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NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING

Lecture - 31
Materials Characterization

Fundamentals of X – ray diffraction

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Hello everyone welcome to this material characterization course in the last class we looked at how to use x-ray diffraction in determining the crystallite size effect and also the effect of strain in the lattice and also we have looked at the method of separating these effects by Williamson Hall's plot, and today's class we will look at some of the fundamental applications of x-ray diffraction I will briefly discuss about the basic principles of each of these applications.

And beyond that the we have to look into much more details in the any specialized to course because in a general characterization course I will not get into the details of the methodology which we are adopting and I will discuss the basic principles of for example crystal structure determination as well as the face identification and also stress measurements. So these things we will look at in the class probably in the later classes I will solve some problems or using these techniques in one of the tutorials if it required. So first and foremost important thing is.

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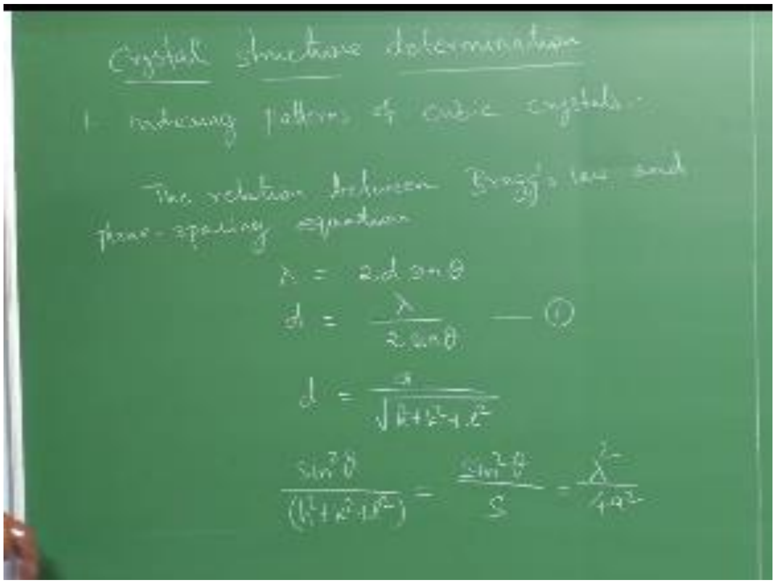

Crystal structure determination

1. Indexing patterns of cubic crystals.

The relation between Bragg's law and plane-spacing equation

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

$$d = \frac{\lambda}{2\sin\theta} \quad \text{— ①}$$

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

$$\frac{\sin^2\theta}{(h^2+k^2+l^2)} = \frac{\sin^2\theta}{S} = \frac{\lambda^2}{4a^2}$$

The crystal structure determination, so the most common method of application of this electron I mean x-ray diffraction is determining the crystal structures the simplest structure being the cubic crystal structures which we will use for indexing them, so the first step is to find out the relation between so this is the Bragg law you can rearrange this equation like this and if you look at the plane spacing equation for the cubic system it is d is equal to8 divided by square root of H square plus K square plus L square and combining these two we can write something like this. So but once you have this relation then we can use this relation to index this cubic pattern we will see how we will do it.

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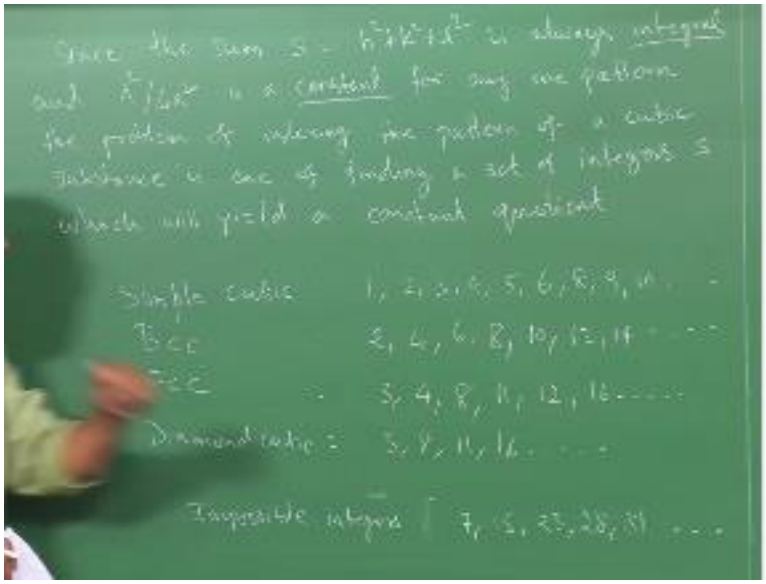

Since the sum $S = h^2+k^2+l^2$ is always integral and $\lambda^2/4a^2$ is a constant for any one pattern the problem of indexing the pattern of a cubic substance is one of finding a set of integers S which will yield a constant quotient

Simple cubic 1, 2, 3, 4, 5, 6, 8, 9, 10 . . .

BCC 2, 4, 6, 8, 10, 12, 14 . . .

FCC : 3, 4, 8, 11, 12, 16 . . .

Diamond cubic : 3, 8, 11, 16 . . .

Impossible integers | 7, 15, 23, 28, 31 . . .

So what I have written is the some H square plus K square plus L square that is s is always an integral and λ square by 4a squared is a constant for a anyone pattern then the problem of indexing the pattern of a cubic substance is one of the finding set of integers yes which will yield a constant coefficient so we can we can write for a simple cubic. So you have with this rule we can form this a kind of selection rule for the cubic system and you cannot choose integers like this because this sum will not add up to these numbers.

So you can exclude them and by this we can simply index this HKL plane from the sine squared theta in fact we can make a table out of this side squared θ versus this kind of a possible HKL plane for a cubic system and similarly you can use some other set of values for tetragonal system.

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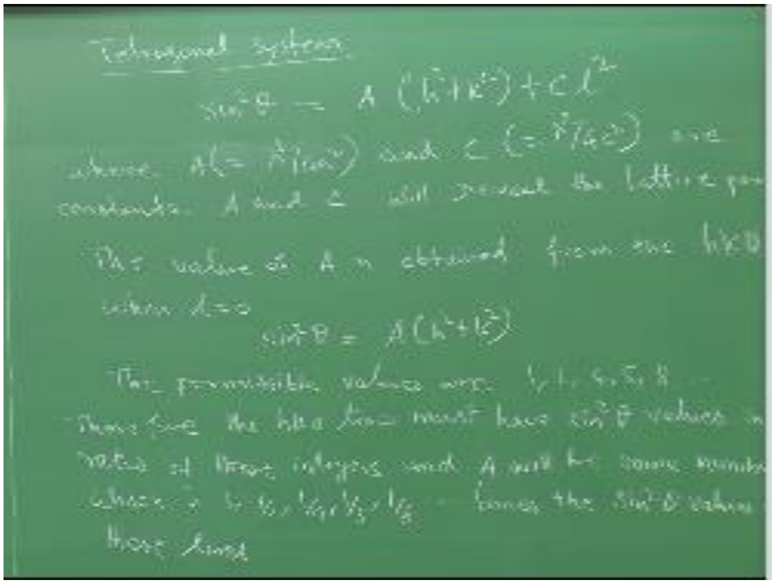

Tetragonal system

$$\sin^2\theta = A(h^2+k^2) + Cl^2$$

where $A (= \lambda^2/4a^2)$ and $C (= \lambda^2/4c^2)$ are constants. A and C will reveal the lattice pa

The value of A is obtained from the hk0 when $l = 0$

$$\sin^2\theta = A(h^2+k^2)$$

The permissible values are 1, 2, 4, 5, 8 ...

Therefore the hk0 lines must have $\sin^2\theta$ values in ratio of these integers and A will be some numb which is 1, 1/2, 1/4, 1/5, 1/8 – times the $\sin^2\theta$ values those lines

So the sine squared theta must obey this is the relation for a tetra gonal system we will see how this is going to help us where so where you have a = λ square by 4 a square plus C is equal to η square by 4 C squared or constants. And then now we have to find out this values using this kind of method so J&C will give your lattice parameters, so what I have written here is in order to find the constants a and C which will give the lattice parameters the value of a is obtained in this manner from hk0lines you put L equal to 0 then your sign span θ should satisfy this condition and then permissible values are 1 2 4 5 8 that kind of a combination.

So now you write so what I have written is these are the per mil permissible values for this condition therefore the HK zero lines must have sine squared values in the ratio of this integers and a will be some number which is 1 1 / 2 1 / 4 1/ 5 1 / 8 times the sine squared θ values of this lights, so that is how you find out the value of a and similarly you will be able to find the values of C α.

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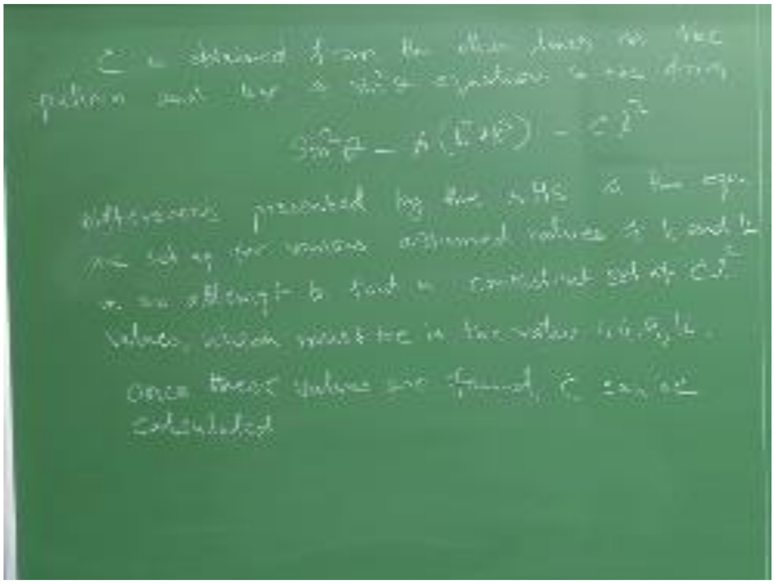

So C is obtained from the other lines on the pattern and the use of sine state equation in this form sine^{2} θ - a into H^{2} plus K^{2} which is equal to CL^{2}, so I will repeat see is obtained from the other lines that means other than h k_{0} lines on the pattern and use the sine squared equation in the form sine^{2} θ -J x H^{2} + K^{2} = CL square and the difference is represented by this equation that is the left hand head side of this equation are set up for various assumed values of H and K in atom to find a consistent set of C L square in fact you can form a table and which must be in the ratio of 1 4 9 16 and so on.

So from there the C value can be found out once these values you so once these values what we are mentioned here is found out C can be calculated so that is how it goes with the tetragonal system.

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Now we will look at other system, so you have for a external system the sine square theta relation is like this sine^2 $\theta = K \times H^2 + HK + K^2 + CL^2$ where a and C are constants where $A = \lambda^2 / 3 a^2$ and $C = \lambda^2 / 4 C^2$ and similar to what we have seen in this tetragonal system we will have the permissible values in hexagonal system like for $H^2 + HK + K^2$ values or 1 3 4 7 9etcetera, again you can make a table and then find out this constant in a similar manner.

For the other crystal systems the sine squared theta relations will have more number of constants for example monoclinic and triclinic system then the calculations procedure becomes little elaborate and we need some kind of a program is programming is required to find out all those things. So this is basic idea behind using the sine^2 θ values to indexing the simple crystal systems.

And one more thing which I have not mentioned how accurately we'll be able to measure this sine^2 θ again depending upon the system of diffract meter we operate and there are set of procedure sin the literature how to correct the sine θ value and after that these kind of calculations are carried out in fact I will show you in the laboratory how some of this calculations are done with the interface of a software you directly get all the indexed pattern readily available and these are some of the basic aspects of indexing the crystal systems.

So I will just move onto the next application called a phase identification which is another very important application of x-ray diffraction for example if you have a material which has a mixture of two three phases so how this phase is identified through x-ray diffraction that we will see with the simple case study.

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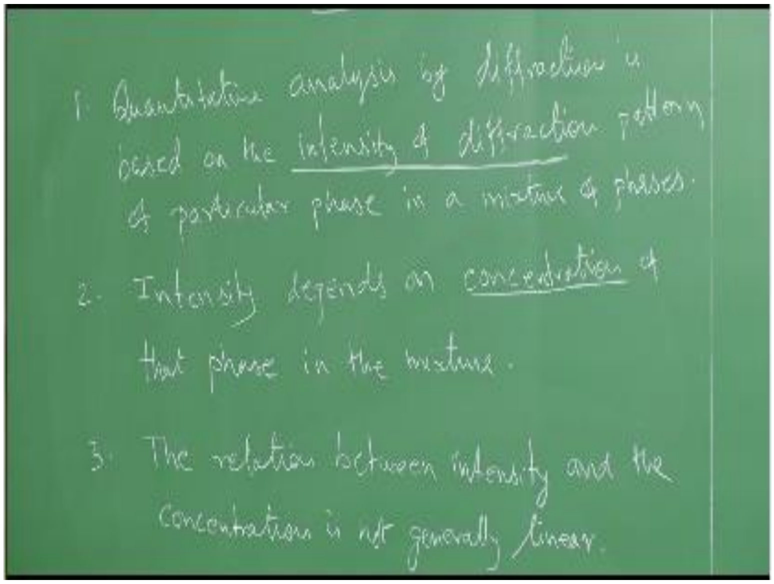

1. Quantitative analysis by diffraction is based on the intensity of diffraction pattern of particular phase in a mixture of phases.
2. Intensity depends on concentration of that phase in the mixture.
3. The relation between intensity and the concentration is not generally linear.

You so what I have written here the quantitative analysis by diffraction is based on the intensity of diffraction pattern of a particular phase in the mixture of phases because we are interested in identifying the phase in a multi-phase system more than one phase system so the basic idea is the quantitative analysis is based on intensity of diffraction pattern from the particular phase in a mixture of phases so what is the next step what is this intensity it depends on that is what we have to write now.

So the intensity in turn depends upon the concentration of the phase of the interest in the mixture so these three points are important so the relationship between the intensity and the concentration is not generally linear. So then it depends upon what it depends upon the mass absorption coefficient of that mixture which itself will vary as a function of concentration so it is not a straight forward here so in order to look at the possibility of identifying the face using the x-ray diffraction we have to keep these three points and also the mass absorption coefficient of the mixture and at and it is variation as a function of concentration also to be considered so to find out the relation between the intensity and the phase contract concentration of the face the starting point is the intensity expression.

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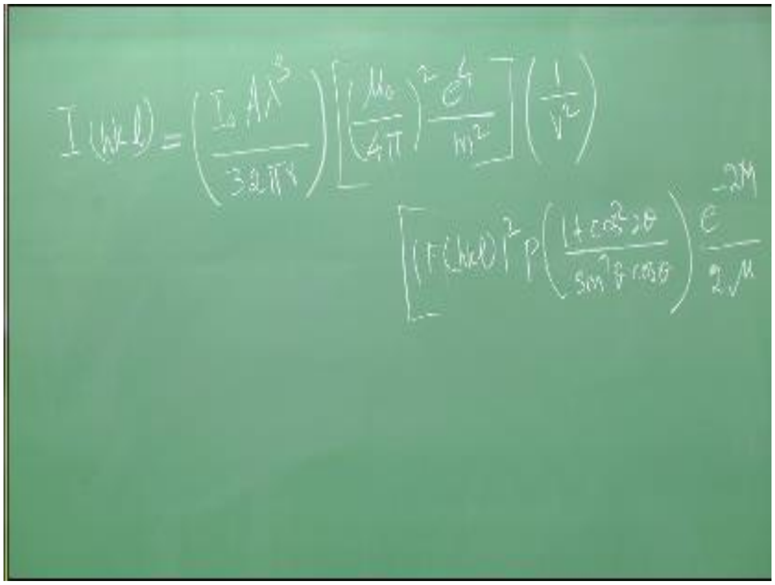

$$I(hkl) = \left(\frac{I_0 A \lambda^3}{32\pi r}\right)\left[\left(\frac{\mu_0}{4\pi}\right)^2 \frac{e^4}{m^2}\right]\left(\frac{1}{v^2}\right)\left[|F(hkl)|^2 p \left(\frac{1+\cos^2 2\theta}{\sin^2\theta \cos\theta}\right) \frac{e^{-2M}}{2\mu}\right]$$

So this is a familiar equation to us because this is what the intensity the final intensity of x-ray diffraction is expressed we have gone through the meaning of each term in the earlier class but this is the standard pattern for the powder specimen we can write intensity.

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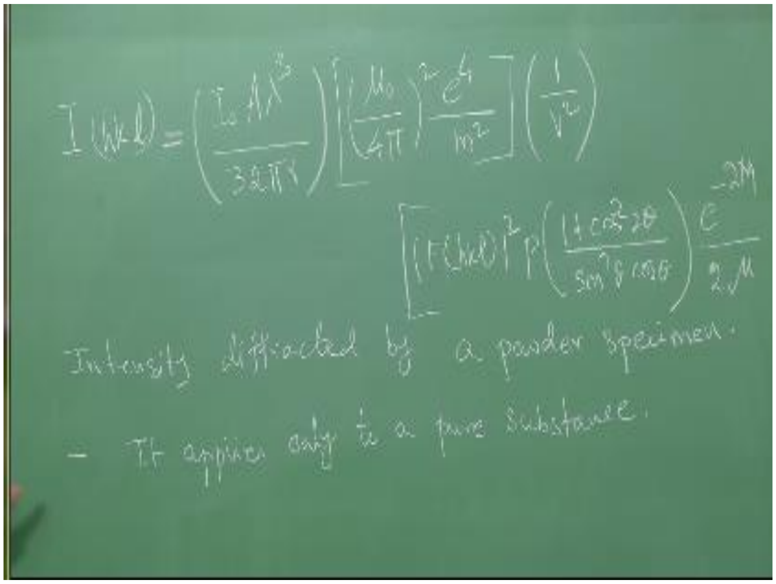

$$I(hkl) = \left(\frac{I_0 A \lambda^3}{32\pi r}\right)\left[\left(\frac{\mu_0}{4\pi}\right)^2 \frac{e^4}{m^2}\right]\left(\frac{1}{v^2}\right)\left[|F(hkl)|^2 p \left(\frac{1+\cos^2 2\theta}{\sin^2\theta \cos\theta}\right)\frac{e^{-2M}}{2\mu}\right]$$

Intensity diffracted by a powder specimen.

- It applies only to a pure substance.

So this is a general expression for an intensity deflected by a powder specimen you have this but what you have to remember is the expression what we have written is for a pure substance we will write this expression is applies only to a pure substance but our interest is to find out the phase in a mixture for example if you take α β mixture, so then this expression need to be written in the other form.

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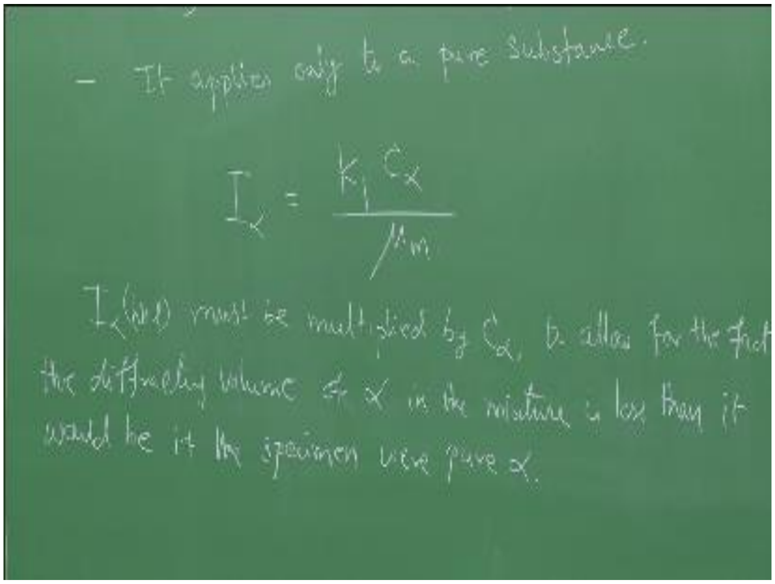

- It applies only to a pure substance.

$$I_\alpha = \frac{K_1 C_\alpha}{\mu_m}$$

$I_\alpha(hkl)$ must be multiplied by C_α, to allow for the fact the diffracting volume of α in the mixture is less than it would be if the specimen were pure α.

So this expression has to be rewritten in this form for a particular phase of interest for example intensity α is equal to K_1 multiplied by C α /μ m the intensity must be multiplied by C α it is a volume fraction of that phase of interest to allow for the fact that the diffracting volume of α in the mixture is less than it would be if the specimen man pure α, so in order to take care of that you have to multiply that expression by C α and then we have to calculate this, so now let us write what is the meaning of this expression.

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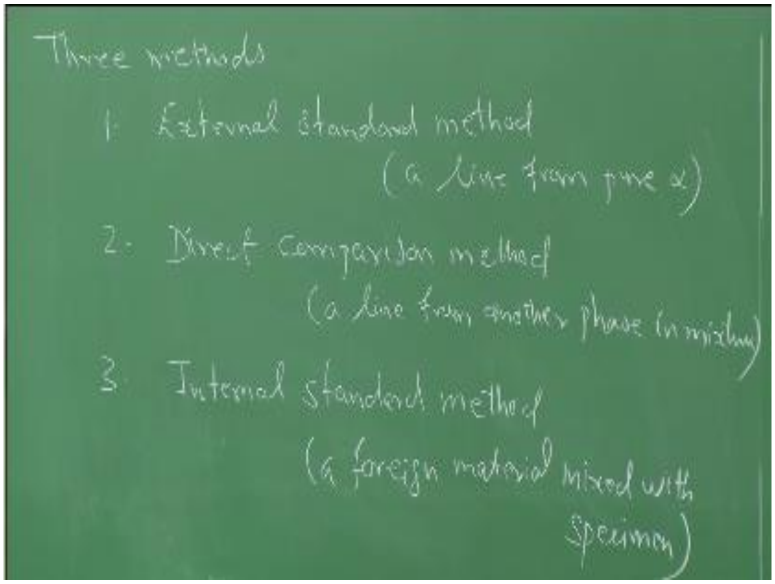

Three methods

1. External standard method
(a line from pure α)
2. Direct comparison method
(a line from another phase in mixture)
3. Internal standard method
(a foreign material mixed with specimen)

So with respect to this expression K is constant the value of K_1 is unknown because I_0 that is incident instant intensity of x-ray is generally unknown but this is unimportant because if the ratio of I α to the intensity of the some standard reference line is form if you can use the ratio between I α and be a standard reference line then this these things can be ignored, so there are three methods in general one is external standard method your line from pure α is used where you have direct comparison method your line from another phase in the mixture is used the third internal standard method where a foreign material is mixed with the specimen.

So there are three methods by which you can do the phase identification in x-ray diffraction using this concept and we will just look at one of the important and very frequently used method to find out the phase fraction and identification that is called a direct comparison method we will take up and then we will look at it.

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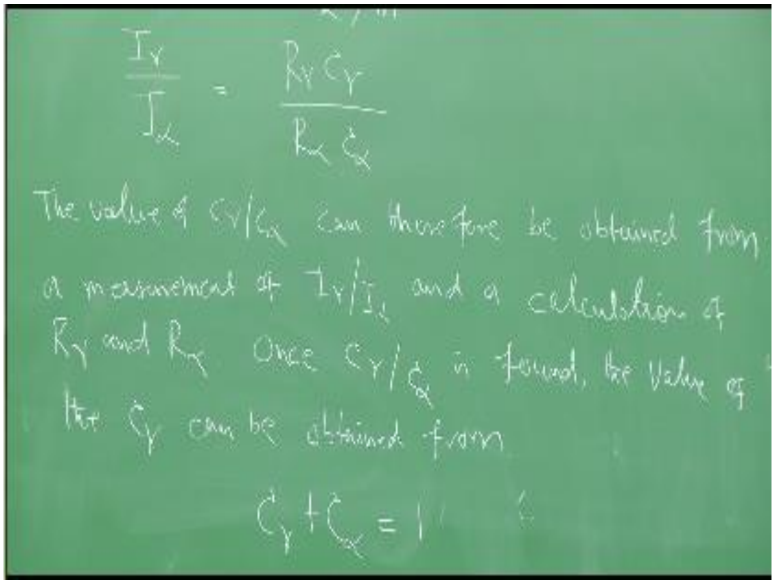

$$\frac{I_\gamma}{I_\alpha} = \frac{R_\gamma C_\gamma}{R_\alpha C_\alpha}$$

The value of C_γ/C_α can therefore be obtained from a measurement of I_γ/I_α and a calculation of R_γ and R_α Once C_γ/C_α is found, the value of the C_γ can be obtained from

$$C_\gamma + C_\alpha = 1$$

Okay what I have written here is suppose if you have a to fix mixture very for example you take a γ and α in a mixture in general, so the you can write this intensity equation in two forms one depend on I mean θ hkl and the kind of substance that is R which is completely substance dependent.

And this is a substance independent term and then you can write this general expression for these two individual phases in a mixture for in this case I γ is equal to k2 R γ C γ divided by 2 μm and I α is equal to k2 to R α C α divided by 2 μm they take the ratio of this which is R γ C γ / R α C α, now the C γ / C α can therefore be obtained from the measurement of I γ / I α and then calculation of R γ and R α can be obtained by the lattice constants and crystal structures and so on.

Once we find that C γ / C α ratio the value of C γ can be found out from this relation C γ + C α is equal to 1, so like that even if you have one more phase you can find out this from this direct comparison method, so like that you can make use of this x-ray diffraction technique for identifying the phase and calculating the phase fraction and another important application is stress measurements I will again discuss the very basic principles of stress measurements in the next class thank you.

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