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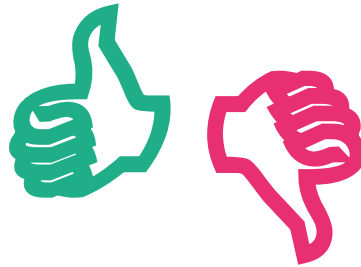
# ***Participation, please.***

**26 Apr – 09 May, 2020**



## **TUCpanel**

Student Poll



**We would like your feedback concerning your studies at CUT!**

The information you provide will help us to improve conditions for you as well as for future students.

To participate, look for the **link to this poll** in your **university e-mail inbox**.

Estimated time: 25 to 30 minutes

*For results and further information: [www.tu-chemnitz.de/tucpanel](http://www.tu-chemnitz.de/tucpanel)*

X-Ray Diffraction basics

&

Multipurpose X-ray diffraction system  
with built-in intelligent guidance

with built-in intelligent guidance

Multipurpose X-ray diffraction system

&

X-Ray Diffraction basics

YES!

We can also see the reciprocal space and the reciprocal structures.

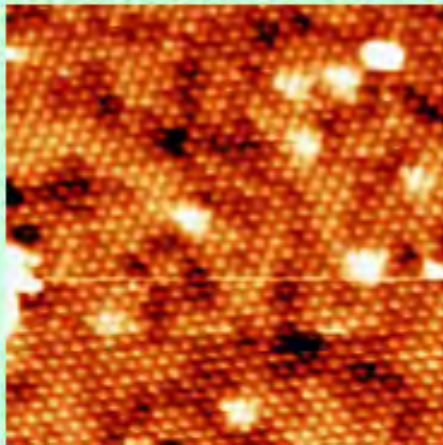


X-Ray Diffraction: Image & spectra

Every crystal structure has **two** lattices associated with it, the *crystal lattice* (or *direct lattice*) and the *reciprocal lattice*.

A diffraction pattern of a crystal is a map of the reciprocal lattice of the crystal.

A microscope image, if it could be resolved on a fine enough scale, is a map of the crystal structure in real space.

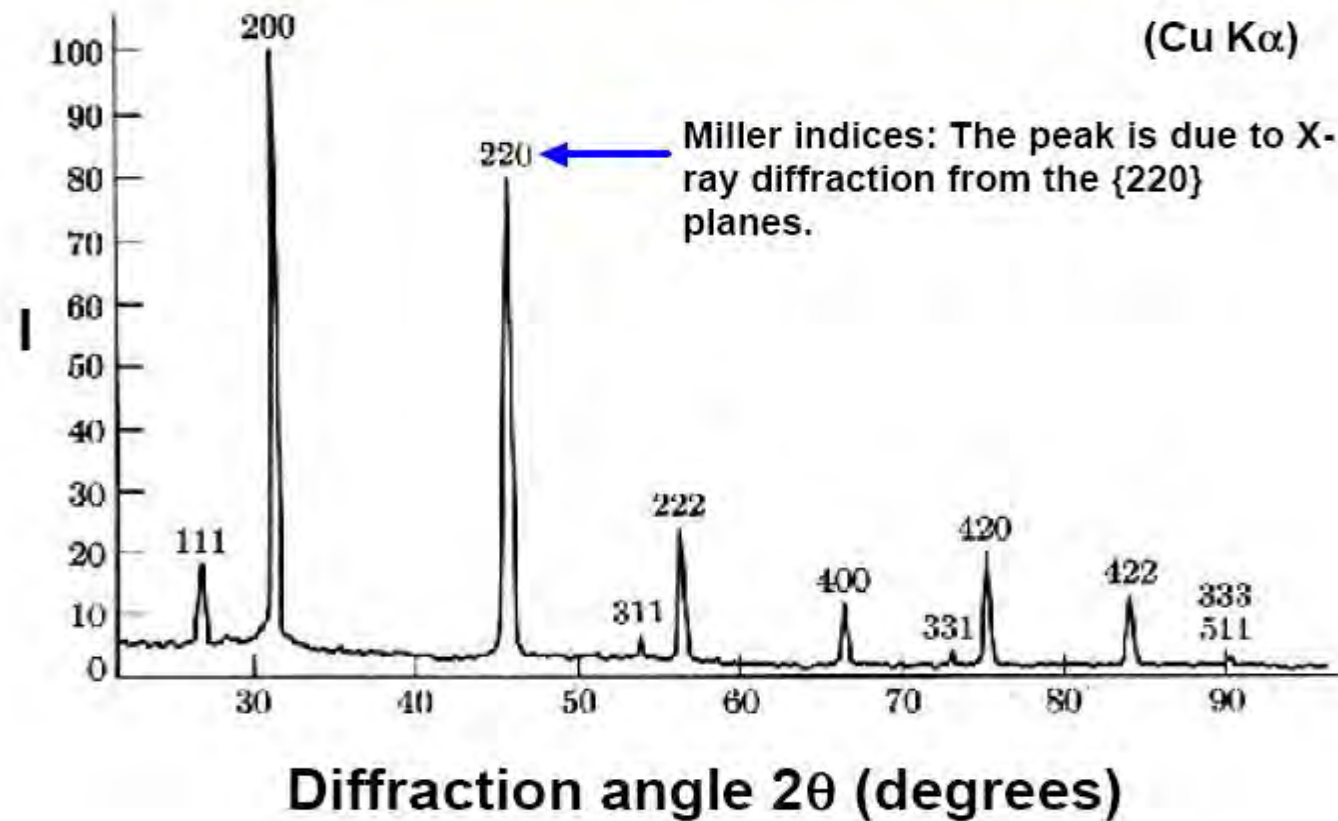


Real  
space  
image



Reciprocal  
space  
image

# XRD Pattern of NaCl Powder



Typical XRD spectra.

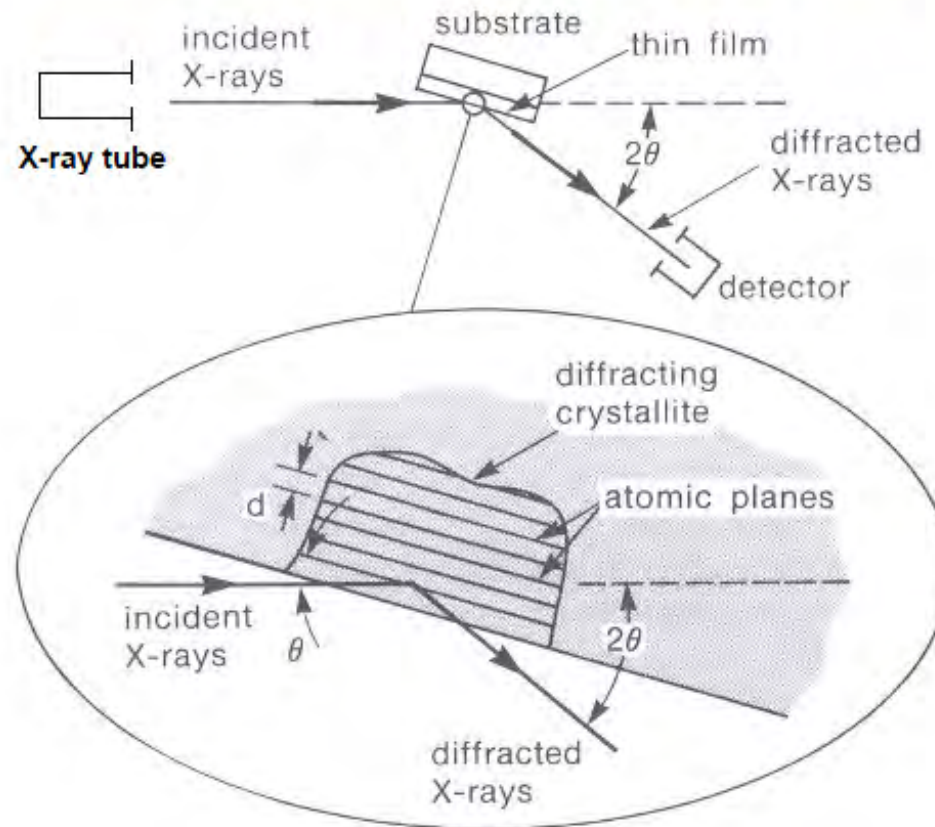
In this case NaCl has a cubic unit cell.

It is best thought of as a face-centered cubic array of anions with an interpenetrating fcc cation **lattice** (or vice-versa).

# XRD – X-ray Diffraction

## Characterization of materials Crystal Structure

### Basic Features of Typical XRD Experiment



- 1) Production
- 2) Diffraction
- 3) Detection
- 4) Interpretation

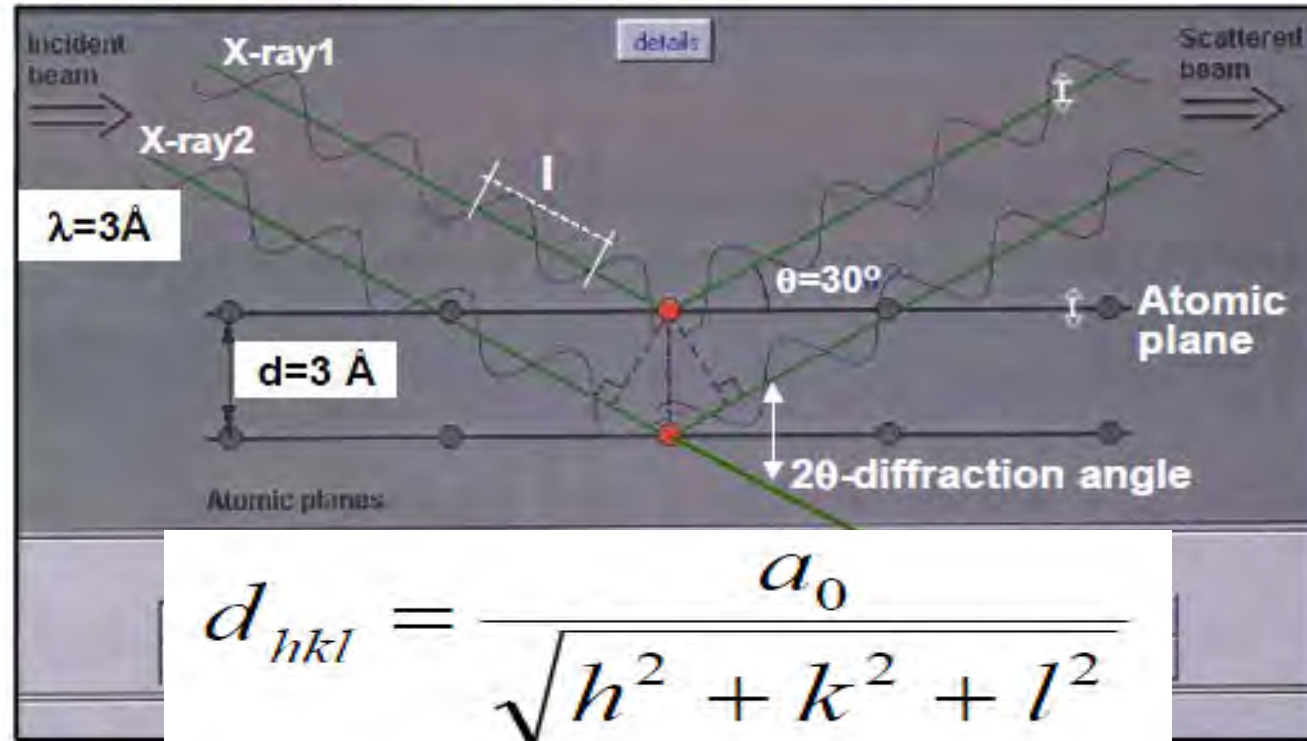


# Bragg's Law and Diffraction:

## How waves reveal the atomic structure of crystals

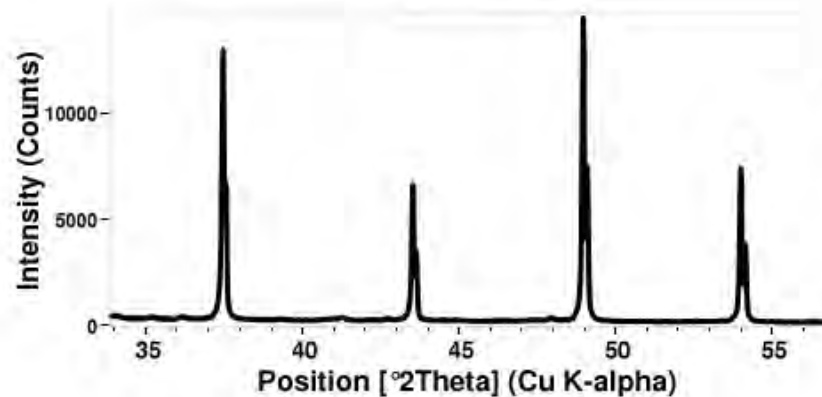
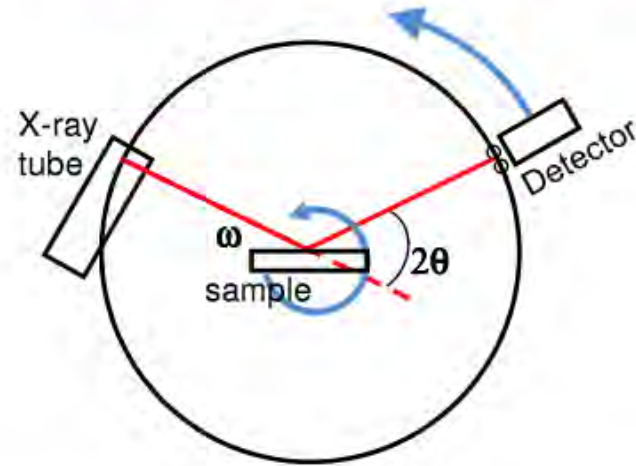
$$n \lambda = 2d_{hkl} \sin \theta_{hkl} \quad n\text{-integer}$$

Diffraction occurs only when Bragg's Law is satisfied Condition for constructive interference (X-rays 1 & 2) from planes with spacing  $d$



Different planes have different spacings  
To satisfy Bragg's law  $\theta$  must change as  $d$  changes  
 $\theta$  increases as  $d$  decreases and vice versa

An X-ray diffraction pattern is a plot of the intensity of X-rays scattered at different angles by a sample



- The detector moves in a circle around the sample
  - The detector position is recorded as the angle  $2\theta$
  - The detector records the number of X-rays observed at each angle  $2\theta$
  - The X-ray intensity is usually recorded as “counts” or as “counts per second”
- To keep the X-ray beam properly focused, the sample will also rotate.
  - On some instruments, the X-ray tube may rotate instead of the sample.

## To calculate unit cell lattice parameters from the diffraction peak positions

- Convert the observed peak positions,  $2\theta$ , into  $d_{hkl}$  values using Bragg's Law:

$$d_{hkl} = \frac{\lambda}{2 \sin \theta}$$

- Determine the Miller indices (hkl) of the diffraction peaks from the published reference pattern
  - If you do not have access to a reference pattern that identifies (hkl) then you will need to index the pattern to determine the (hkl)
- Use the  $d^2$  equation to calculate the lattice parameters
  - Most analysis programs contain an unit cell refinement algorithm for numerically solving the lattice parameters
  - These programs can also calculate and correct for peak position error due to specimen displacement

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} + \frac{2hk}{ab} \cos \gamma + \frac{2hl}{ac} \cos \beta + \frac{2kl}{bc} \cos \alpha$$



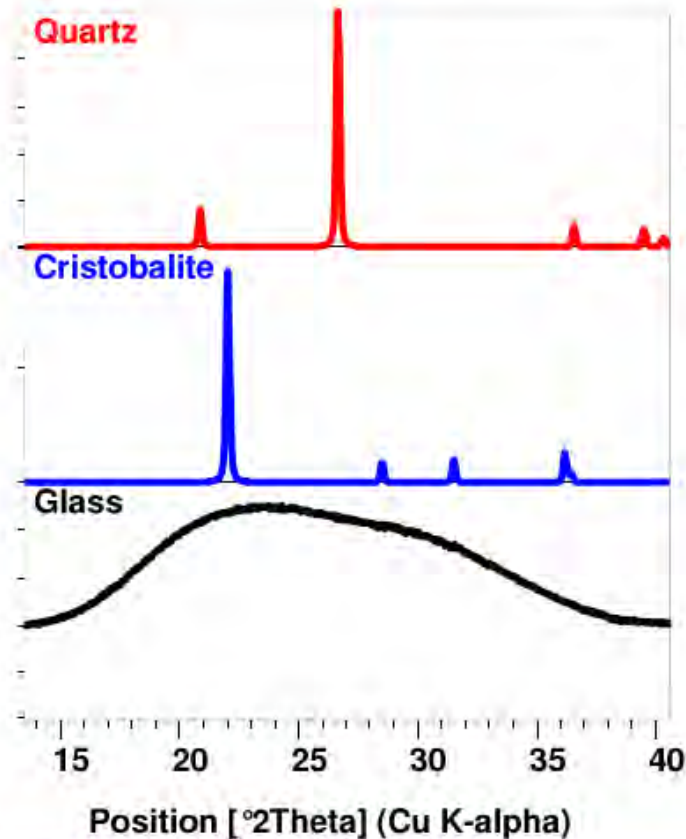
## Diffraction peak lists are best reported using $d_{hkl}$ and relative intensity rather than $2\theta$ and absolute intensity.

- The peak position as  $2\theta$  depends on instrumental characteristics such as wavelength.
  - The peak position as  $d_{hkl}$  is an intrinsic, instrument-independent, material property.
    - Bragg's Law is used to convert observed  $2\theta$  positions to  $d_{hkl}$ .
- The absolute intensity, i.e. the number of X rays observed in a given peak, can vary due to instrumental and experimental parameters.
  - The relative intensities of the diffraction peaks should be instrument independent.
    - To calculate relative intensity, divide the absolute intensity of every peak by the absolute intensity of the most intense peak, and then convert to a percentage. The most intense peak of a phase is therefore always called the "100% peak".
  - Peak areas are much more reliable than peak heights as a measure of intensity.

## Calculations must be executed on the peak list to yield any information about the sample

- This peak list itself does not tell you anything about the sample
  - Additional analysis must be done on the peak list to extract information
- From the peak list you can determine:
  - Phase composition: by comparison to a database of reference patterns
  - Semi-quantitative phase composition: calculated from peak intensities for different phases
  - Unit cell lattice parameters: calculated from peak positions
  - Crystal system: determined by indexing observed peaks and systematic absences
  - Crystallite size and microstrain: calculated from peak widths and/or shapes
  - A number of engineering indexes are also calculated from peak list information

## Each “phase” produces a unique diffraction pattern

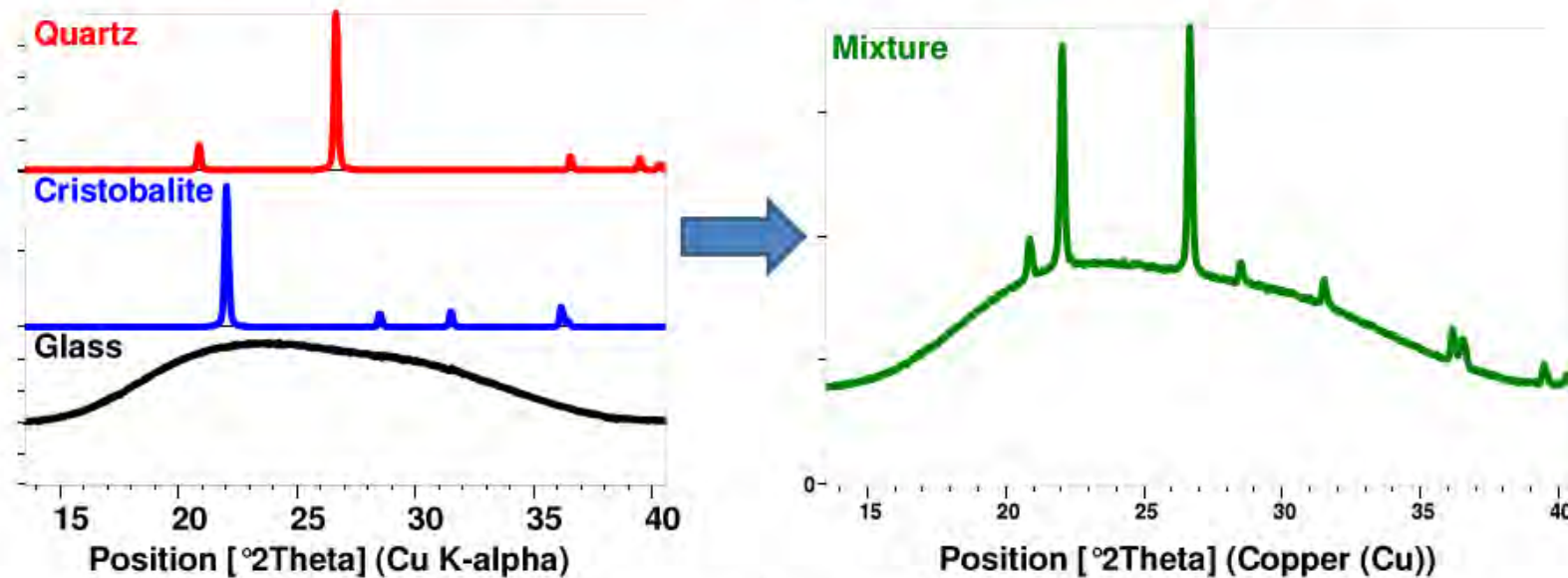


- A phase is a specific chemistry and atomic arrangement.
- Quartz, cristobalite, and glass are all different phases of SiO<sub>2</sub>
  - They are chemically identical, but the atoms are arranged differently.
  - As shown, the X-ray diffraction pattern is distinct for each different phase.
  - Amorphous materials, like glass, do not produce sharp diffraction peaks.

The X-ray diffraction pattern is a fingerprint that lets you figure out what is in your sample.



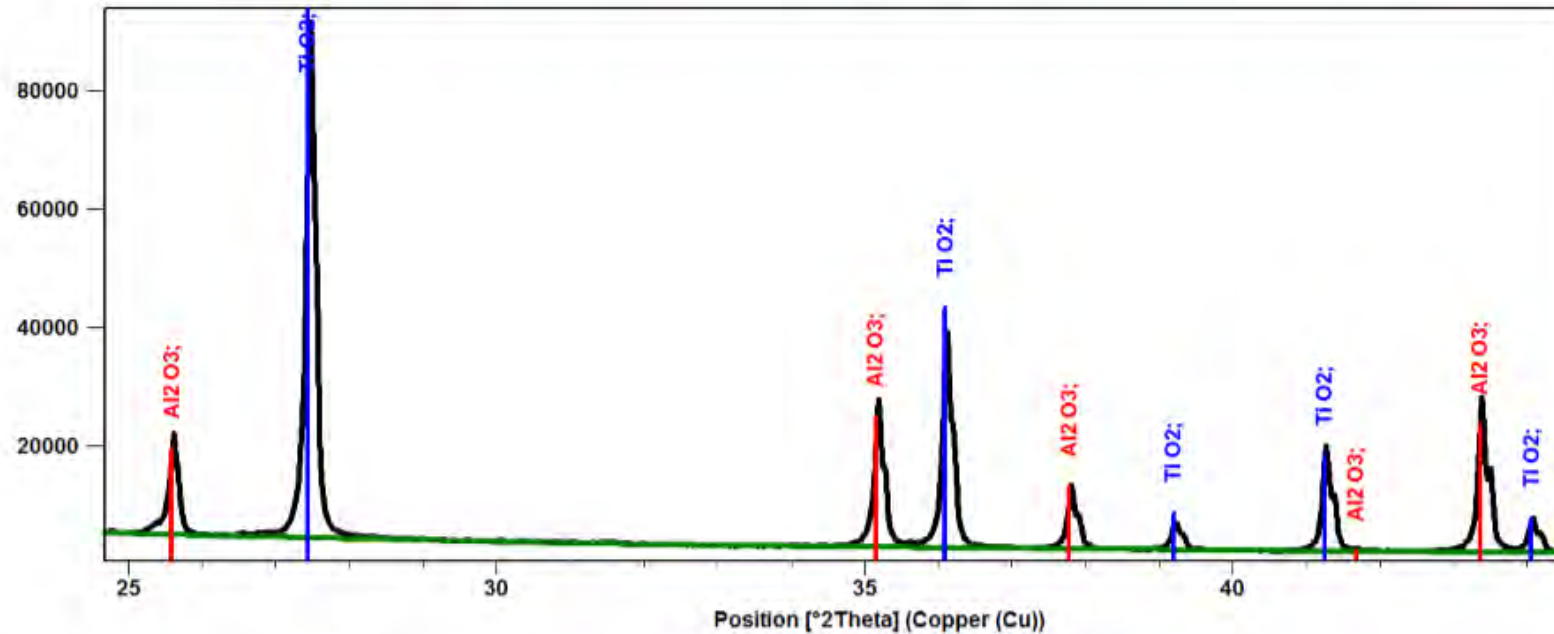
The diffraction pattern of a mixture is a simple sum of the diffraction patterns of each individual phase.



- From the XRD pattern you can determine:
  - What crystalline phases are in a mixture
  - How much of each crystalline phase is in the mixture (quantitative phase analysis, QPA, is covered in another tutorial)
  - If any amorphous material is present in the mixture



You cannot guess the relative amounts of phases based upon the relative intensities of the diffraction peaks



- The pattern shown above contains equal amounts of  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$
- The  $\text{TiO}_2$  pattern is more intense because  $\text{TiO}_2$  diffracts X-rays more efficiently

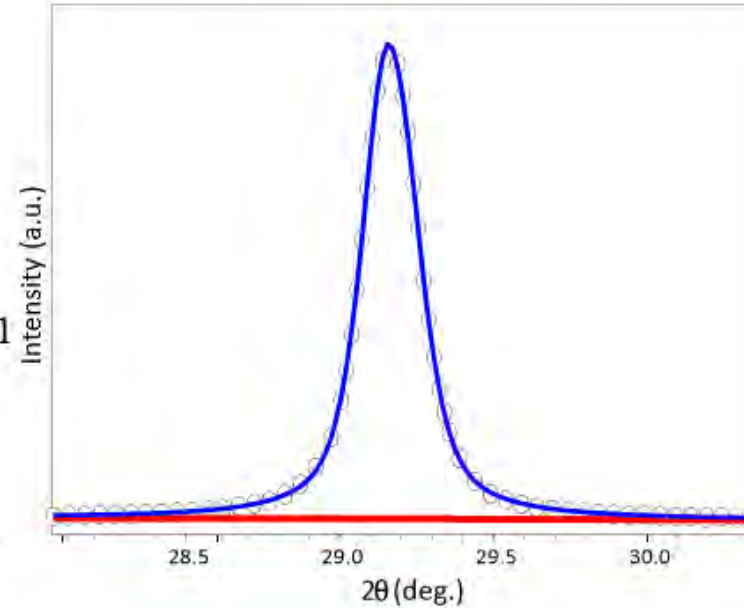
With proper calibration, you can calculate the amount of each phase present in the sample

## There are different ways to extract peak information for quantitative analysis

- Numerical methods reduce the diffraction data to a list of discrete diffraction peaks
  - The peak list records the position, intensity, width and shape of each diffraction peak
  - Calculations must be executed based on the peak list to produce information about the sample
- Full pattern fitting methods refine a model of the sample
  - A diffraction pattern is calculated from a model
  - The calculated and experimental diffraction patterns are compared
  - The model is refined until the differences between the observed and calculated patterns are minimized.
  - The Rietveld, LeBail, and Pawley fitting methods use different models to produce the calculated pattern

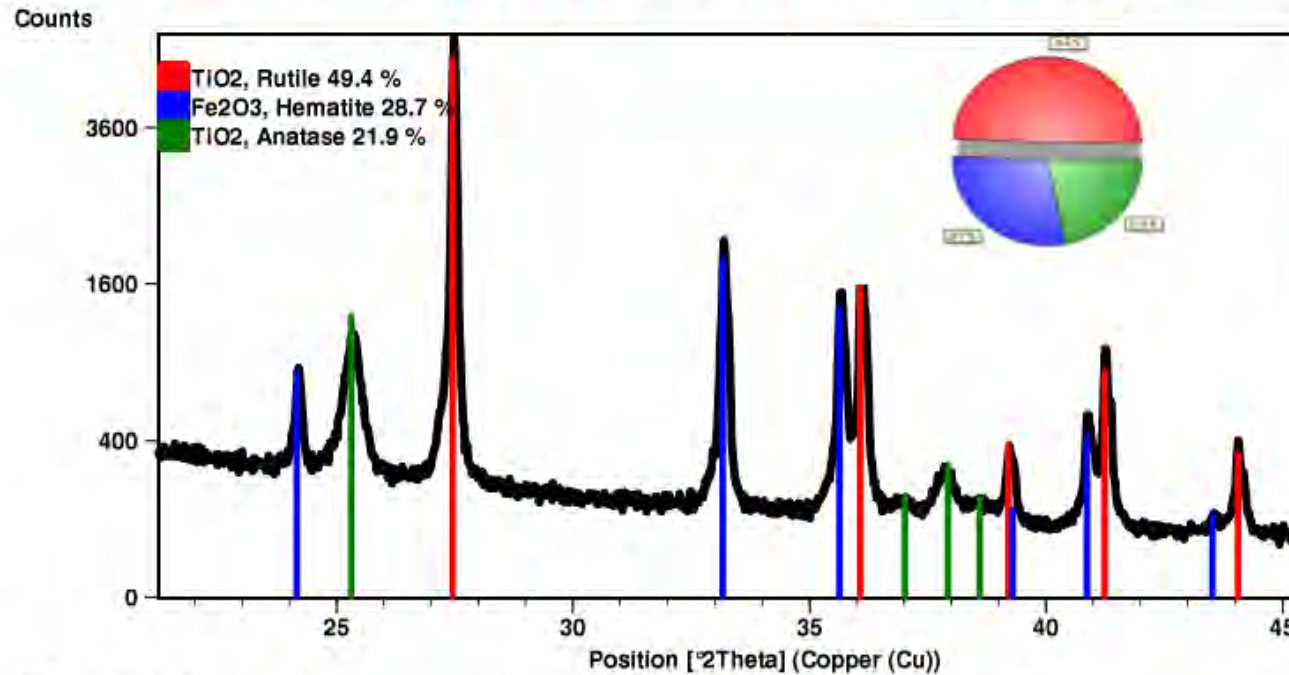
## Profile Fitting produces precise peak positions, widths, heights, and areas with statistically valid estimates

- Empirically fit experimental data with a series of equations
  - fit the diffraction peak using the profile function
    - The profile function models the mixture of Gaussian and Lorentzian shapes that are typical of diffraction data
  - fit background, usually as a polynomial function
    - this helps to separate intensity in peak tails from background
- To extract information, operate explicitly on the equation rather than numerically on the raw data





The weight fraction of each phase can be calculated if the calibration constant is known

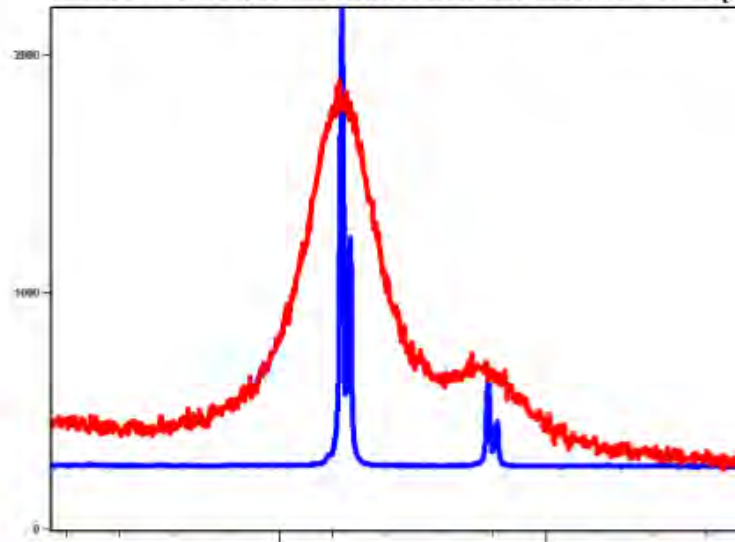


- The calibration constants can be determined:
  - By empirical measurements from known standards
  - By calculating them from published reference intensity ratio (RIR) values
  - By calculating them with Rietveld refinement

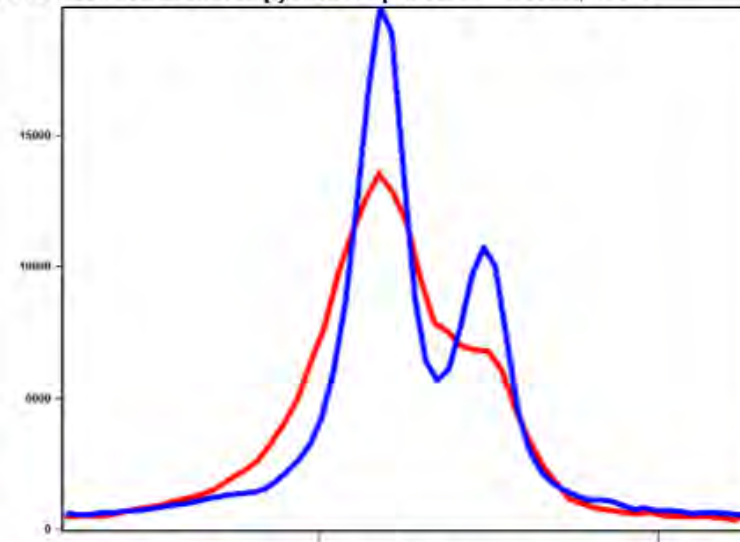


## Diffraction peak broadening may contain information about the sample microstructure

- Peak broadening may indicate:
  - Smaller crystallite size in nanocrystalline materials
  - More stacking faults, microstrain, and other defects in the crystal structure
  - An inhomogeneous composition in a solid solution or alloy
- However, different instrument configurations can change the peak width, too



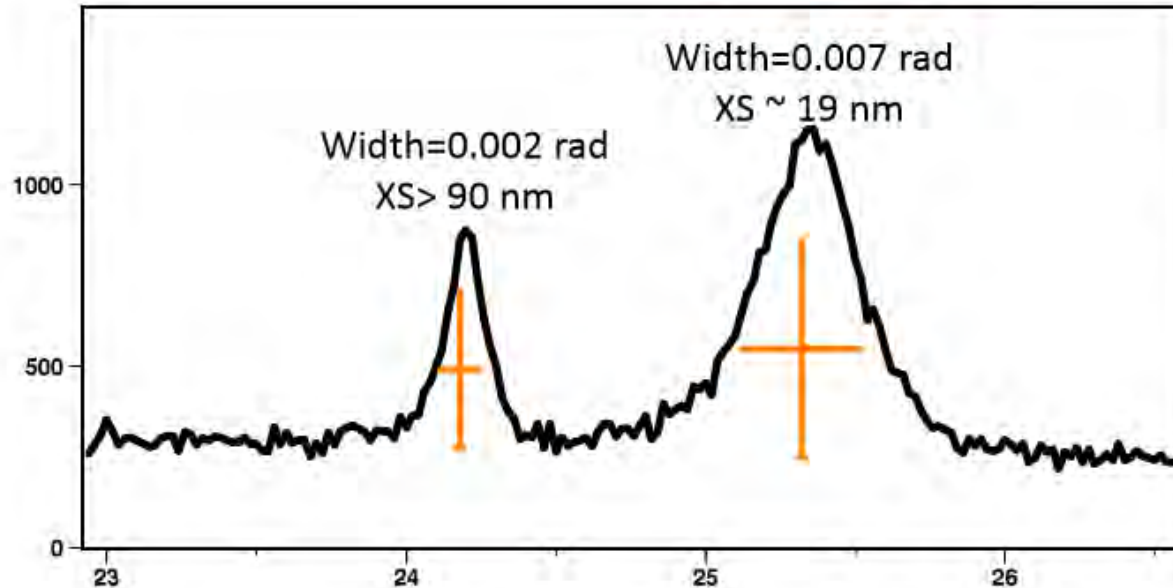
These patterns show the difference between **bulk ceria (blue)** and **nanocrystalline ceria (red)**



These patterns show the difference between the exact same sample run on two different instruments.

When evaluating peak broadening, the instrument profile must be considered.

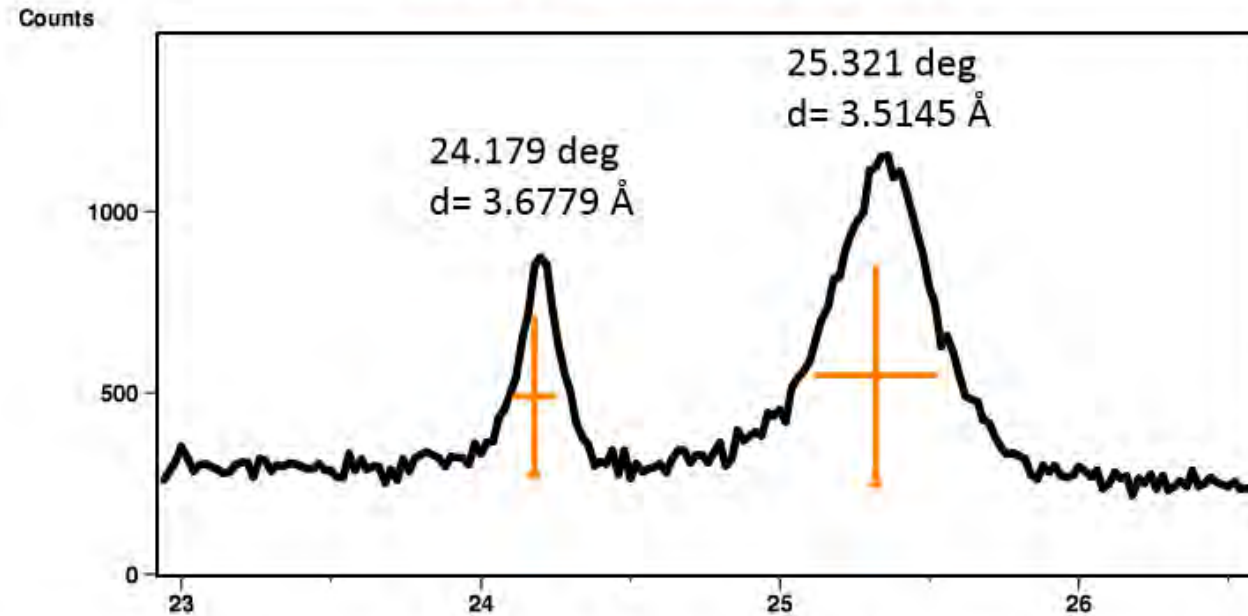
## The diffraction peak width may contain microstructural information



$$\text{Size} = \frac{K\lambda}{\text{Width} \cdot \cos \theta}$$

- Nanocrystallite size will produce peak broadening that can be quantified
  - Once the crystallite size is larger than a maximum limit, the peak broadening cannot be quantified. This creates an upper limit to the crystallite size that can be calculated.
  - The upper limit depends on the resolution of the diffractometer.
- Non-uniform lattice strain and defects will also cause peak broadening
- Careful evaluation is required to separate all of the different potential causes of peak broadening

## Diffraction peak positions can be used to calculate unit cell dimensions



- The unit cell dimensions can be correlated to interatomic distances
- Anything that changes interatomic distances- temperature, substitutional doping, stress- will be reflected by a change in peak positions



Modern XRD machines enable more degrees of freedom and can be used for varied purposes among which **thickness** and **roughness** of thin films and the **size of nanoparticles** in solution, are much used in semiconductor research.

Our lab has one of these machines. Please, click on the links to see how these machines look like and what can be done with them!



[Detailed movement of goniometer](#)

[Automated Multipurpose X-Ray Diffractometer](#)



Next Lecture

## Lattice Vibrations & Phonons

Dispersion Relations & Density of States (DOS)