

Determination of crystallite size (D) of NPs

XRD can provide detailed information about lattice parameters of phases, unit cell dimensions (a, b and c), crystallinity and particle size of materials. The 3D structure of crystalline minerals is defined by regular, repeating planes of atoms to form a crystal lattice. Material properties are highly dependent on their structure.

XRD consists of an X-ray source and detector to read the reflected beam when X-ray beam interacts with these planes of atoms in the sample. Part of the beam is transmitted, absorbed by the sample scattered, refracted and diffracted. Diffraction of an X-ray beam by a crystalline solid is analogous to diffraction of light. X-rays are diffracted by each mineral phase differently, depending on the crystal lattice and how these atoms or ions are arranged. When an X-ray beam hits a sample and is diffracted, one can measure the distances between the planes of the atoms that constitute the sample by applying Bragg's Law (d is the distance between adjacent planes of atoms (the d-spacing), and θ is the angle of incidence of the X-ray beam).

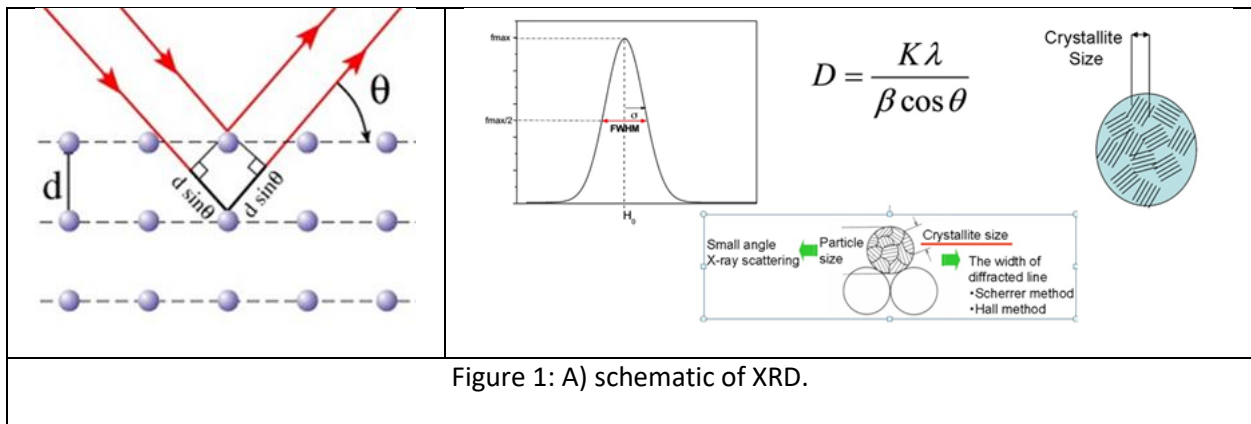


Figure 1: A) schematic of XRD.

Determination of crystal size using the Scherrer Equation

The Scherrer equation can always be used to estimate the size of the crystallite (D) based on the width of the diffraction peak at half intensity, **full-width at half-maximum FWHM** (2θ):

$$D = \frac{K\lambda}{\beta_{1/2} \cos \theta_{hkl}} \quad \text{--- (1)}$$

D = the volume weighted crystallite size (nm),

K = the shape factor ($K= 0.94$),

λ = the radiation wavelength (1.54060 Å for Cu- K_{α}),

β = instrumental-corrected integral breadth of the reflection (in radius) = the broadening (band width) of the hkl diffraction peak at half-height (θ) in radians, and

θ_{hkl} = the Bragg diffraction peak angle

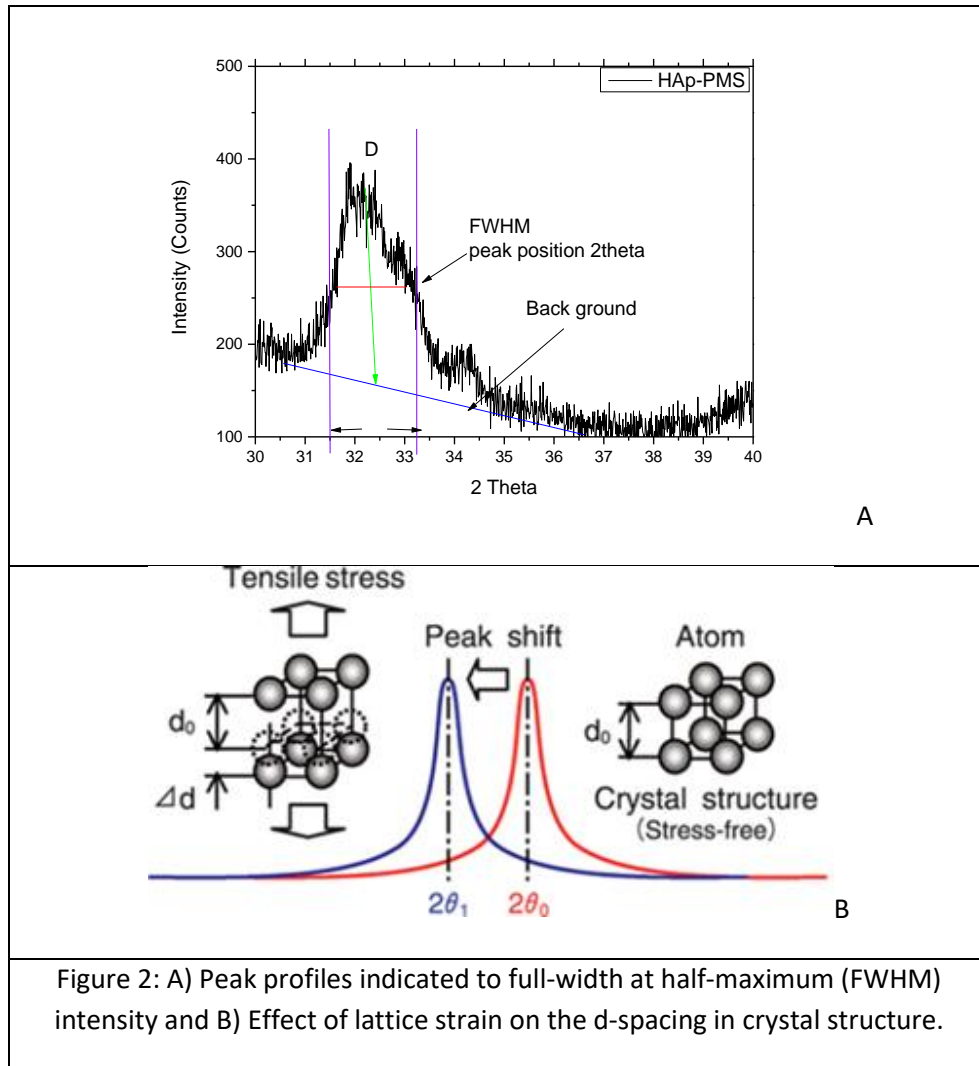
Generally, crystallite size (D) is a measurement of the size coherence diffraction domain and it acts as poly-crystalline aggregates. Crystallite size is not the same as particle size; often, it is smaller.

There are two factors causing deviation from perfect crystallinity and effectiveness of the Bragg peak; crystallite size (D) and lattice strain (ϵ) leading to: (i) increased peak width (broadening), (ii) shift in the position of Bragg angle, (iii) effect of intensity peak. Analysis of XRD peak profiles indicated that width at half-maximum (FWHM) is sensitive to the variation in nanostructure and stress–strain accumulation in the material. The main properties extracted from the width of peak analysis are lattice strain (ϵ) (is a measure of distribution of lattice constants arising from crystal imperfections) and crystallite size (D). The Scherrer method is known to calculate crystallite size.

This equation has not taken account peak broadening reducing from other factors such as instrumental effect and inhomogeneous strain.

$$\beta(hkl) = [(\beta_{hkl})^2_{measured} - (\beta_{hkl})^2_{instrument}]^{1/2} \quad \text{--- (2)}$$

X-ray diffraction peak broadening reveals the β , D , ϵ , Elastic modulus (E_{hkl}) and tensile stress in the materials.



Determination of crystallite size (D) and lattice strain (ε) using the Williamson-Hall approach

The Williamson-Hall approach (W-H) equation is a simple approach both crystallite size (D) and lattice strain (ε) induced broadening are not complex due to considering the peak width as a function of 2θ. The Williamson-Hall approach (W-H) is given by:

$$\beta_{(hkl)} \cos \theta_{hkl} = k\lambda/D + 4\epsilon \sin \theta_{hkl} \quad \text{--- (3)}$$

$$y = z + mX \quad \text{(Linear equation with intercept)}$$

From plot $\beta_{(hkl)} \cos \theta_{hkl}$ along Y-axis and $\sin \theta_{hkl}$ along X-axis, lattice strain (ε) can be calculated from the slope (m) which is equal 4ε. Also, crystallite size (D) can be calculated from the intercept

(Z) of the linear fit made to the plot which is equal to $K \lambda/D$. Assuming the lattice strain (ϵ) is uniform in the materials, this indicates the isotropic nature of the crystal.

Elastic modulus (E_{hkl}) is the constant of proportionality being the modulus of elasticity and it is a Young's modulus in the perpendicular direction to the set of crystal lattice plane (hkl) hexagonal crystal phase. Also, it is related to their elastic compliances S_{ij} and for a hexagonal HAp crystal phase Elastic modulus (E_{hkl}) is according to equation (4).

Hook's Law can be used to determine the lattice deformation stress (σ) by Eq.

$$\sigma = E_{hkl} \epsilon \quad \text{--- (5)}$$

When modified Eq. 5 is given by:

$$\beta \cos\theta = \frac{K\lambda}{D} + 4 \frac{\sigma \sin\theta}{E_{hkl}} \quad \text{--- (6)}$$

Lattice deformation stress (σ) can be extracted from the slope and crystallite size (D) from the intercept of linear fit made to the plot.

Powder samples were supported on a silica wafer and placed on the diffractometer holder which loaded into the instrument. X-Ray diffractometry used was a Bruker Advance D8 including a Cu anode K_{α} ($\lambda=1.54060 \text{ \AA}$) over the 2θ range of $10-70^{\circ}$. The XRD peak positions were calibrated with Al_2O_3 .