X-Ray Diffraction in Nanostructured Materials

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Abstract: *Nanotechnology world is swiftly evolving and opens up a new vista with potential. Characterization of nanostructured materials is necessary to establish the understanding and control of nanoparticle synthesis and application. X-ray diffraction (XRD) is a tool for the investigation of matter. In the case of nanocrystalline material, the average crystallite size (D) of the material is the most predominant factor which influences the physical and chemical properties. X-ray diffraction is the most convenient method for determination of average crystallite size. Simultaneous use of X-ray diffracting techniques and high-resolution microscopy, improves the powder diffraction method to determine the characterization of nanocrystalline material. The X-ray diffraction patterns of nanostructured materials will be broader as compared to single crystal XRD pattern. The broadening of XRD spectrum is an interesting area which give a number of information about nanocrystalline material.*

Keyword: *Nanostructured materials; Size broadening; Strain broadening; X-ray diffraction (XRD)*

1. INTRODUCTION

Nanoscience is the study of nanoscale materials - materials that exhibit remarkable properties, functionality, and the phenomena due to the influence of small dimensions. Nanotechnology is the natural progression of technology miniaturization from the bulk macroscopic world to the millimetre - sized objects to micron dimensions (e.g.: integrated circuits), and, finally, into the nanoworld (e.g.: the quantum dot).

X-ray diffraction (XRD) is a tool for the investigation of the matter. X-rays was discovered in 1895 by Roentgen. The genesis of XRD can be treated to the suggestion of Max Von- Laue in 1912 that a crystal can be considered as a three dimensional diffraction grating, and he observed the characteristic X-ray diffraction from crystals. The suggestion was based on the Ph.D thesis of Paul Ewald, who considered a crystal as three dimensional array of oscillators separated at a distance. At first this technique was used only for the determination of crystal structure. Today this method is applied not only to structure determination but to a number of problems as like chemical analysis, stress and strain measurement, to the shape of phase equilibrium and the measurement of particle size.

In the case of nanocrystalline material, the average crystallite size (D) of the material is the most predominant factor which influences the physical and chemical properties. The XRD patterns of nanostructured materials will be broader as compared to single crystal XRD pattern. The broadening of XRD spectrum is an excellent area which gives large information about the nanocrystalline material. A perfect crystal would extend in all direction to infinity, so no crystals are perfect due to their finite size. This devi-ation from perfect crystallinity leads to the broadening of the diffraction peaks.

2. X-RAY DIFFRACTION ANALYSIS

X-rays are radiations with the wavelength comparable to the size of the atomic dimensions. XRD is a tool for the investigation of the matter. X-rays discovered in 1895 by Roentgen. The genesis of XRD treated to the suggestion of Max Von- Laue in 1912 that a crystal could consider as a three-dimensional diffraction grating, and he observed the characteristic X-ray diffraction from crystals. The suggestion based on the Ph. D thesis of Paul Ewald, who considered a crystal as a three dimensional array of oscillators separated at a distance. At first, this technique was used only for the determination of crystal structure. Today this method is applied not only to structure determination but some problems as like chemical analysis, stress and strain measurement, to the shape of phase equilibrium and the measurement of particle size [1].

A few years later, W.L Bragg & W.H Bragg came with the idea of treating diffraction from a crystal as reflection from the lattice planes, and that planes identified with a set of integers h, k, l called Miller indices [2]. Bragg considers, X-ray diffraction was originating due to the interference of X-ray reflections. Each plane reflects only a very small fraction of radiation. In a plane, each atom becomes a source of scattered X-ray radiation, and in general, the scattered X-ray from all atoms in a crystal will combine destructively as they fall on the top of one another in a random manner. In a perfect crystal, X-ray scatters without loss of energy, the incident waves reflected secularly from the parallel planes of atoms in the crystal, and constructive interference may occur in

certain directions.

Partial reflection followed by interference is called Bragg reflection. So the words diffraction and reflection are mutually interchangeable in Bragg treatment. Based on these considerations Bragg derived a simple mathematical relationship, which serves as the condition for Bragg reflection to occur [3]. If 'd' is the interplanar spacing, λ is the wavelength of incident X-ray beam, and θ is the angle of incidence, then according to Bragg's law,

$$n\lambda = 2d \sin\theta; \quad n = 1, 2, 3...... \quad (1)$$
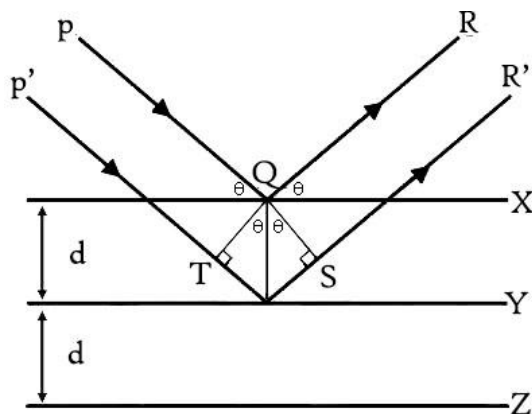
Where 'n' is the order of the spectrum.

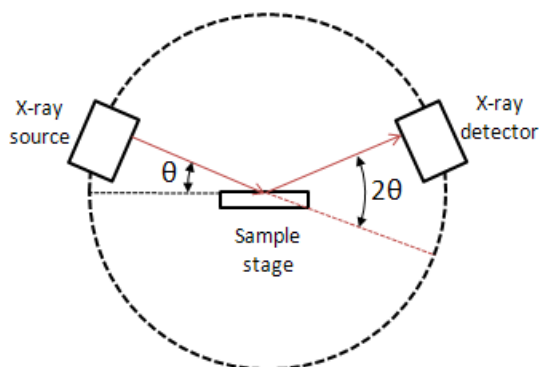*Figure 1 Reflection of X-rays from a crystal*
[Courtesy: https://www.kullabs.com]

Figure 2 Powder X-ray diffraction
[Courtesy: https://www.pinterest.com]

This diffraction condition can be written in vector form as,

$$2 \mathbf{k} \cdot \mathbf{G} + G2 = 0 \quad (2)$$

Where **G** is a reciprocal lattice vector such that where the diffraction condition is met, is defined as,

$$\mathbf{G} = \Delta\mathbf{k} = \mathbf{k} - \mathbf{k'} \quad (3)$$

Where **k** is the incident wave vector and **k'** is the reflected wave vector.

There are three X-ray diffraction methods by which the crystal structure to be analyzed. They are Laue method, Rotating crystal method and the powder method. The diagram of powdered X-ray diffraction shown in Figure 2. In this approach powdered form of the sample is used to obtain the diffraction patterns. Diffracted X-rays are detected, processed and counted. By scanning the sample through a range of 2θ angle, all possible directions of the lattice should be attained due to random orientation of the powdered material.

2.1. X-Ray Diffraction in Nanostructured Materials

In the case of nanocrystalline material, the average crystallite size (D) of the material is the most predominant factor which influences the physical and chemical properties. X-ray diffraction is the most convenient method for determination of average crystallite size. Simultaneous use of X-ray diffracting techniques and high-resolution microscopy improves the powder diffraction method to determine the characterization of nanocrystalline material [4]

The X-ray diffraction patterns of nanostructured materials will be broader as compared to single crystal XRD pattern. The broadening of XRD spectrum is an exciting area which gives some information about the nanocrystalline material. A perfect crystal would extend in all direction to infinity, so no crystals are perfect due to their finite size. This deviation from perfect crystallinity leads to the broadening of the diffraction peaks

2.2. The Broadening Of X-Ray Diffraction Lines for Small Crystallites

The measurement of crystallite size in nanocrystalline specimens using X-ray diffraction technique is based on the broadening of the diffraction lines when the crystallite size becomes very tiny [1]. For crystallites with size greater than 100nm, there is no measurable broadening of diffraction lines. In the nanosize regime, where the linear dimension is less than 100nm, the estimations based on the line broadening is applicable. The cause of broadening of XRD lines from small crystallites is understood by extending the method of deduction of Bragg's law to cover the incomplete reinforcement of waves scattered by successive lattice planes [12].

Bragg's law deduced by finding the conditions under which the waves reflected from all the planes in a crystal are in phase with each other. However, there will be an appreciable amount of radiation scattered, even if the law is not precisely obeyed. For small crystals, the deviation may be quite large and

reflections may appear over a range of angle and the diffraction lines are broadened. The order of magnitude of broadening can be estimated as follows. Consider a beam of X-rays falling up on a set of 2m lattice planes at an angle θ+δθ and scattered at same angle. δθ is the deviation from the correct Bragg angle for particular reflections from the lattice planes. So the path difference for the waves scattered from successive planes is 2dsin (θ+δθ). The condition for total reinforcement of the wave is, suppose that δθ is such that the plane (m+1) scatters 180˚ out of phase with the first plane. Then

$$2d \sin(\theta+\delta\theta) = [m + 1/2] \lambda \ ; \ m = 1,2,3.... \qquad (4)$$

Also Bragg's law is,

$$2d\sin\theta = m\lambda \qquad (5)$$

If the Equation (5) is true for the first plane and the plane (m+1), it will also be true for any two planes with the corresponding separation up to the plane m and 2m. Thus the crystal can be divided into two parts, the scattering from which will be 180˚ out of phase and so cancels out exactly. The value of δθ is given by Equations (4) and (5). The value of δθ can be found by subtracting Equation (5) from Equation (4). Thus gives,

$$2d \cos\theta. \ \delta\theta = \lambda/2 \qquad (6)$$

$$\delta\theta = \lambda/(2D \cos\theta) \qquad (7)$$

Where D= 2d, is the thickness of the crystal. The angular separation β=2θ+δθ of the directions in which the scattering is zero is λ/ (D cosθ), β is referred as the breadth of the X-ray diffraction peak. Then from above equation,

$$D = \lambda/\beta\cos\theta \qquad (8)$$

2.3 Scherrer Equation

Equation (8) does not take into account the actual geometric shape of the crystallite and also, not defined the breadth β. In 1918 Scherrer found that the broadening of X-ray diffraction line is related to the finite size of the material. Scherrer introduced a shape factor K which lies between 0.9 and 1.15 depending on the shape of grains. (K= 1 for spherical crystallites) and, the Scherrer equation is,

$$D_{hkl} = K\lambda/ (\beta \ Cos\theta) \qquad (9)$$

This is one of the modified forms of Bragg's equation and it is an extension of Equation (8). Where 'D' is the thickness of crystallite or the average crystallite size, K is a constant dependent on crystallite size, β is the full width at half maximum (FWHM), λ is the x-

ray wavelength and θ is the Bragg angle. From this equation it is clear that peak width is inversely proportional to crystallite size. Many factors may contribute to the observed peak profile, some of them are,

- Instrumental Peak Profile
- Crystallite Size
- Microstrain, because of
  - Non-uniform Lattice Distortions
  - Faulting
  - Dislocations
- Temperature Factors

Simply the peak profile is a convolution of the profiles from all of these contributions [5].

2.4 Crystallite Size Broadening

Peak width due to crystallite size varies inversely with crystallite size. i.e., crystallite size gets smaller; the peak gets broader and also the peak width varies 2θ as cos θ. The crystallite size broadening is most pronounced at large angles 2θ. However, the instrumental profile width and Microstrain broadening are also largest at large angles 2θ. If using a single peak, often get better results from using diffraction peaks between 30˚ and 50˚ 2θ.

To estimate the crystallite size from X-ray diffraction line broadening should be described quantitatively. There are different quantitative measure for the breadth of X-ray diffraction peak viz., full width at half maximum (FWHM) and integral breadth. The most commonly used quantitative measure of line broadening is the FWHM or half peak breadth [6]. This is illustrated in Figure 3.
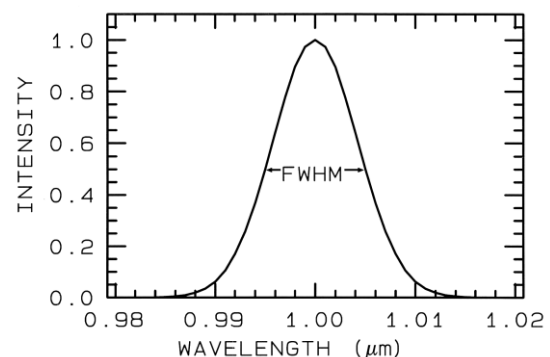

Figure 3 Full width at half maximum
[Courtesy: https://speclab.cr.usgs.gov]

Although FWHM is used as a quantitative measure of line broadening for most calculation, it suffers from disadvantage that it doesn't take into account the lower part of the line profile. The best fit taken into account the minimum errors as well as the realistic values of the individual variables [7].

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2.5 Correction to Strain Broadening

The crystallite size of the particle is not generally the same as the particle size, due to the presence of poly crystalline aggregate. Lattice strain is a measure of the distribution of lattice constants arising from crystal imperfection, such as lattice dislocation. X-ray line broadening is used for the investigation of dislocation distribution. Change in d value is referred as the lattice strain. Due to this, only the shifting in 'd' values or 2θ values occur but not contribute for broadening. Strain, which extends over few lattice space is called microstrain. Microstrain only contribute to broadening. Microstrain are very common in nanocrystalline materials. Anisotropy of the crystallite should be taken in to account while separating the strain and particle size contributions to line broadening. Williamson –Hall analysis is a simplified integral breadth method where both size induced and strain induced broadenings are deconvoluted by considering peak width as a function of 2θ.

Modified Hall-Williamson models are Uniform Deformation Stress Model (UDSM) and Uniform Deformation Energy Density Model (UDEDM). These two models give an idea of the stress-strain relation and the strain as a function of energy density, 'U'. Uniform deformation model does not take into account the anisotropic nature of the crystal. UDS and UDED models take into account the anisotropic nature, hence they are more realistic methods. However UDSM and UDEDM are essentially different [8]. Sometimes these models are not able to produce better result. A better evaluation of the size-strain parameters can be obtained by considering an average 'size-strain plot' (SSP).

2.5.1 Uniform Deformation Model (UDM)

Uniform deformation model does not take into account the anisotropic nature of the crystal. Here the microstrain is assumed to be uniform in all crystallographic axes. Strain induced broadening is given by Wilson formula as,

$$\beta_{hkl} = 4 <\varepsilon> \tan\theta \qquad (10)$$

Where ε is the root mean square (RMS) value of the microstrain. Hence the strain induced in powders due to crystal imperfections and distortion can indicated as

$$<\varepsilon> = \beta / (4 \tan\theta) \qquad (11)$$

Assuming the particle size and strain contributions to line broadening are independent to each other and both have a Cauchy like profile (Lorentzian), then the observed line breadth is simply the sum of size induced broadening and strain induced broadening.

$$i.e., \beta_{hkl} = \beta D + \beta \varepsilon \qquad (12)$$

$$\beta_{hkl} = K\lambda / (D \cos\theta) + 4 <\varepsilon> \tan\theta \qquad (13)$$

By multiplying both sides by cos θ, the Equation (13) became,

$$\beta_{hkl} \cos\theta = K\lambda / (D) + 4<\varepsilon> \sin\theta \qquad (14)$$

This equation is Williamson –Hall equation. [12], [13]. β_{hkl} values used here is the instrumental corrected values. From Equation (9) and (12), confirm that the peak width and crystallite size varies as (1 / cosθ), strain varies as (1 / tanθ). By plotting the value of β_{hkl} cos θ as a function of 4Sinθ, the microstrain (ε) may be estimated from the slope of the line and the crystallite size from the intersection with the vertical axis (Y – intercept).

2.5.2 Uniform Deformation Stress Model (UDSM)

Uniform deformation stress model take in to account the anisotropic nature of young's modulus. So, UDSM is more realistic than UDM. Here the cause of anisotropic microstrain is assumed to be a uniform deformation stress. Young's modulus,

$$E_{hkl} = stress / strain \qquad (15)$$

Hence in this model the isotropic microstrain is replaced by,

$$\varepsilon_{hkl} = \sigma / E_{hkl} \qquad (16)$$

So in this approach Williamson – Hall equation has the form,

$$\beta_{hkl} \cos\theta = K\lambda/(D) + (4\sigma \sin\theta)/E_{hkl} \qquad (17)$$

Where, σ is the uniform deformation stress. Stress and strain are related to each other by Hooke's Law where the strain is assumed to be sufficient small that stress and strain depend linearly on each other. Such a medium is called linear elastic. In its general form Hooke's law reads:

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl} \quad ; with \ i, j, k, l = 1,2, 3 \qquad (18)$$

The fourth-rank tensor C_{ijkl} is called the stiffness tensor and consists of 81 entries. These components of stiffness matrix are called elastic constants. This tensor actually links the deformation of to an applied stress. The stress tensor is symmetrical,

$$i.e., \sigma_{ij} = \sigma_{ji} .$$

Alternatively, one may express the strain in terms of stress as,

$$\varepsilon_{ij} = S_{ijkl}\, \sigma_{kl} \qquad (19)$$

In this case, S_{ijkl} is called the elastic compliance tensor and its elements are called elastic compliances. For an anisotropic cubic crystal system the 81 components of elastic compliance have been reduced to three independent ones. They are S_{11}, S_{12} and S_{44}. In a cubic material, the elastic moduli can be determined along any orientation from the elastic compliances, by the application of the following equation,

$$E_{hkl}^{-1} = S_{11} - [(2 S_{11} - S_{12} - S_{44})\,(h^2 k^2 + k^2 l^2 + h^2 l^2)] / [(h^2 + k^2 + l^2)^2] \qquad (20)$$

For a cubic crystal also the elastic constants are reduced to three, they are C_{11}, C_{12} and C_{44}. Hence anisotropy ratio (also called the Zener anisotropy ratio, in honor of the scientist who introduced it) is defined as,

$$A = 2 C_{44} / (C_{11} - C_{12}) \qquad (21)$$

By plotting the value of $\beta_{hkl} \cos \theta$ as a function of $(\frac{4\sigma\, Sin\theta}{E})$, the uniform deformation stress (σ) may be estimated from the slope of the line and the crystallite size from the intersection with the vertical axis (Y – intercept). Then also the anisotropic microstrain can be calculate by using the Equation (11) [8].

2.5.3 Uniform Deformation Energy Density Model (UDEDM)

Uniform deformation energy density model take in to account the anisotropic nature of young's modulus. So UDSM is more realistic than UDM. Here the cause of lattice strain is assumed to be density of deformation of energy (U). Thus deformation energy density to be uniform in all crystallographic directions. According to Hooke's law,

$$U = (E_{hkl}.\,\varepsilon_{hkl}^2) / 2 \qquad (22)$$

Hence in this model the isotropic microstrain is replaced by,

$$\varepsilon_{hkl} = \sqrt{(2u / E)} \qquad (23)$$

So in this approach Williamson – Hall equation has the form,

$$\beta_{hkl} \cos \theta = \frac{K\lambda}{D} + 4\, Sin\theta\, \sqrt{(2u / E)} \qquad (24)$$

$$\beta_{hkl} \cos \theta = \frac{K\lambda}{D} + 4\, Sin\theta\, (2\, U / E)^{1/2} \qquad (25)$$

By plotting the value of $\beta_{hkl} \cos \theta$ as a function of $(2^{5/2}\, Sin\theta\, E\, hkl^{-1/2})$ the uniform deformation energy density (U) may be estimated from the slope of the line and the crystallite size from the intersection with the vertical axis (Y– intercept). Then also the anisotropic microstrain can be calculate by using the Equation (12) [8].

Though the models UDSM and UDEDM take into account the anisotropic nature elastic constants, they are essentially different. This is because in the UDS model it is assumed that the deformation stress has the same value in all crystallographic direction, allowing energy density to be anisotropic. But in UDED model energy density is assumed to be uniform [9].

2.6 Size – Strain Plot (SSP)

It is reported that in some cases a better evaluation of the size-strain parameters can be obtained by considering an average 'size-strain plot' (SSP). This has a benefit that less importance is given to data from reflections at high angles, where the precision is usually lower. In this approximation it is assumed that the crystallite size broadening is described by a Lorentzian function and strain broadening by a Gaussian function [10] hence we have,

$$(d_{hkl}\,\beta_{hkl} \cos \theta)^2 = \frac{K}{D}\,(d_{hkl}^2\,\beta_{hkl} \cos \theta) + (\mathcal{E}/2)^2 \quad (26)$$

Where K is a constant, shape of the particles for spherical particles it is given as 3/4. Similar to the W-H methods, the term (dhkl β hkl cosθ)2 is plotted with respect to (dhkl2 β hkl cos θ) for the all orientation of peaks. In this approximation the particle size is determined from the slope of the linearly fitted data and the root of the y –intercept gives the strain [11].

3. CONCLUSION

In the case of nanocrystalline material, the average crystallite size (D) of the material is the most predominant factor which influences the physical and chemical properties. The broadening of X-ray diffraction line is related to the finite size of the material. Lattice strain is a measure of the distribution of lattice constants arising from crystal imperfection, such as lattice dislocation. Change in d value is referred as the lattice strain. Due to this only the shifting in d values or 2θ values occur but not contribute for broadening. Strain, which extends over few lattice space is called microstrain. Microstrain only contribute to broadening. Microstrain are very common in nanocrystalline materials. Williamson –Hall analysis is a simplified integral breadth method where both size induced and strain induced broadenings are deconvoluted by considering peak width as a function of 2θ. A better evaluation of the size-strain parameters can be obtained by considering an average 'size-strain plot' (SSP).

4. ACKNOWLEDGEMENTS

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