

**Indian Institute of technology Madras  
Presents**

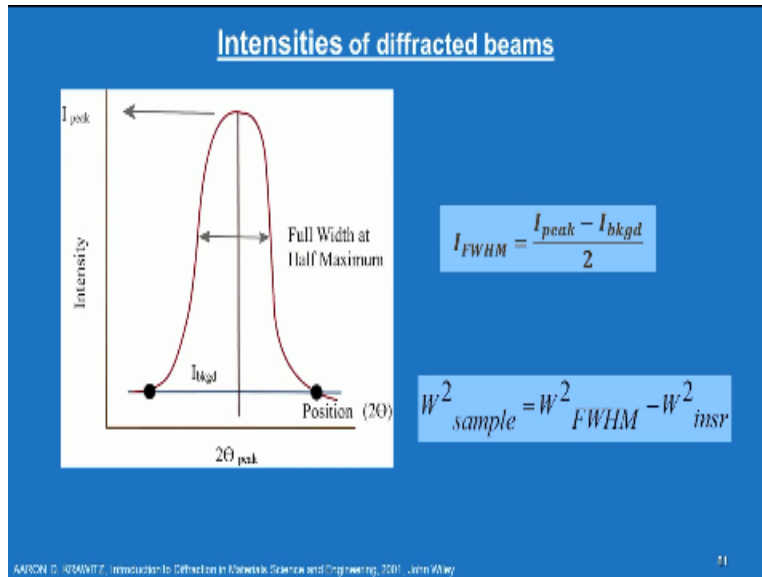
**NPTEL  
NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING**

**Lecture - 30  
Materials Characterization  
Fundamentals of X-ray diffraction**

**Dr. S. Sankaran  
Associate Professor  
Department of Metallurgical and Materials Engineering  
IIT Madras  
Email: [ssankaran@iitm.ac.in](mailto:ssankaran@iitm.ac.in)**

Hello everyone welcome to this material characterization course in the last class we looked at the effect of crystallite size on the peak intensity of x-ray diffraction similarly we also looked at the effect of strain on the x-ray intensity of peak after diffraction and before we get into the details further details I would like to show you a little bit about the intensity big details because we always say that whether it is the effect of crystal size as well as strain or instrumental broadening everything we account for be the breadth of the peak so how to understand this and how to correct this peak for the required intensity from which you either calculate the crystallite size or characterize the strain in the materials so look at this slide this is a typical x-ray diffraction peak where you have a peak.

(Refer Slide Time: 01:21)



Intensity as well as the integrated intensity which is under area under the peak and then you have the typically we always measure the full width at half maximum and then this is the background you have to subtract  $I_{background}$  and you have the intensity at full width of maximum is equal to  $I$  that means intensity peak minus intensity background / 2 and we also discuss about this peak broadening is due to sample as well as the instrumentation reasons so that can be represented by this  $W_{sample}^2$  is equal to  $W_{FWHM}^2 - W_{instr}^2$  so this is a typical peak representation of x-ray diffraction.

So from there how do I mean separate all this effects that is exactly we want to see before that we would like to see some of the models.

(Refer Slide Time: 02:32)

| Intensities of diffracted beams |  |
|---------------------------------|--|
| Function (Symbol)               | $I(2\theta)_i$   |
| Gaussian (G)                    | $I_p \frac{(4 \ln 2)^{1/2}}{\pi^{1/2} W_{FWHM}} \exp \left\{ \frac{-(2\theta_i - 2\theta_p)^2}{W_{FWHM}^2} \right\}$ |
| Lorentzian (L)                  | $I_p \frac{2}{\pi W_{FWHM}} \left\{ 1 + \frac{(2\theta_i - 2\theta_p)^2}{W_{FWHM}^2} \right\}^{-1}$                  |
| Pseudo Voigt                    | $\eta L + (1 - \eta)G$   |

Note:  $I(2\theta)_i$  is the intensity at the  $i$ th point on the peak,  $I_p$  is the peak intensity,  $(2\theta)_i$  is the position along the profile,  $(2\theta)_p$  is the peak position,  $W_{FWHM}$  is FWHM of the peak, and  $\eta$  is a mixing fraction having a value between 0 and 1.

AAEPON ID: 1024WIT2 - Introduction to Diffraction in Materials Science and Engineering, 300 - John Wiley

Typical models for x-ray diffraction show it is very clear that if you want to quantify some of these effects you need to model them first and then some of the models which are represented in this table for an x-ray diffraction you see that the first column is a function second column is the intensity so you see the first the Gaussian if your peak can be fitted into the Gaussian this middle based upon this expression then we can do certain type of calculations and then secondly if your peak can be modeled with the Lorentzian function.

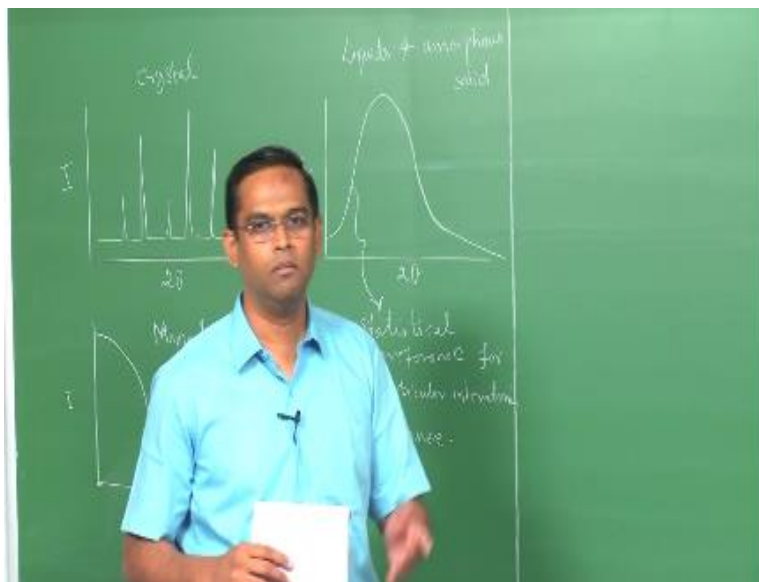
Like this then that has got some advantage we will see and then you also have a pseudo white model which is represented by this equation I will not get into the details of this but you should know the basic idea of the fitting the x-ray diffraction then how it can be utilized so let us look at the meaning of the details of the terms which is given in this equation  $I(2\theta)_i$  is the intensity at point on the peak that means any point on the peak  $I_p$  is the peak intensity to  $\theta_i$  is the position along the profile to  $\theta_p$  is the peak position.

FWHM is the full width half maximum of the P and E time is the mixing fraction having a value between 0.2 and 1 so if you have this kind of an expression then we have some advantage of using this mathematical model to separate some of the effects namely instrumentation or a

crystal size effect or the strain in the lattice and so on so we will have a look at those aspects today and before we really look into the separation of these effects from an x-ray diffraction I would like to go back to little more fundamental aspects of x-ray diffraction itself and I would like to draw.

Some of the typical x-ray diffraction pattern for a crystalline material as well as for a liquid and an amorphous material and then you will have a gas how the x-ray diffraction peak will look like and then how do we understand them so let me draw some of the typical x-ray diffraction peak then we will continue our discussion.

(Refer Slide Time: 05:15)



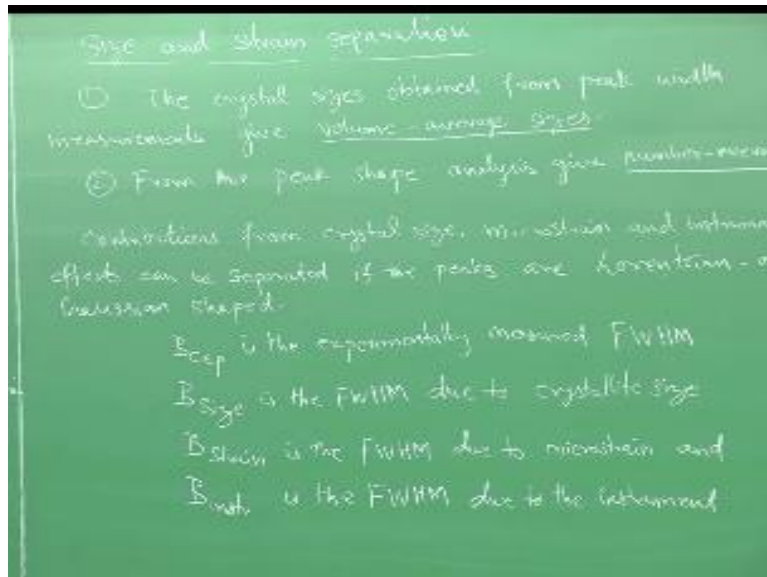
So what I have drawn is a typical x-ray diffraction pattern from three different kind of materials what is crystal the other is for the lipids and amorphous solid and then you have a monatomic gas so what do we understand from this is this is now well known to us the intensity is zero almost zero except at particular to theta value typically known as a brag and ale so one thing you have to understand from this very important you see you take a single atom then you assume that x rays are interacting with this atom but atoms scatters the x-rays in all directions and in a periodic lattice.

You just assume that you get only with certain  $2\theta$  angle this intensity is seen that means rest of the all directions the intensity is canceled by the destructive interference so which is also very important aspects of a diffraction as much as the constructive interference you have to appreciate that so the destructive interference plays a crucial role in appreciating this the constructive interference that happens only at particular angle of I mean Bragg law that is Bragg angle rest all the other direction is completely canceled by the period all the atoms which is arranged in a period three dimensional periodic lattice.

So that is point number one if you look at the intensity versus  $2\theta$  peak for liquids and anamorphous solid it is quite interesting to note that you do not have a very sharp peak for a given  $2\theta$  so it is quite random you say it is something called you know it is the lack of order you see that there is no a concrete order or a three-dimensional periodicity what you see the peak is one or two peak statistically chosen by the system and then what you really observe is a very broad peak okay so you can so it is only a statistical preference of particular interest distance which will give a to preferential.

And peak and then eventually you see only a broad peak which is true for anamorphous solid and liquids which really lacks the order the crystal order lines and if you look at the monatomic gas it is much more interesting you do not even see that any kind of peak broadening because of the a complete randomness so you can write that the features no periodicity at all I would say no structural periodicity no structural periodicity and the curve is this is point number one point number two is it is featureless horizontal and it is since it does not have any structural periodicity you will have the featureless a curve or a peak like this you will obtain for a monatomic type of a gas so now let us look at the let us come back to the x-ray diffraction peak where you have the contribution from a crystal size as well as the strain effect of the lattice so how to separate them that we will see now.

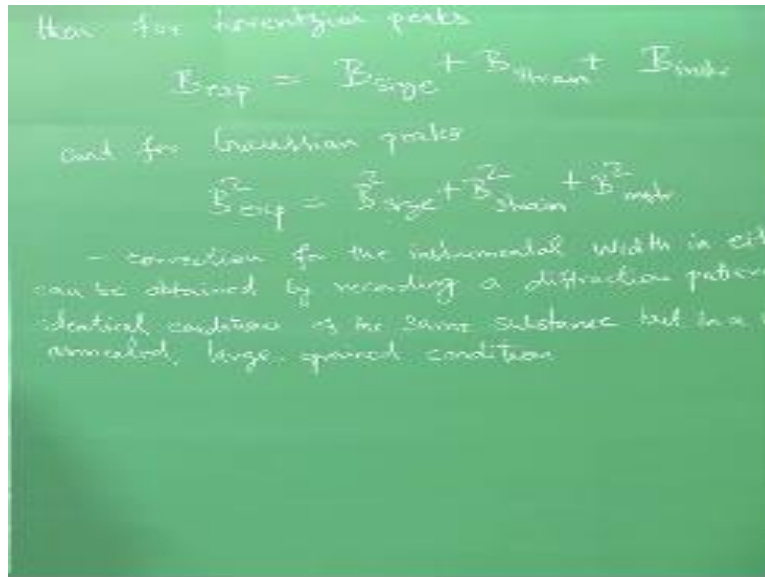
(Refer Slide Time: 12:22)



Oh you so the first point to note down here is when we talk about the crystal size which you obtained from the x-ray diffraction experiments if you are the crystal sizes obtained from a peak width measures give volume average sizes whereas from the peak shape analysis give the number averages so these two subtle things you have to appreciate whether it is peak shape analysis or from the peak width analysis, so now let us look at the contribution from so the contributions from crystal size micro strain and an instrumental effects can be separated if the peaks are Lorentzian in our Gaussian shaped.

So just like just before we have seen in the slides where we have how this speaks our model and if your peak is close to this models then separating this effects are straight forward so we will see how suppose you are be experiment is the experimental I measured B experiment that is full width half maximum be sized you so you have different contribution to the peak width B be experiment is the experiment a measured full width half maximum B size is the FWHM due to the crystallite size B strain is the FWHM due to micro strain and B instrument is the FWHM due to the instrument effects.

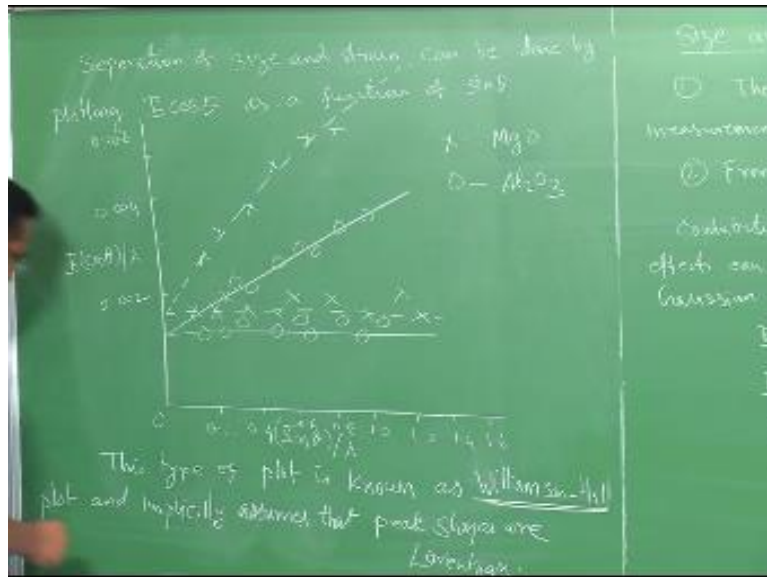
(Refer Slide Time: 19:50)



Now if it is for Lorentzian for Lauren chin Peaks be experiments equal to  $B_{size} + B_{strain} + B_{instrumental}$  and for Gaussian peaks you so for a Gaussian fix it is a square of the these terms that is  $B^2$  experiments equal to  $B^2$  size +  $B^2$  strain +  $B^2$  instrument so now correction for the instrument is done you can write that also as a point so how to get this instrumental width contribution the correction for the instrumental with in either case that is both these cases can be obtained by recording a diffraction pattern under identical conditions of the same substance but in a well annealed large grained condition.

So that you do not have a contribution from the crystallite size itself that is why it is emphasized a large grain condition that means you obtain that by complete annealing treatment you relieve all the strain and then record this peak that is considered as the instrumentation contribution and then we have these two alone sighs and string.

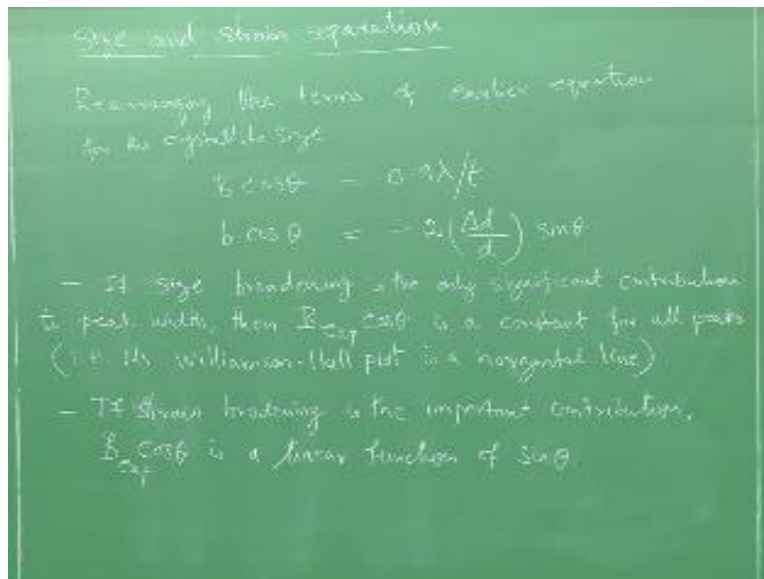
(Refer Slide Time: 24:36)



So now let us write us so what I have drawn here is a plot of  $B \cos \theta$  by  $\lambda$  versus  $\sin \theta$  by  $\lambda$  that is  $B \cos \theta$  versus  $\sin \theta$  that is what I have written here separation of size and strain can be done by plotting  $B \cos \theta$  as a function of sine theta so let us try it you, so this type of plot that is  $B \cos \theta$  versus  $\sin \theta$  is known as Williamson and Hall plot Williamson whole plot and implicitly assumes that the peak shape our Lorentzian Gn. So let us now try to understand this how this separates the size and strain.



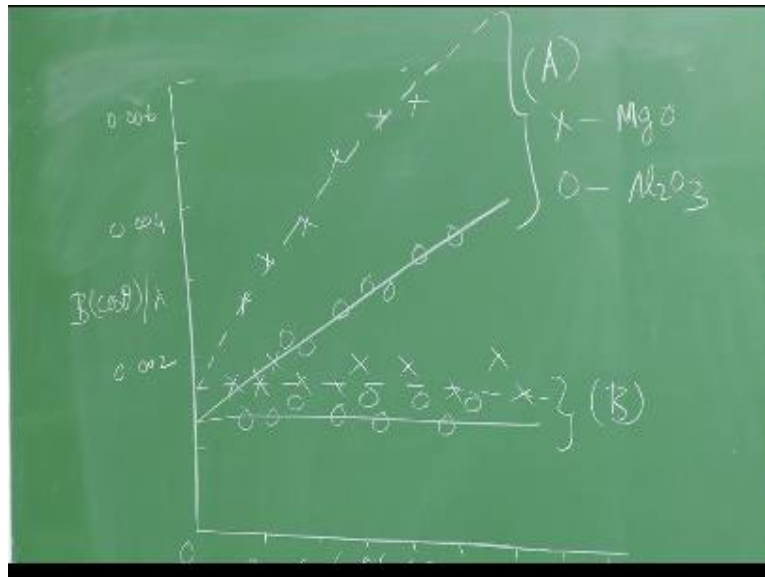
(Refer Slide Time: 31:13)



Terms of what is the crystallite size equation I am saying here rearranging the terms of earlier equation for crystallite size the dash error formula we can write  $B \cos \theta$  is equal to  $0.9 \lambda$  divided by  $T$  and this one equation we know and we also done the other equation that is strain equation -  $2 \Delta B$  by  $B \sin \theta$  so these two equations are quite familiar to us this one is a sheriff formula I have just rearranged and this one is again rearranged if you differentiate the Bragg's law with respect to  $\theta$  and  $D$  you get this expression that we have seen in the last class.

So combine these two we can now explain this plot how this separates the first remark is if you so let us look at what is that details of this using these two equations if the size broadening is the only significant contribution to the peak width then  $B \cos \theta$  is the constant for all peaks that means it is Williamson Hall plot is a horizontal line so like this you have a straight line and if the strain broadening is the important contribution then  $B \cos \theta$  is a linear function of  $\sin \theta$  so like this so what you have the data points here plotted for magnesium oxide as well as aluminum oxide magnesia and then this is for Alumina so now we can see that this portion.

(Refer Slide Time: 37:06)



(Refer Slide Time: 37:41)



Let me erase this so now let us complete that discussion this plot as I mentioned belong to two materials magnesia and alumina after two conditions after ball milling and ball milling followed by an annealing at 13 15<sup>0</sup> centigrade for two hours so you have the when you say ball milling that means you are basically trying to make the powders more fine that means you are you are straining the system are straining the lattice so you have the strain accumulation is there then after this annealing the complete strain is relieved so you will have only the size contribution or the strain contribution.

And that is how this two effects are separated in these two examples so if you look at the complete procedure it is the first you have to measure the instrumental broadening subtract them and then use these two equations one for strain 14 sorry one for size and one for strain and then plot this because theta versus  $\sin\theta$  then you will be able to separate these two effects so this is one typical examples of application of x-ray diffraction where we have demonstrated how this size effect as well as strain effect can be measured.

And then other typical applications of x-ray diffraction is a crystal structure determination which everybody commonly used this technique and also the x-ray diffraction is primarily used for the

phase identification suppose if you have a mixture of two or three phases in a substance and then how to identify each phase that is again a primary application of this technique and then finally people use this technique quite often for stress measurements that is residual stress measurements of all the engineering compounds that is one of the vital industrial application and also x-ray diffraction is used for crystal orientation determination namely a texture analysis so we will touch upon all this application part with small case studies in the coming classes thank you.

**IIT Madras Production**

Funded by

Department of Higher Education

Ministry of Human Resource Development

Government of India

[www.nptel.ac.in](http://www.nptel.ac.in)

Copyrights Reserved