite: ~45: (101), ~54: (004) reflection, ~70: (104), ~77: (110)
- (002) peak is observable in all graphitic carbons, with a broadening as the disorder increases
- (100) peak is present in most heat-treated carbons, with a broadening as the disorder increases
- The (101) peak is only observed for perfect graphite

As per the IUPAC, if a clear peak for planes can be observed during XRD, a material can be termed “graphitic”. This does not mean that the material contains perfect graphite crystals.

Now, what are the different peak positions for graphite for different planes? So, the 002 palne as I already mentioned is between 26 and 28, that is where you will typically observe the value. Of course, for different types of carbon materials, it can also be slightly shifted.

For example, non-graphitizing carbons may have a broader peak which will also be probably left shifted a little bit, but this is the range where you will typically observe the peak. Of course, this will also depend on the wavelength that you have used for your analysis. So, most of the things that I will tell you in this lecture or assuming that we are using CuKα wavelength. So, this is the first one.

What else the other important peak? So, in the previous slide, we also saw that in the Scherrer equation, for calculation of Lc, you will use the 002. And for calculation of L a, you will use this 100 peak. So, this peak is observed in most of the heat treated carbon.

You will also have it in some porous carbons in glass like carbon. So, as long as you have heat treated it to a reasonably high temperature, you should be able to see this peak. However, this will be present in a broad, it becomes broader reasonably fast, but you will have this peak available for you for the calculation of La.

If the carbon materials become very curve then turbostatic or the sheets are too far from each other; in that case, you are seeing is actually not the 3D structure right. When even though I say 100 plane it is not really 100 plane; it is 10 plane. It is not h, k, l; it is just h K that I am measuring. Because this is more of a 2D structure, in that case we do not really have any 3D arrangements.

So, in that case, you will also find 10 plane written here and there; instead of 100 you will say 10. This plane basically tells you more about the inter atomic arrangement within a layer. So, the arrangement of hexagonal rings whether you have defects or not, so this is more information of one plane, and it is more of a 2D information and that is why this is also sometimes called h k plane rather than h, k, l plane. However you will see the peak at approximately 42 or 43.

There are other possible peaks which are mostly present in graphite rather than other non-graphitizing carbons. Some of them can be observed here and there, but in most cases if you have a perfect graphite crystal, then you should be able to see all of these peaks. So, 002 peaks almost always available, but definitely it broadens as the disorder increases in a material.

100 peak, as I mentioned, in most heat treated carbons it is present, but again this also becomes broad reasonably fast as your disorder increases. 101 peak, which is almost always absent if the material is not graphite; in perfect graphite only you should be able to see this 101 peak.

And this 111 is approximately at 44 or 45, you will practically see it almost right after if your spectrum is going from left to right, if your diffraction pattern is going from left to right. In that case, you should be able to almost always see it for graphite just after 100 peak. So, this 101 peak, however, is missing from all non-graphitizing carbons because even slight disorder can make this peak disappear.

So, maybe it will become more clear from here. So, this is a typical diffraction pattern. These are the positions. These are not realistic peaks because there you will see the broadening, but these are just the positions that I have mentioned here. If you will see I have mentioned Bragg distances rather than Bragg rather than 2θ values because this you can very easily calculate from your Bragg's law.

In fact, this will be a nice little exercise for you. And the relative intensity is on the y-axis, the intensity in most cases is mentioned in arbitrary units because this is a relative intensity. And that will depend on your crystal size sample size and everything. So, this is always a relative value that is why it is arbitrary units. The Bragg distances here are in nanometer.

One more important thing is that as per IUPAC, materials in the X-ray diffraction studies, if you can observe a peak for graphite which is specially the 002 peak, then you can call them graphitic. But, on the other hand, that is not always true because if it is too broad, what is the limit to which you should call it graphitic material that is also very interesting question?

However, this is the IUPAC definition often we will use this the XRD studies as I said to understand how the graphitic content of a certain carbon increases.

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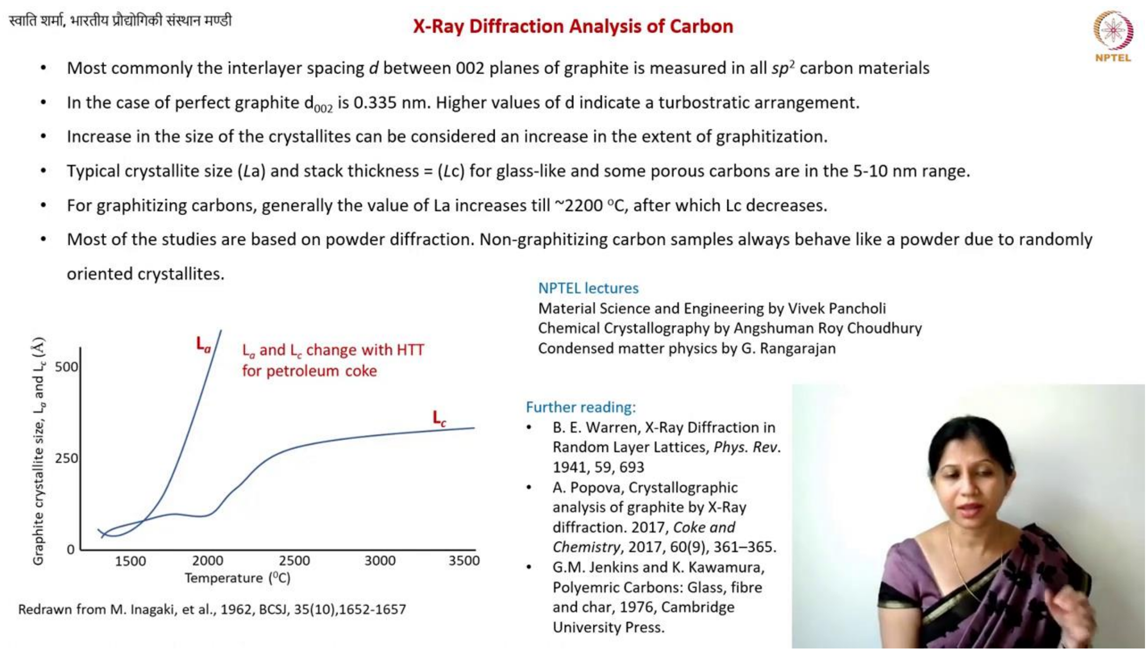

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X-Ray Diffraction Analysis of Carbon

- Most commonly the interlayer spacing *d* between 002 planes of graphite is measured in all *sp*^{2} carbon materials
- In the case of perfect graphite d_{002} is 0.335 nm. Higher values of d indicate a turbostratic arrangement.
- Increase in the size of the crystallites can be considered an increase in the extent of graphitization.
- Typical crystallite size (*La*) and stack thickness = (*Lc*) for glass-like and some porous carbons are in the 5-10 nm range.
- For graphitizing carbons, generally the value of La increases till ~2200 °C, after which Lc decreases.
- Most of the studies are based on powder diffraction. Non-graphitizing carbon samples always behave like a powder due to randomly oriented crystallites.

Redrawn from M. Inagaki, et al., 1962, BCSJ, 35(10),1652-1657

NPTEL lectures
Material Science and Engineering by Vivek Pancholi
Chemical Crystallography by Angshuman Roy Choudhury
Condensed matter physics by G. Rangarajan

Further reading:

- B. E. Warren, X-Ray Diffraction in Random Layer Lattices, *Phys. Rev.* 1941, 59, 693
- A. Popova, Crystallographic analysis of graphite by X-Ray diffraction. 2017, *Coke and Chemistry*, 2017, 60(9), 361–365.
- G.M. Jenkins and K. Kawamura, Polyemric Carbons: Glass, fibre and char, 1976, Cambridge University Press.

Now, you understand that 002 peak is your most important peak that helps you calculate your Lc value. You also know that in the case of perfect graphite, it is 0.335 nanometer. But as it increases, then you have turbostatic carbon. So, these are some basic things that you can immediately do.

Now, the increase in the size of crystallites, size of crystallites means La values. That becomes a little more tricky to understand rather than Lc value as I had also said before. But the increase in La and the decrease in Lc is what will tell you how much graphitic your material is.

So, if you keep on heating your material, let us say you will have a graphitizing type carbon and you will have a non-graphitizing. Non-graphitizing carbon even if you heat-treated at 3000 °C, you will never see the values that you would have for perfect graphite, you will always have a peak broadening.

But in the case of graphitizing carbon, first you will have an increase in La up to let us say 2000 degrees, and then you will rather see more organization and either decrease in Lc, but if not significant decrease at least with more and more order you will see that the Lc value will stay there will not in a change further.

But also Lc value about 2200 °C, they do not further increase. Then what we have is the graphitization process. And for that purpose, you should see the lecture on the kinetics of graphitization. So, you will know that this is a kinetic process and what actually takes place.

we know how to calculate La and L c. For most of the non-graphitizing carbon, these values are between 5 and 10 nm. They can also be smaller than 5 nm, which is then very short-range order, let us say glass like carbons are in the order of 5 nm.

This is what we call crystallites. Although they are not really spherical crystallites, but these are regions where you have the order, and these regions are then randomly oriented in all directions similar to polycrystalline material. But the difference is that in the case of polycrystalline material it is one crystal and the other two crystals are not connected.

But in the case of non-graphitizing carbons, all the crystals are connected, they are not just crystals, but you also have curved structures. You have very long sheets maybe some part of that one particular sheet is forming a layer in another crystal.

But the rest of the same sheet might be curved and might be going somewhere else, and maybe participating in another crystallite that we do not know. The point is that we have these regions the short-range order, that is of the order of 5 to 10 nanometer. This is something that you can increase by increasing the heat treatment temperature.

So, you will start with 2 nanometers crystallite size, you can go all the way up to 10 nanometers. For non-graphitizing carbons, not easy to go above 10; typically you cannot get crystallite sizes of above 10 nanometer because this is what we mean by the short range order.

Here is simple is the diagram which I have taken from this reference that I have mentioned where you will see that for petroleum coke, if you keep on increasing the early treatment temperature, how do the values of La and Lc change. So, you can see that up to let us say 2000, 2100 and so on, you have pretty sharp increase in L a.

So, what is happening is basically your crystalline diameter is increasing. That means, if you had a lot of non 6 membered rings, then they are annealing out and this network of 6 membered rings int 2D is increasing that is the increase in L a.

And change in Lc of course, at some point it becomes a little bit stable because it does not change too much because the minimum value of b can only be 3.35, but also initially you will have the sheets too far from each other; they will come closer.

But at some point, then it takes a lot of energy for them to convert into graphite-like sheets or AB AB A type sheets because that requires pretty much all the defects to anneal out. So, that is a very slow process. So, you can see here how with respect to the temperature heat treatment temperature the values of La and Lc change.

One more important thing is that most of the studies that we do are powder diffraction studies. Carbon single-crystal studies can be done on perfect graphite, natural graphite crystals. In fact, often you can do single crystal studies, but the intensities are pretty low and you can actually get pretty good information also from the powder diffraction.

So, if you have a non-graphitizing carbon, then you already have the crystallites oriented in all directions. Even if you take a solid piece of that material as a sample, still you are going to get a value of what you would get in powder diffraction pattern. So, basically you will have the diffraction in all directions, in all possible angles which are detectable anywhere. So, in most cases, you will do powder diffraction for carbon materials.

I would like you to also go through some of these other NPTEL lectures, and also there were some other lectures which I had mentioned in the basic material science and engineering courses I have mentioned in a couple of other slides and initial lectures especially.

In that case, you can just go through all of these lectures maybe you will get much more information about crystallographic aspects, and also the generation of X-rays from different viewpoints; from a physics viewpoint, from an engineering viewpoint and from material science. So, you can go through other NPTEL lectures.

There are certain papers and books that are mentioned here. There are various books because X-ray diffraction is a very common technique for carbon analysis. So, you will find a lot of literature on this topic, there is an overwhelming amount of literature. But this the book and papers that I mentioned are more specific to graphite and bulk carbons rather than carbon nanomaterials.