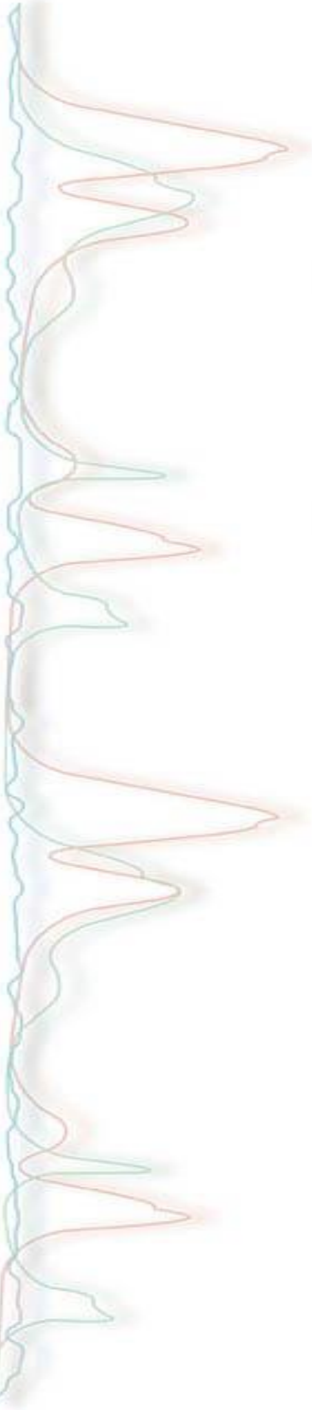


chem 5390

Advanced X-ray Analysis

LECTURE 16

Dr. Teresa D. Golden
University of North Texas
Department of Chemistry

Diffraction Theory

Diffraction Methods

3. Diffractometer (Powder) Method

What can we learn from the diffractometer experiments?

- **Phase Analysis**
- **Texture Analysis**
- **Lattice Parameters**
- **Crystallite Size**
- **Stress Analysis**
- **Strain Analysis**

Diffraction Theory

Crystallite Size

Diffraction Theory

Diffractometer (Powder) Method

Crystallite Size

Crystallite (Grain) size in materials has an effect on the material’s properties, i.e., strength, hardness, etc…

When size of the individual crystals is less than ~ 0.1 mm (1000 Å) the term “particle size” or “crystallite size” is used.

Diffraction Theory

Diffractometer (Powder) Method

Crystallite Size

The widths of the peaks in a particular pattern provide an indication of the average crystallite size.

Large crystallites give rise to sharp peaks, while the peak width increases as crystallite size reduces.

Diffraction Theory

Diffractometer (Powder) Method

Crystallite Size

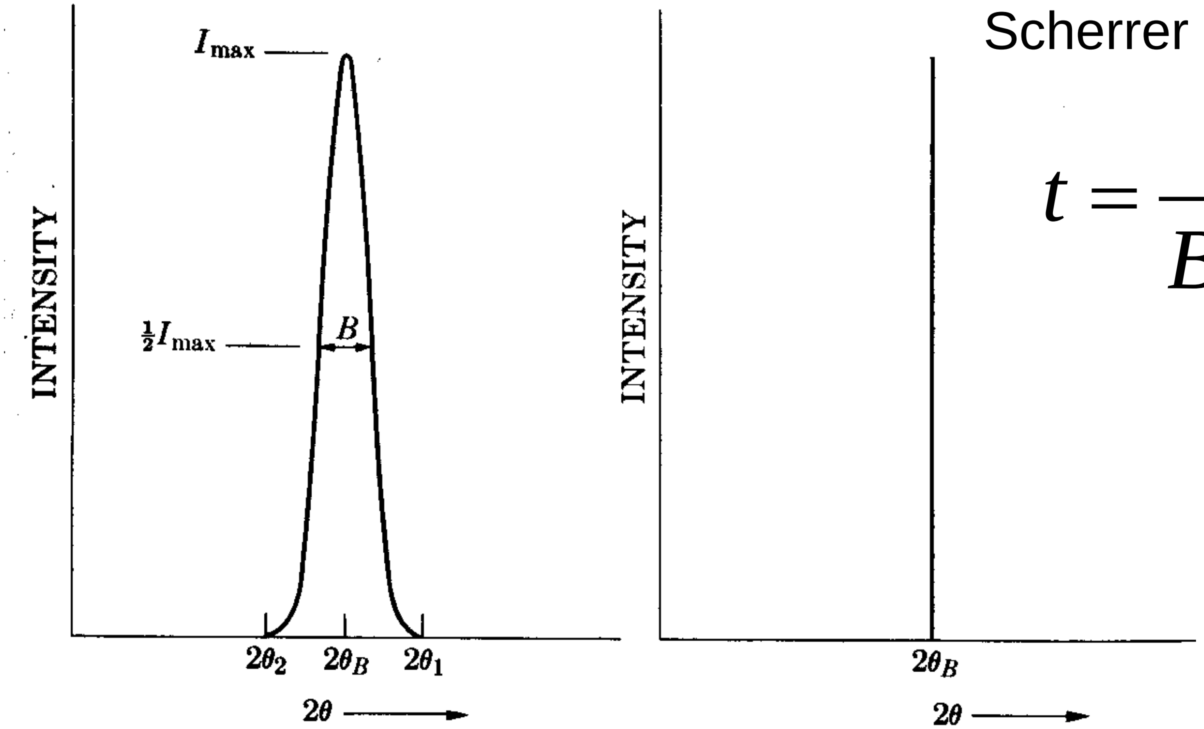
This peak broadening can be used to quantify the average crystallite size of nanoparticles using the Scherrer equation, must know the contribution of peak width from the instrument by using a calibration curve.

Diffraction Theory

Crystallite Size

Crystallite size can be calculated using Scherrer Formula

$$t = \frac{0.9\lambda}{B\cos\theta_B}$$



Instrumental broadening must be subtracted

Diffraction Theory

Crystallite Size

Scherrer equation

$$\tau = \frac{K\lambda}{\beta_\tau \cos\theta}$$

Where

τ is the mean crystallite dimension,
K is the shape factor (typically about 0.9),
λ is the wavelength,

and

β_τ is the line broadening

(equal to the B – b, B being the breadth of the observed diffraction line at its half-intensity maximum, and b the instrumental broadening)

Diffraction Theory

Crystallite Size

Scherrer equation

$$\tau = \frac{K\lambda}{\beta_\tau \cos\theta}$$

P. Scherrer, “Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen,” Nachr. Ges. Wiss. Göttingen 26 (1918) pp 98-100.

J.I. Langford and A.J.C. Wilson, “Scherrer after Sixty Years: A Survey and Some New Results in the Determination of Crystallite Size,” J. Appl. Cryst. 11 (1978) pp 102-113.

Diffraction Theory

Crystallite Size

- The peak width varies with 2θ as cos θ
- The crystallite size broadening is most pronounced at large angles 2Theta
- However, the instrumental profile width and microstrain broadening are also largest at large angles 2theta
  - Peak intensity is usually weakest at larger angles 2theta
- If using a single peak, often get better results from using diffraction peaks between 30 and 50 deg 2theta
  - below 30deg 2theta, peak asymmetry compromises profile analysis

Diffraction Theory

Crystallite Size

In order to analyze crystallite size, we must deconvolute:

Instrumental Broadening from Sample Broadening

We must then separate the different contributions to sample broadening:

Crystallite size and microstrain broadening of diffraction peaks

Diffraction Theory

Crystallite Size

Instrument broadening is the line width shown by a standard sample diffraction peak that is of large crystallite size ~> 1 μm.

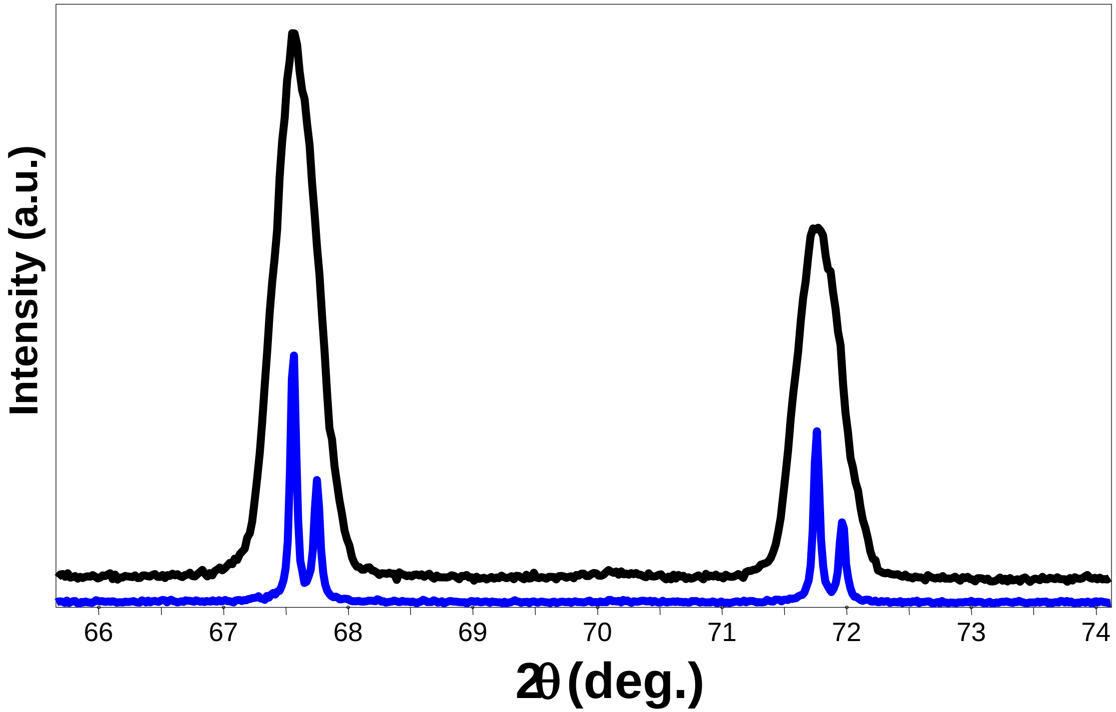
It is a characteristic of the individual xrd instrument being used to make measurements and not related to the specimen.

Crystallite or particle size broadening is related to deviation of crystallite size from ideality.

Broadening related to crystallite size is measurable in the nm region and not significant for larger sizes.

Diffraction Theory

Which of these diffraction patterns comes from a nanocrystalline material?



-These diffraction patterns were produced from the exact same sample

-The apparent peak broadening is due solely to the instrumentation

0.0015° slits vs. 1° slits

Diffraction Theory

Crystallite Shape

Though the shape of crystallites is usually irregular, we can often approximate them as:

-sphere, cube, tetrahedra, or octahedra

-parallelepipeds such as needles or plates

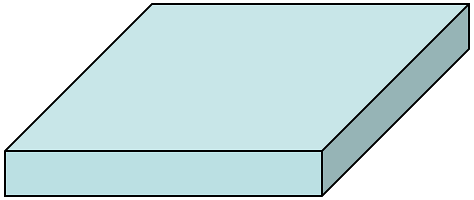
-prisms or cylinders

Most applications of Scherrer analysis assume spherical crystallite shapes

If we know the average crystallite shape from another analysis, we can select the proper value for the Scherrer constant K

Anisotropic peak shapes can be identified by anisotropic peak broadening

-if the dimensions of a crystallite are 2x * 2y * 200z, then (h00) and (0k0) peaks will be more broadened then (00l) peaks.



Diffraction Theory

Crystallite Size

The constant of proportionality, K (the Scherrer constant) depends on the how the width is determined, the shape of the crystal, and the size distribution.

The most common values for K are 0.94 (for FWHM of spherical crystals with cubic symmetry), 0.89 (for integral breadth of spherical crystals with cubic symmetry, and 1 (because 0.94 and 0.89 both round up to 1).

K actually varies from 0.62 to 2.08

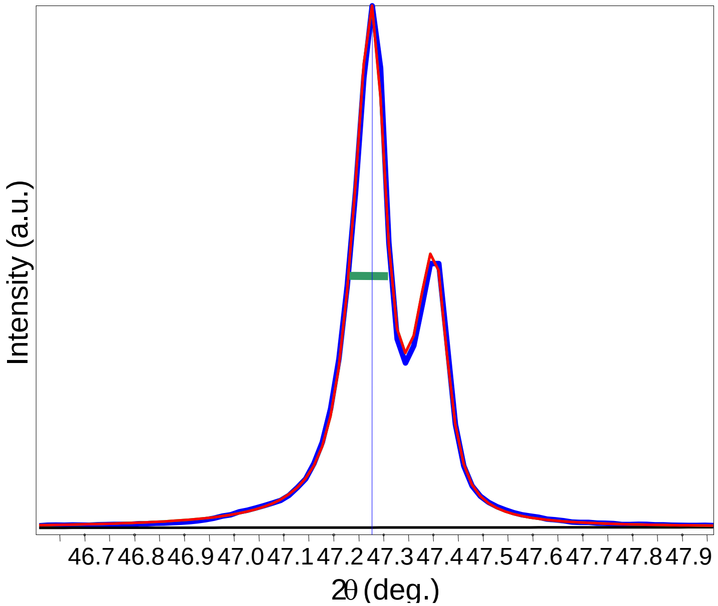
For an excellent discussion of K,

JI Langford and AJC Wilson, “Scherrer after sixty years: A survey and some new results in the determination of crystallite size,” J. Appl. Cryst. 11 (1978) p102-113.

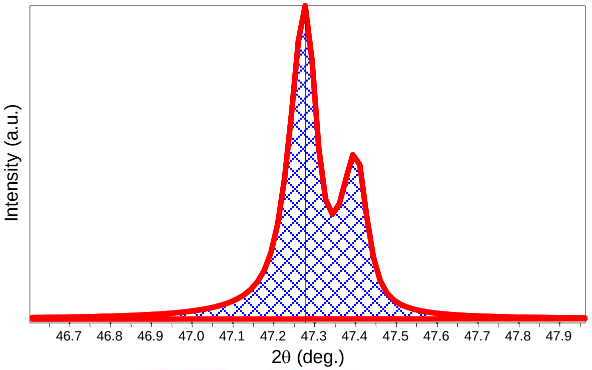
Diffraction Theory

Methods used to Define Peak Width

Full Width at Half Maximum (FWHM)
-the width of the diffraction peak, in radians, at a height half-way between background and the peak maximum



Integral Breadth
-the total area under the peak divided by the peak height
-the width of a rectangle having the same area and the same height as the peak
-requires very careful evaluation of the tails of the peak and the background

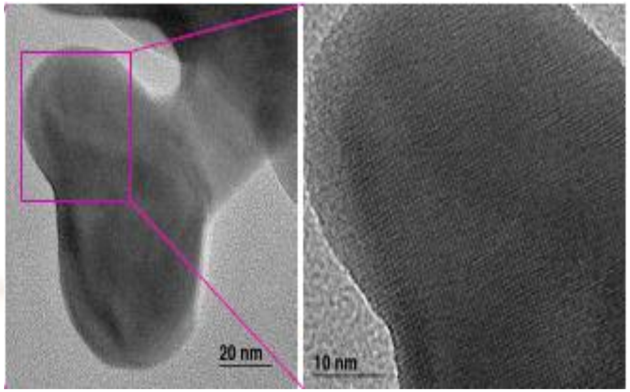


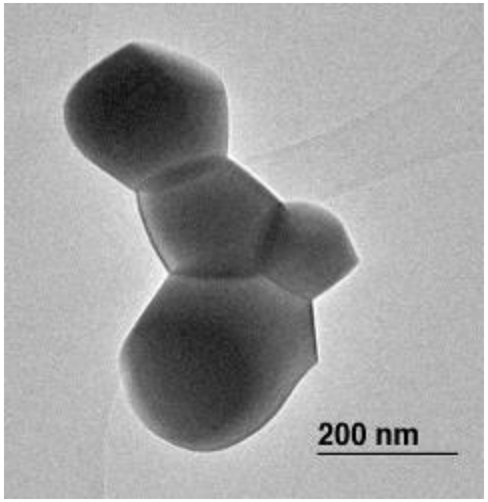
Diffraction Theory

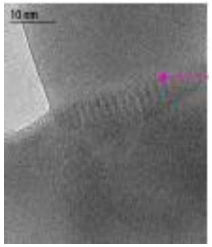
Remember, Crystallite Size is Different than Particle Size

-A particle may be made up of several different crystallites

-Crystallite size often matches grain size, but there are exceptions



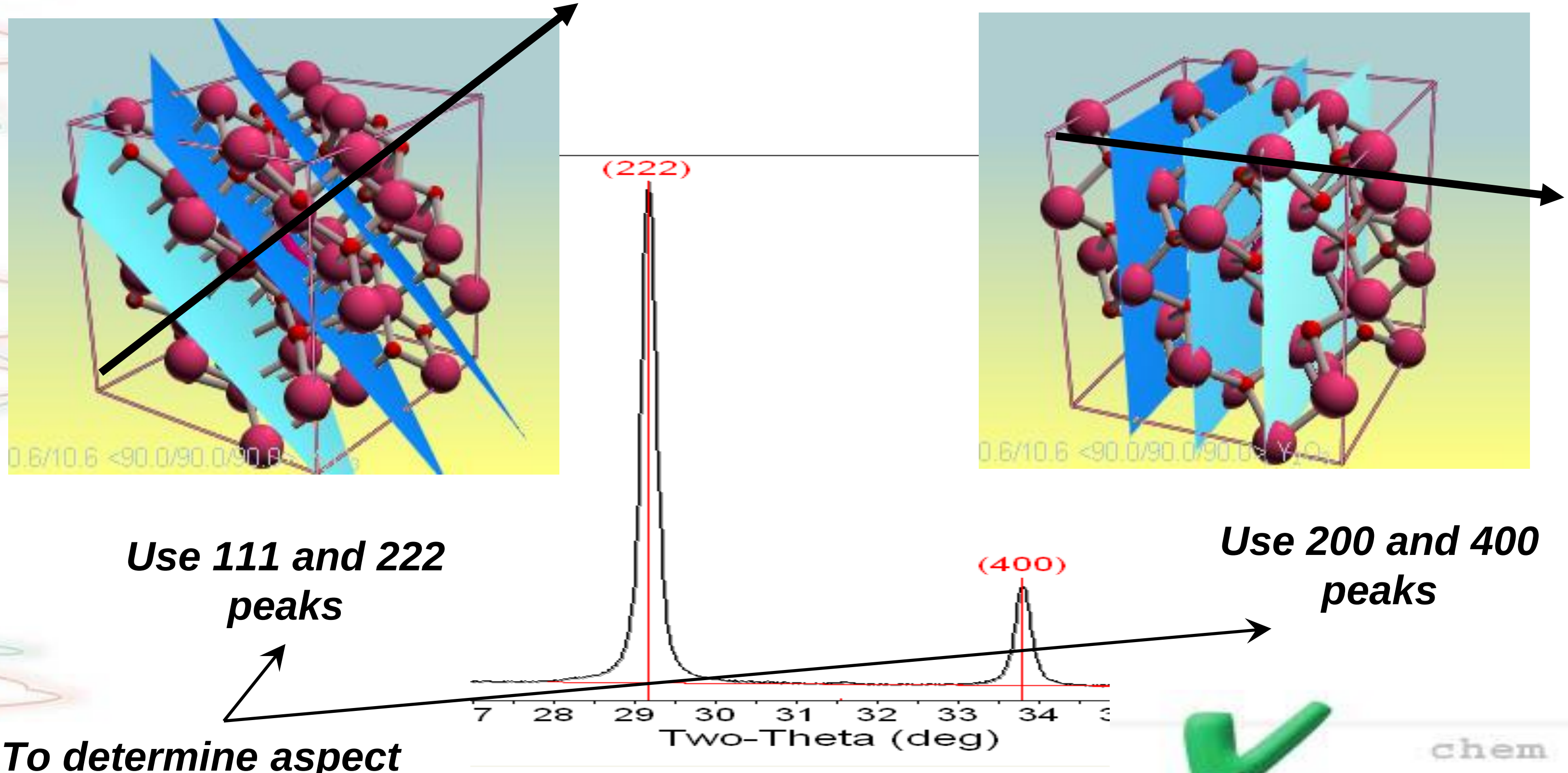




Diffraction Theory

Crystallite Size – Anisotropic Size Broadening

-The broadening of a single diffraction peak is the product of the crystallite dimensions in the direction perpendicular to the planes that produced the diffraction peak.



Use 111 and 222 peaks

Use 200 and 400 peaks

To determine aspect ratios

Diffraction Theory

Crystallite Size

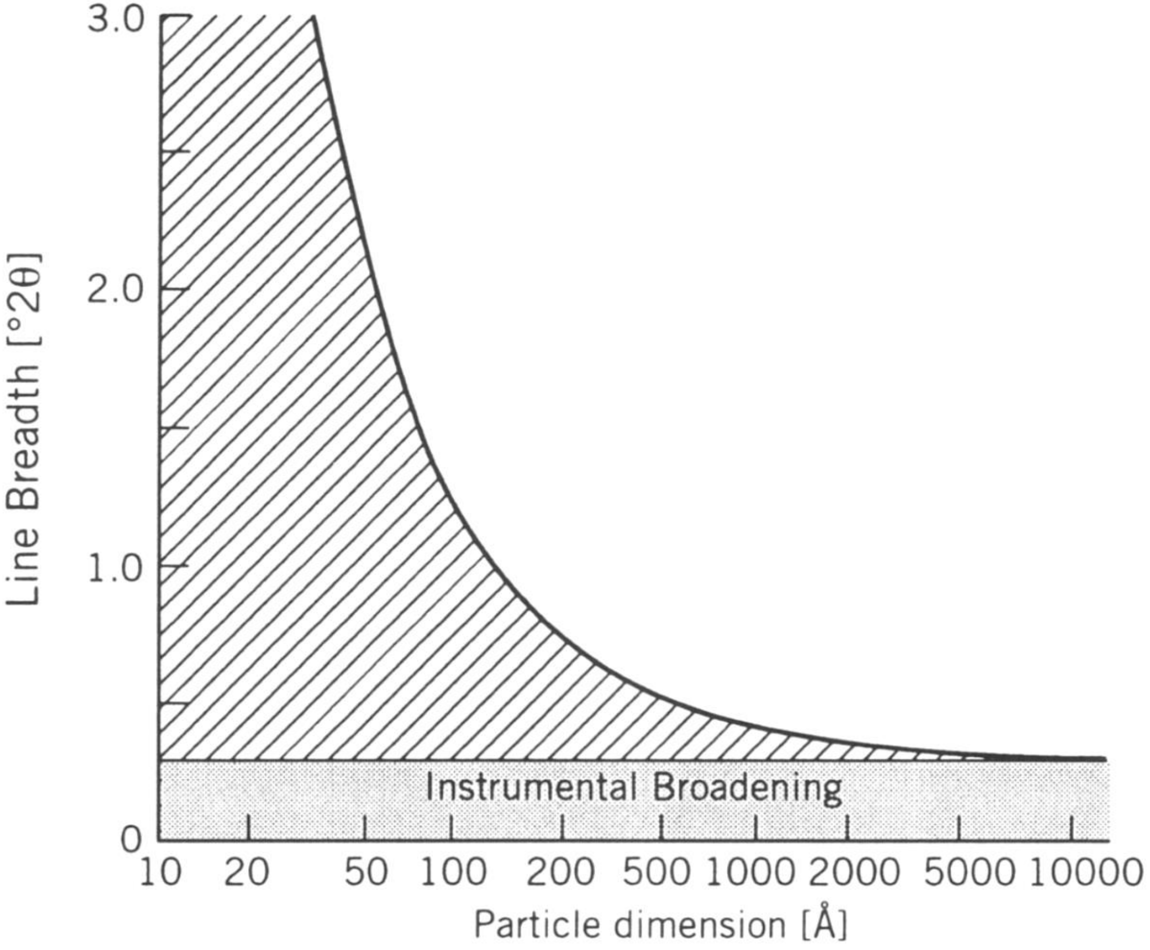


Figure 3.21. Line width as a function of particle dimension.

Diffraction Theory

Diffraction Methods

3. Diffractometer (Powder) Method

What can we learn from the diffractometer experiments?

- **Phase Analysis**
- **Texture Analysis**
- **Lattice Parameters**
- **Crystallite Size**
- **Stress Analysis**
- **Strain Analysis**

Diffraction Theory

Strain Analysis

Strain in the crystal lattice will produce a distortion of the diffraction line.

Macrostrain when stress if uniformly compressive or tensile to cause the distance within the unit cell to become smaller or larger.

Causes the lattice parameters to change resulting in a peak shift.

Glycolation or heating of clay minerals are examples of induced macrostrains.

Diffraction Theory

Strain Analysis

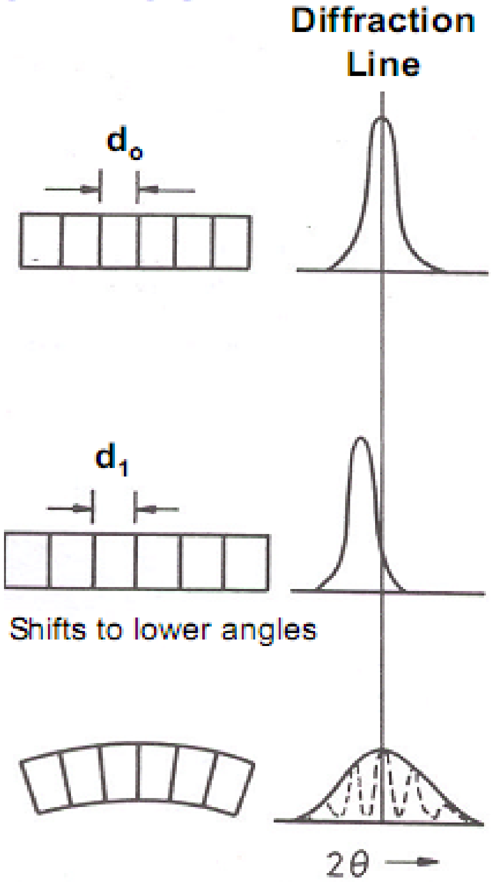
Strain in the crystal lattice will produce a distortion of the diffraction line.

Microstrain – produces a distribution of both tensile and compressive forces in the material. Results in a broadening of the diffraction peaks or peak asymmetry in some cases.

Dislocations, vacancies, shear planes, thermal expansion or contractions, etc can produce Microstress. The result can be a distribution of peaks around the unstressed peak location, appearing like a crude broadening of the peak.

Diffraction Theory

Effect of Lattice Strain on Diffraction Peak Position and Width



No Strain

Uniform Strain
$(d_1\text{-}d_o)/d_o$
Peak moves, no shape changes

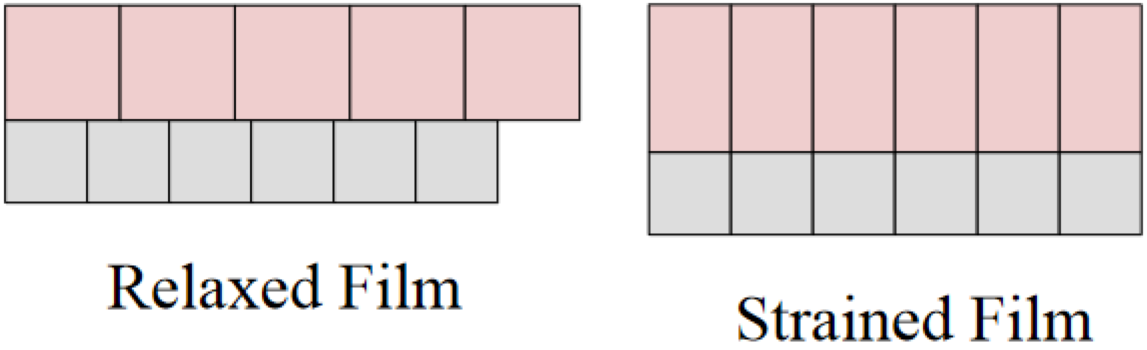
Non-uniform Strain
$d_1 \neq \text{constant}$
Peak broadens

RMS Strain

Exceeds d_0 on top, smaller than d_0 on the bottom

Diffraction Theory

Relaxation and Lattice Strain



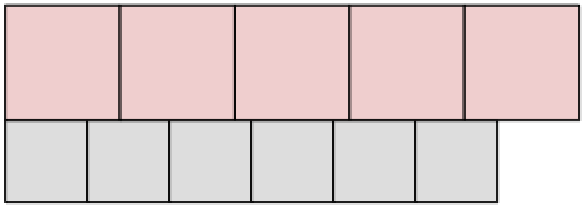
- If the film is mismatched to the substrate, then the film might be strained so that the lattice parameters in the lateral direction (ie within the plane of the film) are forced to match the lattice parameters of the substrate

- This distorts the unit cell of the film

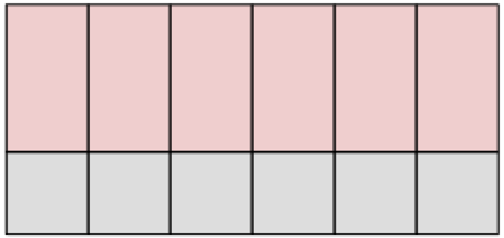
– A formerly cubic unit cell is now tetragonal

Diffraction Theory

Relaxation and Lattice Strain



Relaxed Film



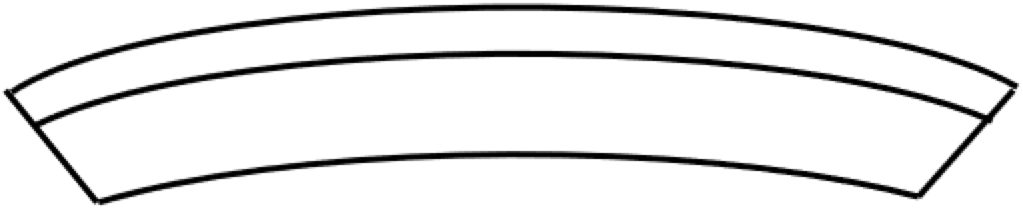
Strained Film

Determine the degree of relaxation

- **No relaxation (fully strained)- the lateral lattice parameters of the film are strained to be identical to the substrate**
- **Fully relaxed- the lateral lattice parameters of the film are equal to the bulk values**

Diffraction Theory

Lattice Strain



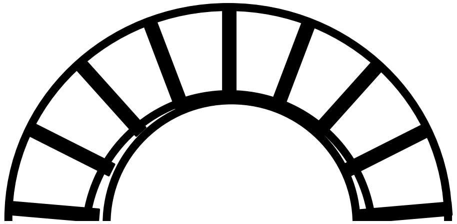
The film and substrate may become slightly curved rather than perfectly flat

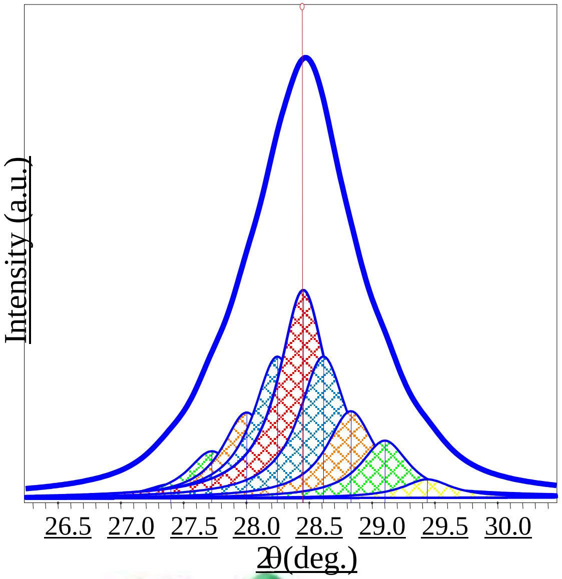
This may be the result of deposition process, thermal expansion mismatch between the film and substrate, etc

Diffraction Theory

Non-Uniform Lattice Distortions

Rather than a single d-spacing, the crystallographic plane has a distribution of d-spaces.





This produces a broader observed diffraction peak.

Such distortions can be introduced by:

- **-surface tension of nanocrystals**
- **-morphology of crystal shape, such as nanotubes**
- **-interstitial impurities**

Diffraction Theory

Dislocations

Can try to analyze by separating the Lorentzian and Gaussian components of the peak profile

Can also determine using the Warren-Averbach method

measure several orders of a peak

001, 002, 003, 004, …

110, 220, 330, 440, …

The Fourier coefficient of the sample due to dislocations has a strong hkl dependence

broadening will contain

an order independent term due to size broadening

an order dependent term due to strain

Diffraction Theory

Faulting

Broadening due to deformation faulting and twin faulting will convolute with the particle size Fourier coefficient

The particle size coefficient determined by Warren-Averbach analysis actually contains contributions from the crystallite size and faulting

-the fault contribution is hkl dependent, while the size contribution should be hkl independent (assuming isotropic crystallite shape)

-the faulting contribution varies as a function of hkl dependent on the crystal structure of the material (fcc vs bcc vs hcp)

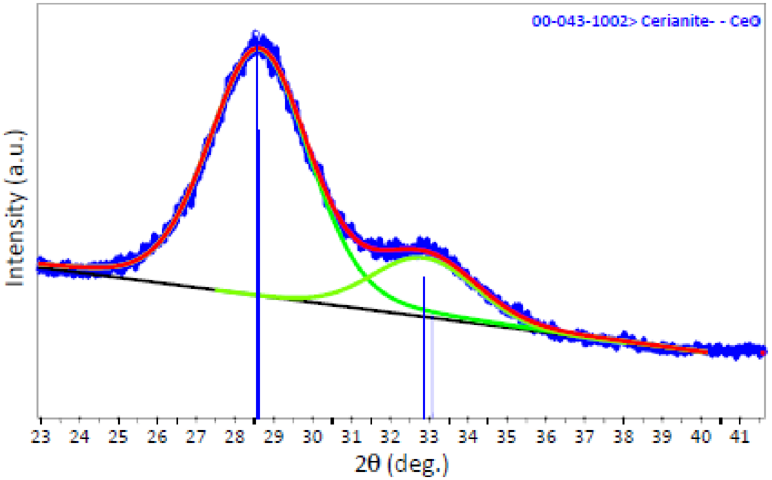
See Warren, 1969, for methods to separate the contributions from deformation and twin faulting

Diffraction Theory

Strain Analysis

Peak broadening also occurs as a result of variations in d-spacing caused by micro-strain.

Analyzing the peak widths over a long range of 2theta using a Williamson-Hall plot can let you separate microstrain and crystallite size.



$$B(2\theta)=\frac{K\lambda}{L\cos\theta}$$

Diffraction Theory

Strain Analysis

Broadening of a diffraction line due to stress can be represented by:

$$\beta_{\varepsilon} = 4\varepsilon\tan\theta$$

where,

- ε **– residual strain (also represented as** η**)**
- β_{ε} **– (radians) – broadening of observed diffraction peak.**

Diffraction Theory

Williamson-Hall Plot

Dealing With Different Integral Breadth/FWHM Contributions

-Lorentzian and Gaussian Peak shapes are treated differently

-B=FWHM or β in these equations

-Williamson-Hall plots are constructed for both the Lorentzian and Gaussian peak widths.

-The crystallite size is extracted from the Lorentzian W-H plot and the strain is taken to be a combination of the Lorentzian and Gaussian strain terms.

Lorentzian (Cauchy)

$$B_{Exp} = B_{Size} + B_{Strain} + B_{Inst}$$

$$\left(B_{Exp} - B_{Inst}\right) = B_{Size} + B_{Strain}$$

Gaussian

$$B_{Exp}^2 = B_{Size}^2 + B_{Strain}^2 + B_{Inst}^2$$

$$\left(B_{Exp}^2 - B_{Inst}^2\right) = B_{Size}^2 + B_{Strain}^2$$

Integral Breadth (PV)

$$\beta_{Exp}^2 = \beta_{Lorentzian}\beta_{Exp} + \beta_{Gaussian}$$

If not sure

$$B_{Size} + B_{Strain} = (B_{Exp} - B_{Inst})(B^2{}_{Exp} - B^2{}_{Inst})$$

Diffraction Theory

Selecting a standard for building the Instrument Peak Profile Calibration Curve

Standard should share characteristics with the nanocrystalline specimen

– Similar linear absorption coefficient

- **similar mass absorption coefficient**
- **similar atomic weight**
- **similar packing density**

Diffraction Theory

Selecting a standard for building the Instrument Peak Profile Calibration Curve

- The standard should not contribute to the diffraction peak profile
  - macrocrystalline: crystallite size larger than 500 nm
  - particle size less than 10 microns
  - defect and strain free

- There are several calibration techniques
  - Internal Standard
  - External Standard of same composition
  - External Standard of different composition

Diffraction Theory

Internal Standard Method for Calibration

- Mix a standard in with your nanocrystalline specimen
- a NIST certified standard is preferred
  - use a standard with similar mass absorption coefficient
  - NIST 640c Si
  - NIST 660a LaB6
  - NIST 674b CeO2
  - NIST 675 Mica

- standard should have few, and preferably no, overlapping peaks with the specimen
  - overlapping peaks will greatly compromise accuracy of analysis

Diffraction Theory

Internal Standard Method for Calibration

Advantages:

– know that standard and specimen patterns were collected under identical circumstances for both instrumental conditions and

sample preparation conditions

– the linear absorption coefficient of the mixture is the same for

standard and specimen

Disadvantages:

– difficult to avoid overlapping peaks between standard and

broadened peaks from very nanocrystalline materials

– the specimen becomes contaminated

– only works with a powder specimen

Diffraction Theory

External Standard Method for Calibration

If internal calibration is not an option, then use external calibration

Run calibration standard separately from specimen, keeping as many parameters identical as is possible

The best external standard is a macrocrystalline specimen of the same phase as your nanocrystalline specimen

– How can you be sure that macrocrystalline specimen does not contribute to peak broadening?

Diffraction Theory

Qualifying your Macrocrystalline Standard

Select powder for your potential macrocrystalline standard

– if not already done, possibly anneal it to allow crystallites to grow and to allow defects to heal

Diffraction Theory

Qualifying your Macrocrystalline Standard

Use internal calibration to validate that macrocrystalline specimen is an appropriate standard

- mix macrocrystalline standard with appropriate NIST SRM
- compare FWHM curves for macrocrystalline specimen and NIST standard
- if the macrocrystalline FWHM curve is similar to that from the NIST standard, than the macrocrystalline specimen is suitable
- collect the XRD pattern from pure sample of you macrocrystalline specimen
  - do not use the FHWM curve from the mixture with the NIST SRM

Diffraction Theory

External Calibration with a Standard of the Same Composition

- **Advantages:**
  - will produce better calibration curve because mass absorption coefficient, density, molecular weight are the same as your specimen of interest
  - can duplicate a mixture in your nanocrystalline specimen
  - might be able to make a macrocrystalline standard for thin film samples

- **Disadvantages:**
  - time consuming
  - desire a different calibration standard for every different nanocrystalline phase and mixture
  - macrocrystalline standard may be hard/impossible to produce
  - calibration curve will not compensate for discrepancies in instrumental conditions or sample preparation conditions between the standard and the specimen

Diffraction Theory

External Standard Method of Calibration using a NIST Standard

As a last resort, use an external standard of a composition that is different than your nanocrystalline specimen

– This is actually the most common method used

– Also the least accurate method

• Use a certified NIST standard to produce instrumental FWHM calibration curve

– Use the standard that has the most similar linear absorption coefficient

Diffraction Theory

External Standard Method of Calibration using a NIST Standard

Advantages

– only need to build one calibration curve for each instrumental configuration

– NIST standard diffraction patterns for each instrument and configuration available for download from literature/database

– know that the standard is high quality if from NIST

– neither standard nor specimen are contaminated

- **Disadvantages**

– The standard may behave significantly different in diffractometer than your specimen

  - different mass absorption coefficient
  - different depth of penetration of X-rays

– NIST standards are expensive

– cannot duplicate exact conditions for thin films

Diffraction Theory

When is good calibration most essential?

FWHM of Instrumental Profile at 48° 2θ is

0.061 deg

Crystallite Size	B (2theta) (rad)	FWHM (deg)
100 nm	0.0015	0.099
50 nm	0.0029	0.182
10 nm	0.0145	0.871
5 nm	0.0291	1.745

For a very small crystallite size, the specimen broadening dominates over instrumental broadening

Only need the most exacting calibration when the specimen broadening is small because the specimen is not highly nanocrystalline

Diffraction Theory

Williamson-Hall Plot

Plot $\beta\cos\theta$ versus $\sin\theta$ (Williamson-Hall Plot)

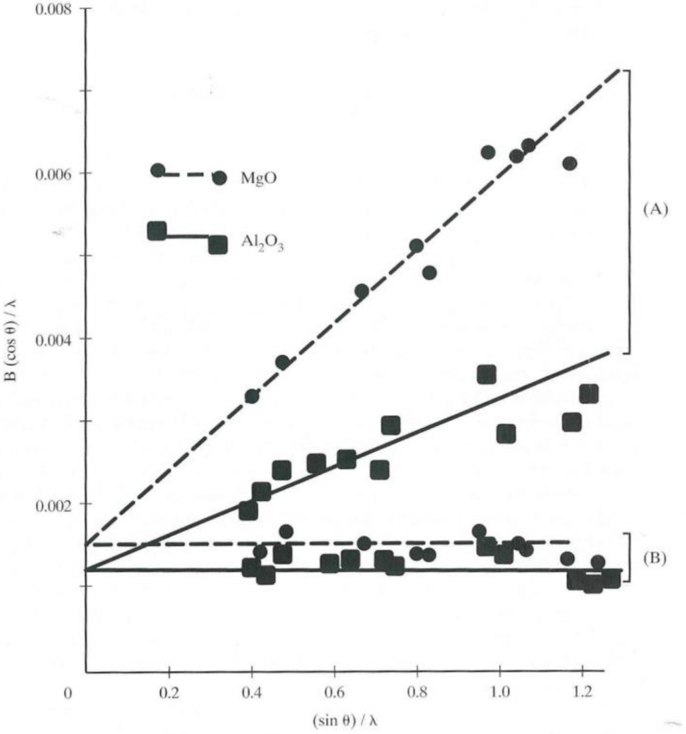


Figure 14-8 Williamson-Hall plot for MgO and Al_2O_3, curves (A) ball milled for 2 hours and (B) ball milled for 2 hours, then annealed for 2 hours at 1350° C. After Lewis and Lindley [14.10].

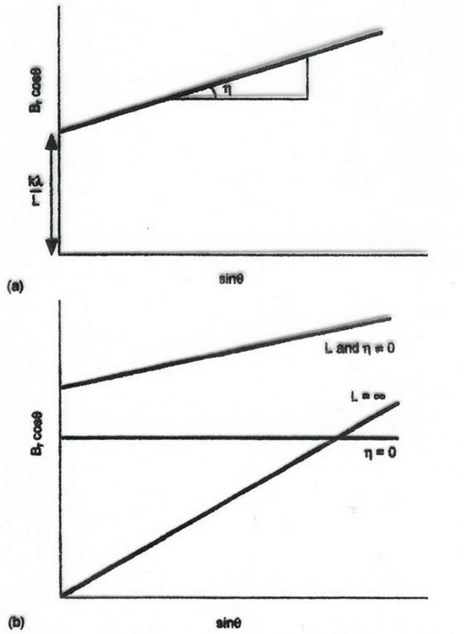
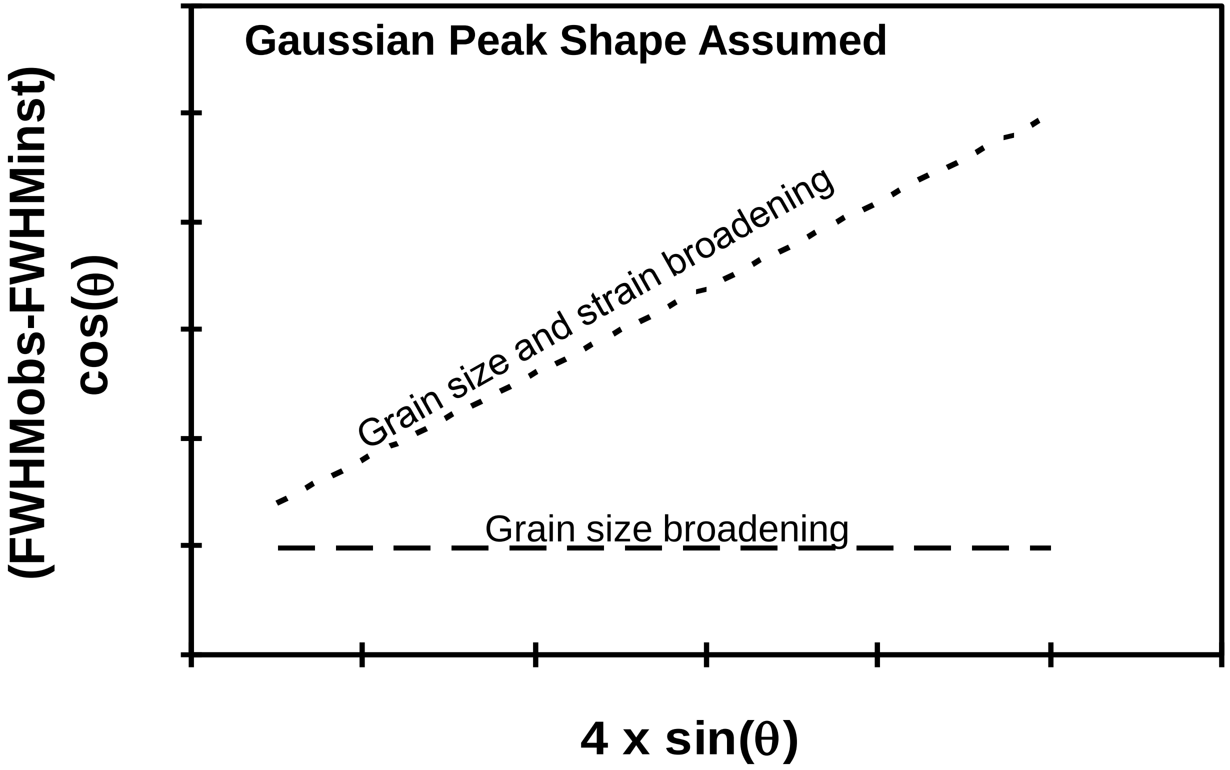


FIG. 6.4. (a) Plot of $B_r \cos\theta$ against $\sin\theta$, indicating that the intercept ($k\lambda/L$) and slope (η) can be used to calculate the crystallite size (L) and lattice strain (η), respectively. (b) Typical plots to show the relative positions of the straight line for very large crystallite sizes ($L = \infty$), no strain ($\eta = 0$), and when both lattice strain and crystallite size contribute to peak broadening.

Diffraction Theory

Williamson-Hall Plot

$$FWHM \times \cos(\theta) = \overset{\text{y-intercept}}{\overset{\downarrow}{\frac{K \times \lambda}{Size}}} + Strain \times \overset{\text{slope}}{\overset{\downarrow}{4}} \times \sin(\theta)$$



Diffraction Theory

Broadening Effects – Ex: CeO_2

Contributions of crystallite size and strain are given by the following equation:

$$\beta_r \cos\theta = \frac{k\lambda}{L} + \eta \sin\theta$$

where

λ is the wavelength of the x-rays,

θ is the diffraction angle,

η is the strain,

L is the crystallite size,

k is a constant (0.94 for gaussian line profiles and small cubic crystals of uniform size)

β_r is the corrected full width at half maximum of the peak

Diffraction Theory

Broadening Effects

β_r is the corrected full width at half maximum of the peak given by,

$$\beta_r{}^2 = \beta_m^2 - \beta_s^2$$

where

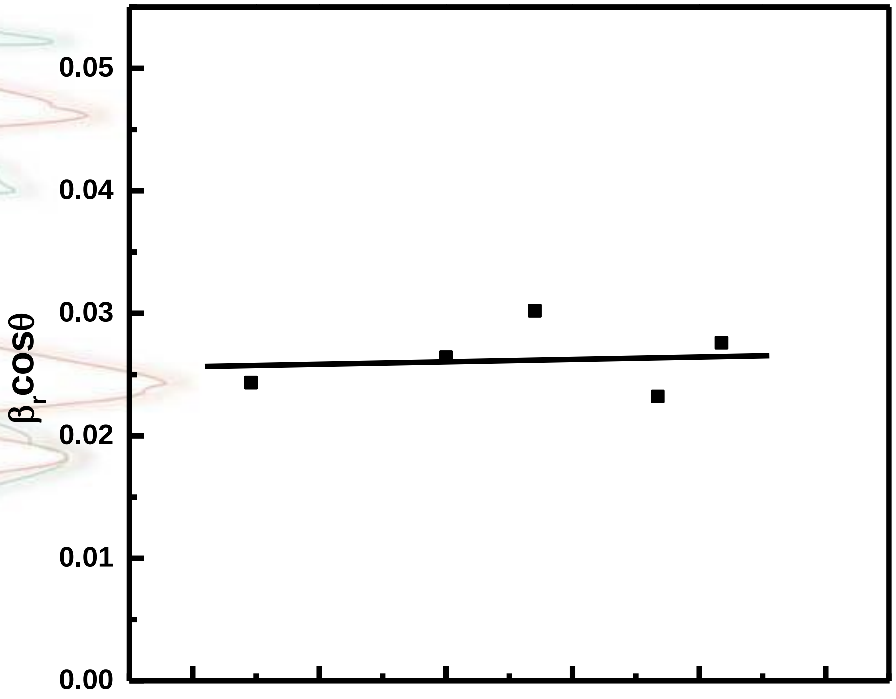
β_m is the experimental measured half width

β_s is half width of a silicon powder standard with peaks corresponding to the same 2θ region.

Diffraction Theory

Broadening Effects

Williamson-Hall Plot



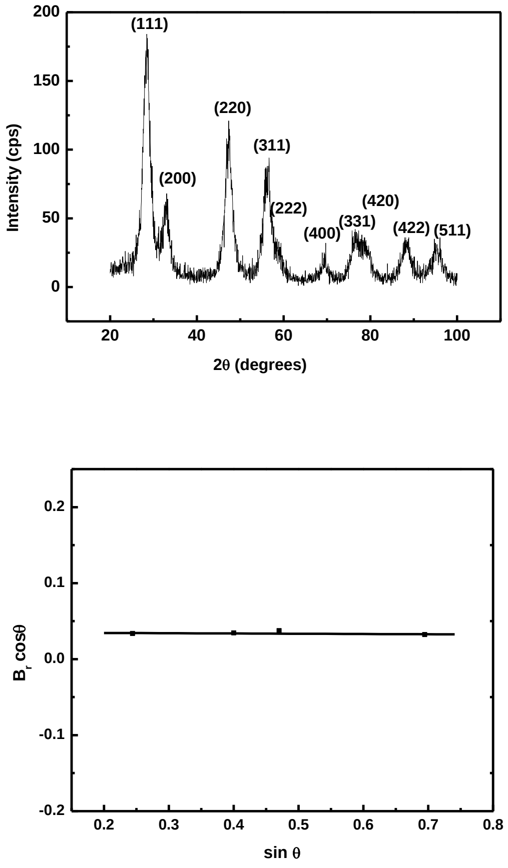


Figure 4. (a) X-ray diffraction pattern of CeO_2 powder produced from a solution of 0.1 M $Ce(NO_3)_3$ and 0.5 M acetate at pH ~ 11 at applied potential of 1.10V vs SCE. The synthesis was operated at room temperature. (b) Williamson-Hall plot βcosθ versus sinθ for the XRD pattern for (a).

Diffraction Theory

Other Methods

Most alternative XRD crystallite size analyses use the Fourier transform of the diffraction pattern

- **Variance Method**
  - **Warren Averbach analysis- Fourier transform of raw data**
  - **Convolution Profile Fitting Method- Fourier transform of Voigt profile function**

- **Whole Pattern Fitting in Fourier Space**
  - **Whole Powder Pattern Modeling- Matteo Leoni and Paolo Scardi**
  - **Directly model all of the contributions to the diffraction pattern**
  - **each peak is synthesized in reciprocal space from it Fourier transform**
    - **for any broadening source, the corresponding Fourier transform can be calculated**

Diffraction Theory

Other Methods

Most alternative XRD crystallite size analyses use the Fourier transform of the diffraction pattern

- **Fundamental Parameters Profile Fitting**

– combine with profile fitting, variance, or whole pattern fitting techniques

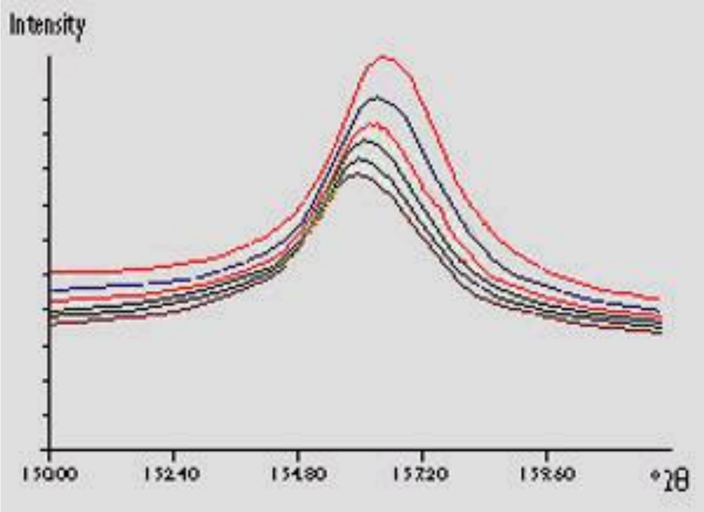
– instead of deconvoluting empirically determined instrumental profile, use fundamental parameters to calculate instrumental and specimen profiles

Diffraction Theory

Other Methods

Stress Analysis

Stress is determined by recording the angular shift of a given Bragg reflection as a function of sample tilt (psi). This actually provides a measure of strain in the sample from which the stress can then be calculated by plotting the change in d-spacing against sin2psi.



Lab 5 – Due today

Lab 6 – Due 12-07-21

Reading Assignment:

Read Chapter 8 from:

-X-ray Diffraction Procedures by Klug and Alexander

Read Chapter 13 from:

-Elements of X-ray Diffraction, 3rd edition, by Cullity and Stock