

Introduction to X-Ray Powder Diffraction Data Analysis

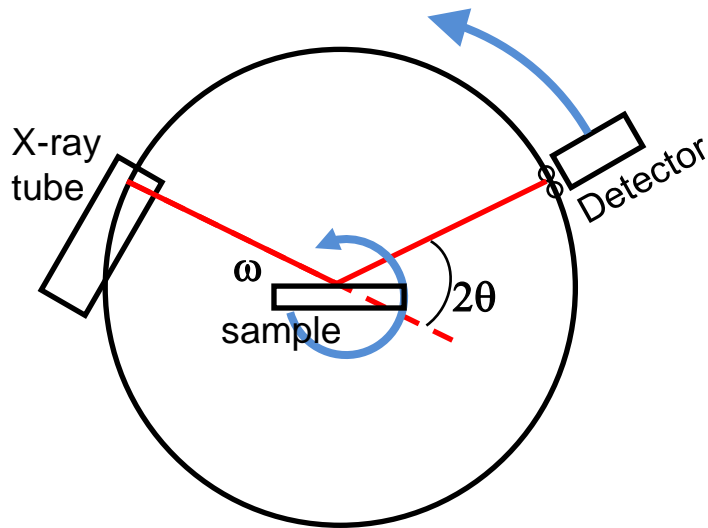
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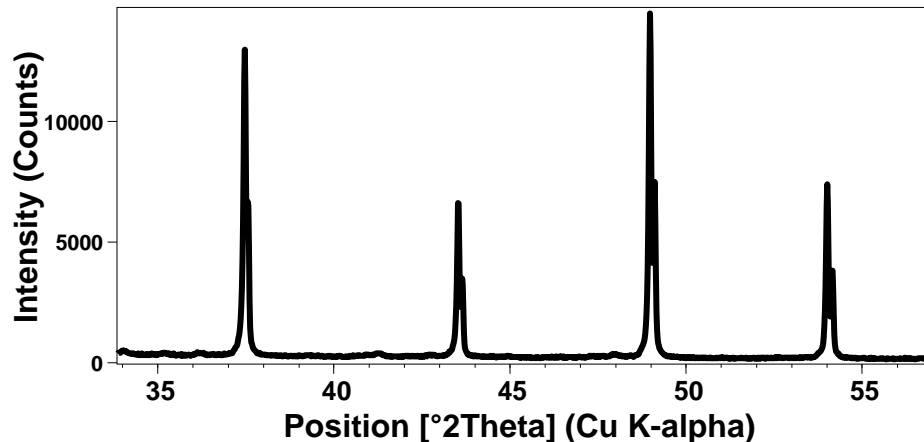
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<http://prism.mit.edu/xray>

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

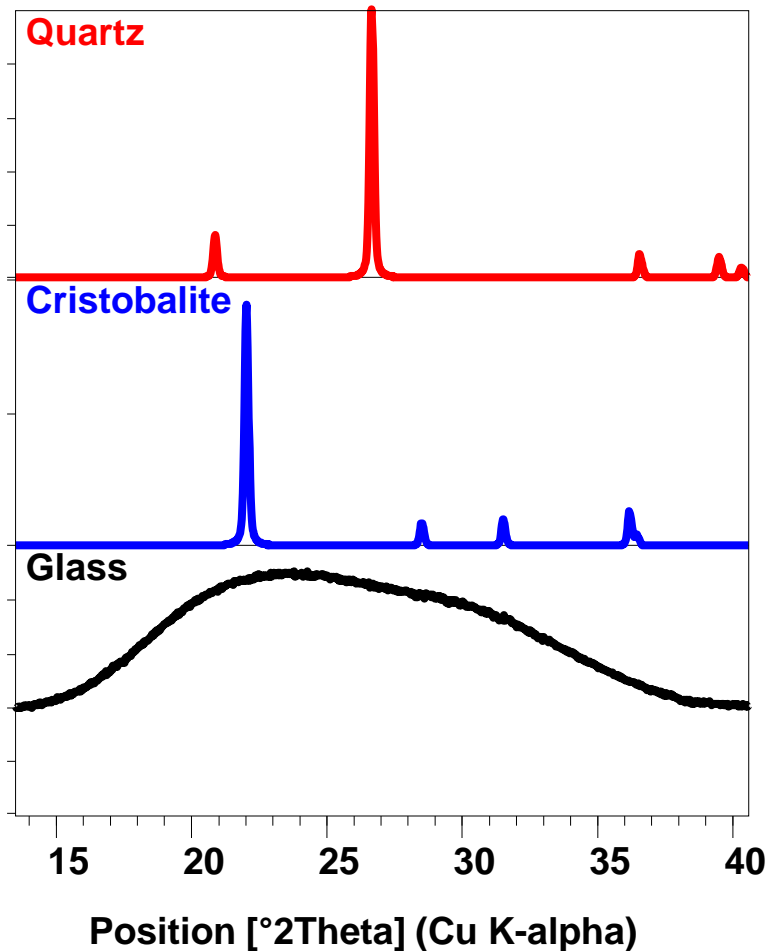


- The detector moves in a circle around the sample
 - The detector position is recorded as the angle 2θ
 - The detector records the number of X-rays observed at each angle 2θ
 - The X-ray intensity is usually recorded as “counts” or as “counts per second”



- 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.

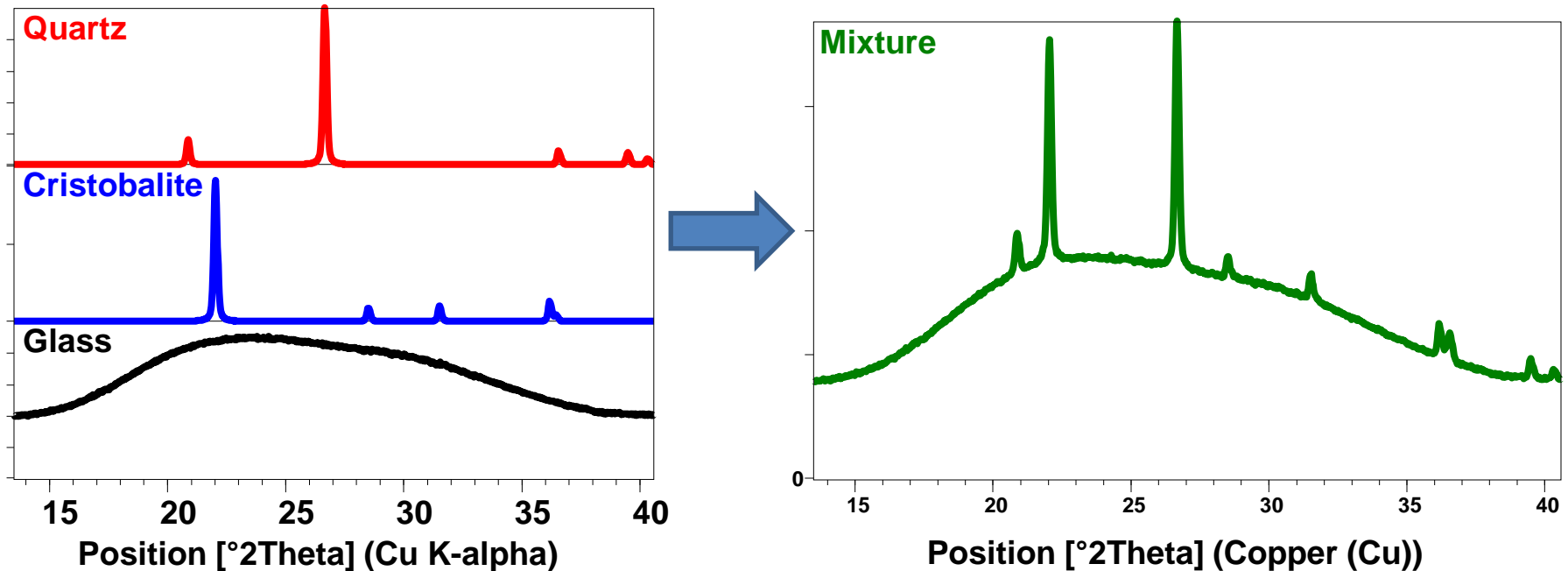
Each “phase” produces a unique diffraction pattern



- A phase is a specific chemistry and atomic arrangement.
- Quartz, cristobalite, and glass are all different phases of SiO₂
 - 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.

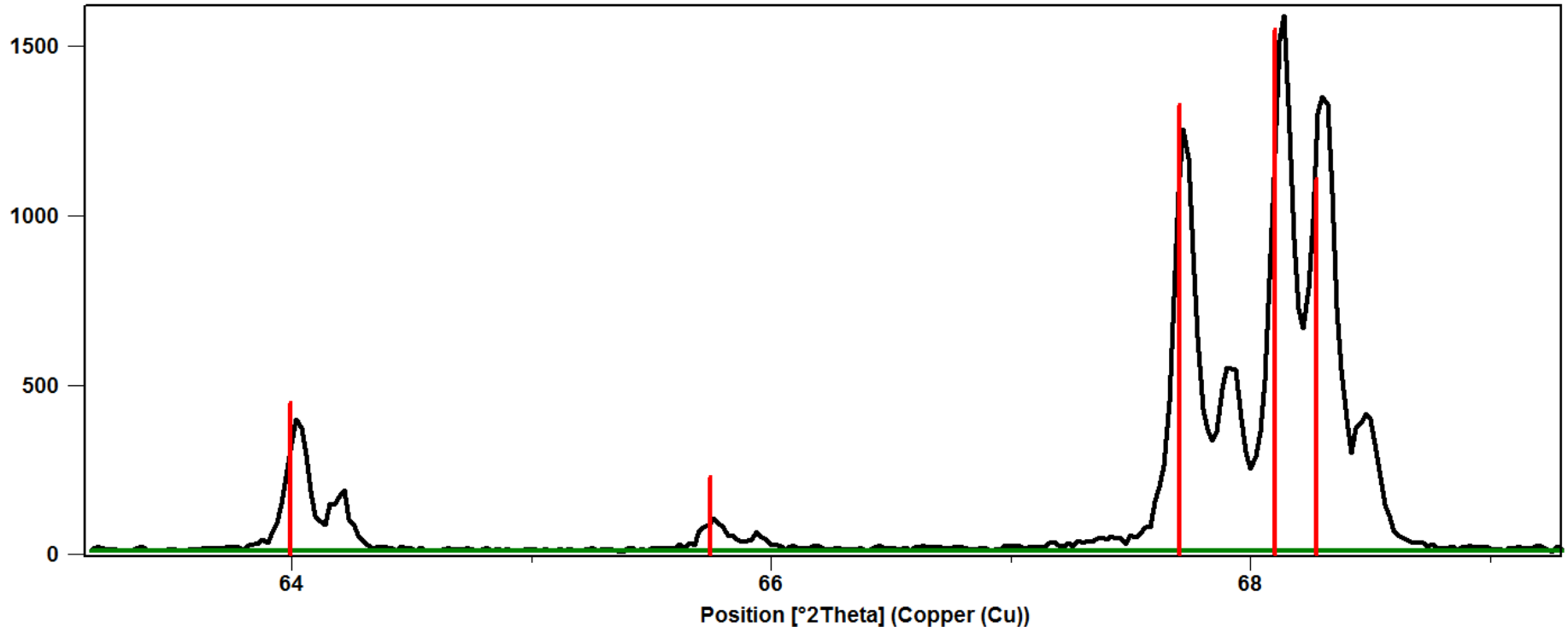
The diffraction pattern of a mixture is a simple sum of the diffraction patterns of each individual phase.



- 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

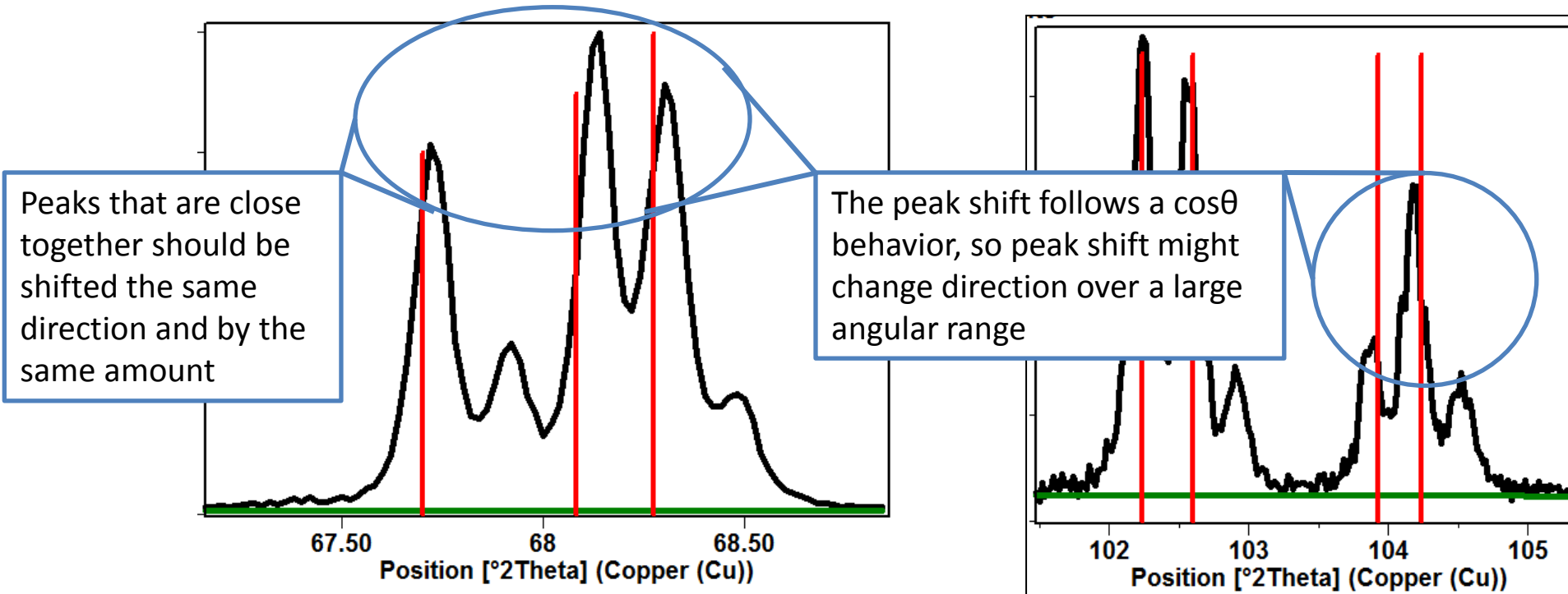
Qualitative Analysis of XRD Data

Experimental XRD data are compared to reference patterns to determine what phases are present



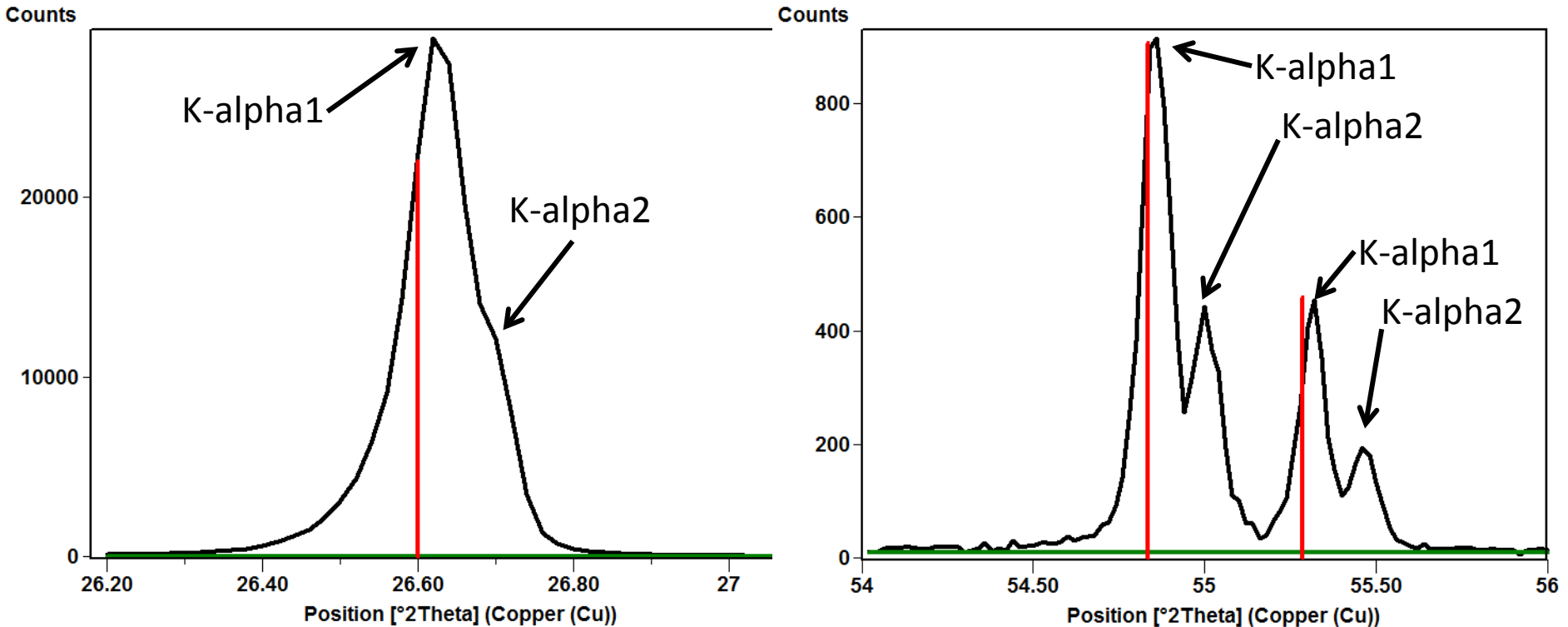
- The reference patterns are represented by sticks
- The position and intensity of the reference sticks should match the data
 - A small amount of mismatch in peak position and intensity is acceptable experimental error

Specimen Displacement Error will cause a small amount of error in peak positions



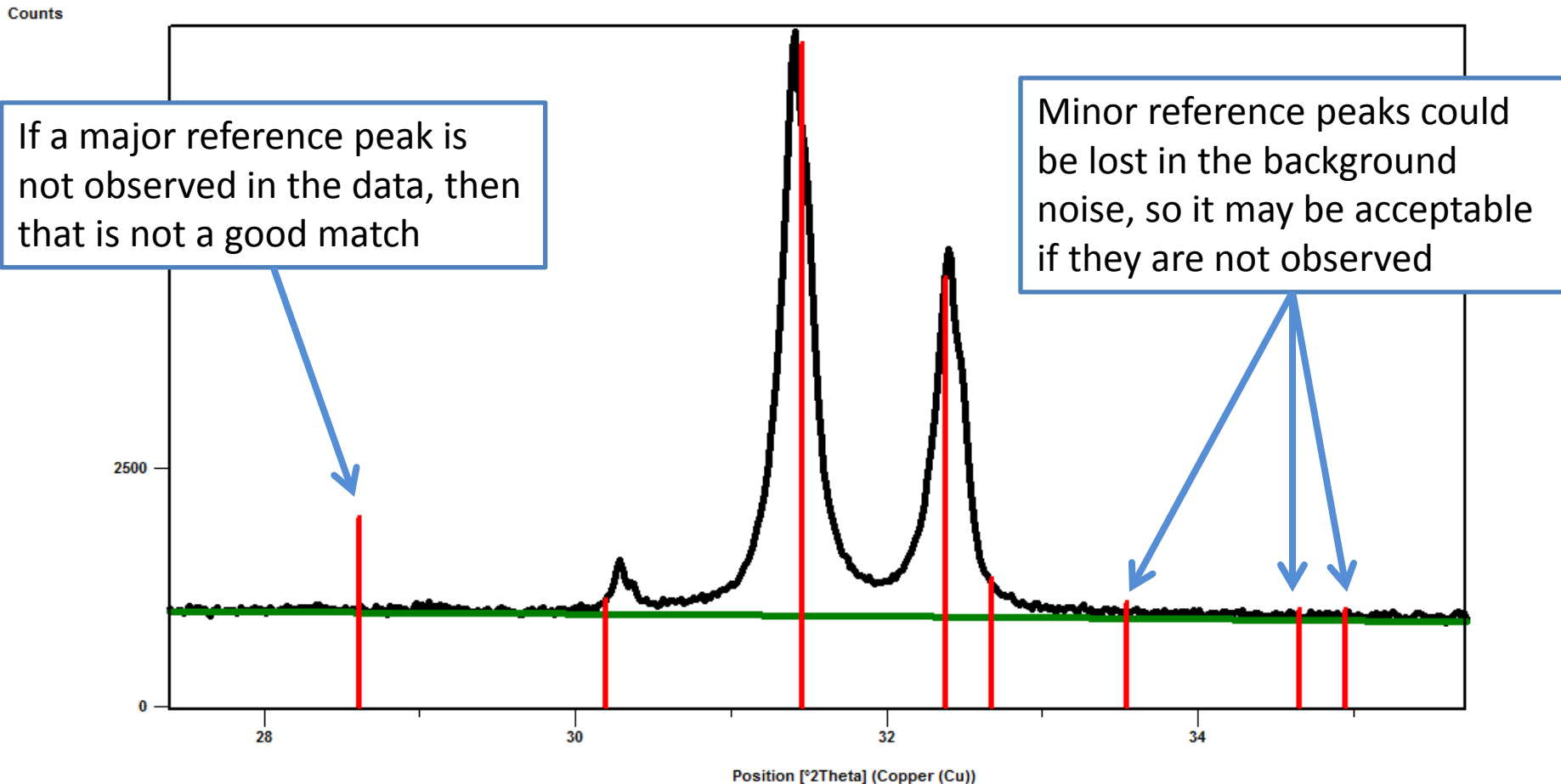
- Specimen displacement is a systematic peak position error due to misalignment of the sample.
- The direction and amount of peak shift will vary as $\frac{-2s \cos \theta}{R}$

Most diffraction data contain K-alpha1 and K-alpha2 peak doublets rather than just single peaks



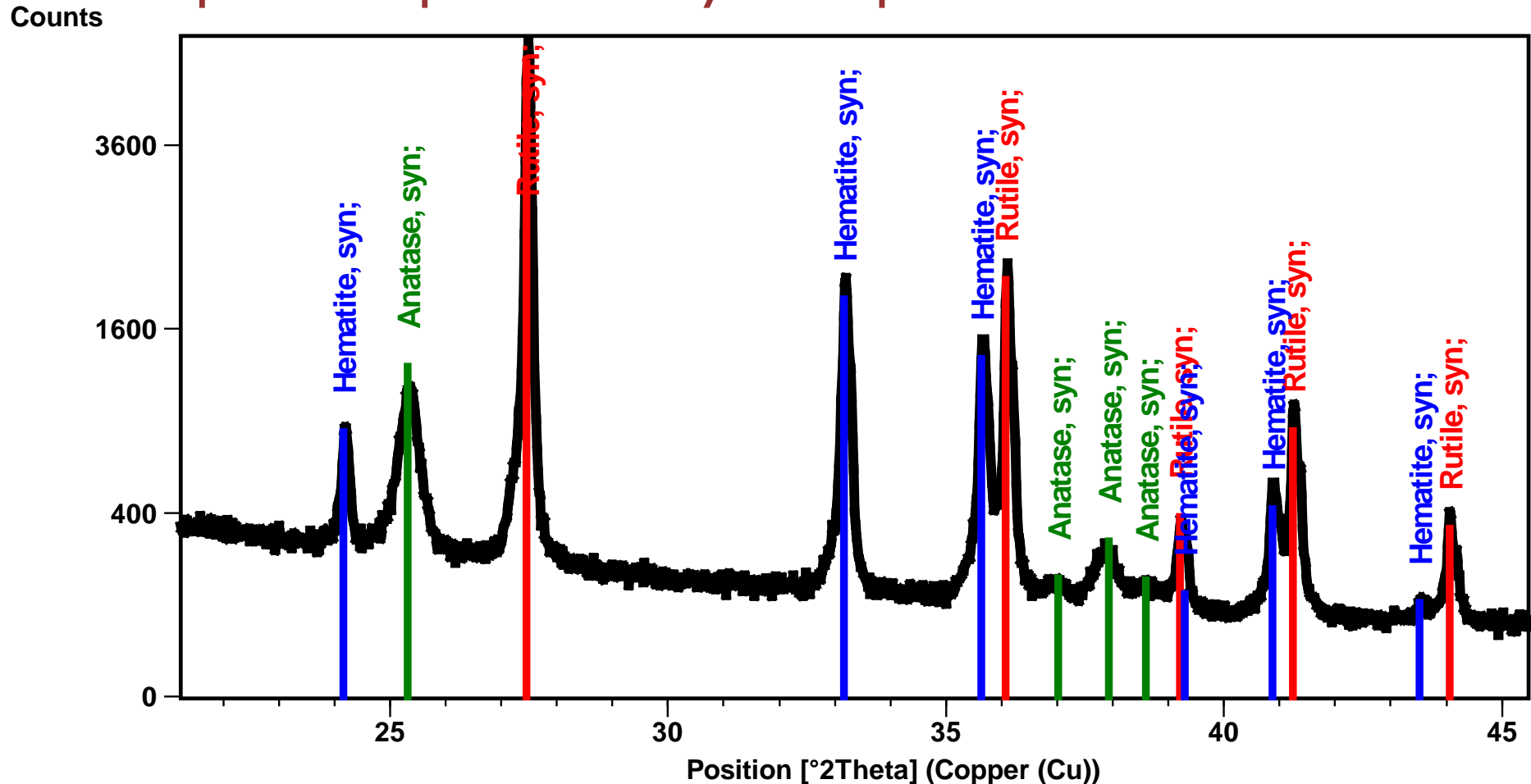
- The k-alpha1 and k-alpha2 peak doublets are further apart at higher angles 2theta
- The k-alpha1 peaks always as twice the intensity of the k-alpha2
- At low angles 2theta, you might not observe a distinct second peak

The experimental data should contain all major peaks listed in the reference pattern



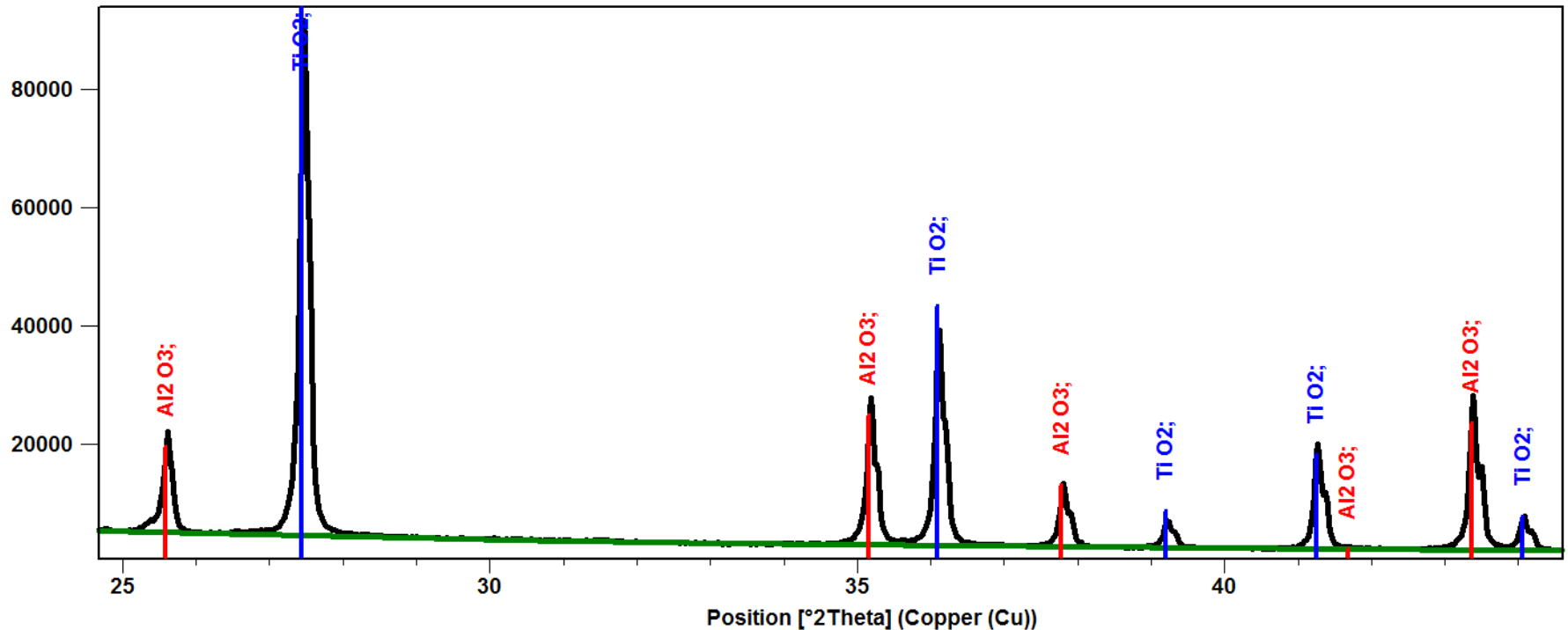
This is an example of a bad match between the data and the reference pattern

The X-ray diffraction pattern is a sum of the diffraction patterns produced by each phase in a mixture



Each different phase produces a different combination of peaks.

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

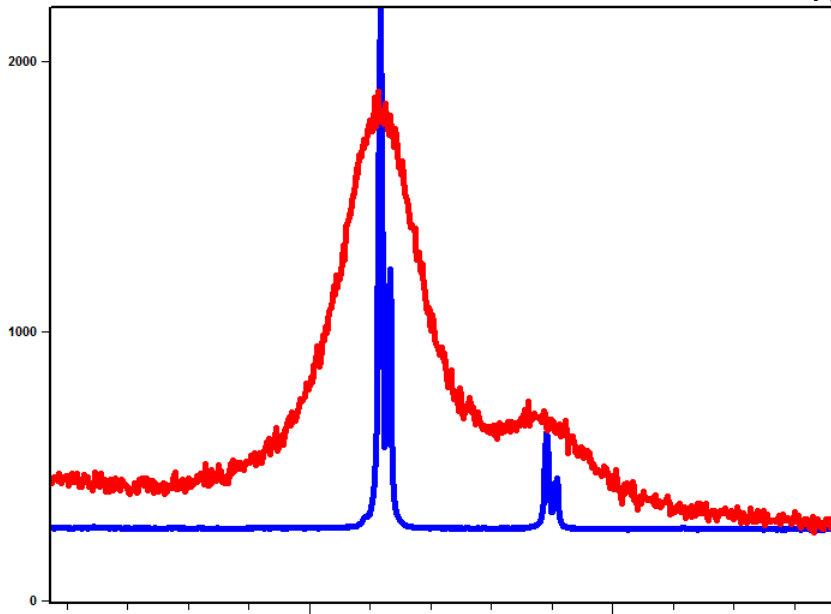


- The pattern shown above contains equal amounts of TiO₂ and Al₂O₃
- The TiO₂ pattern is more intense because TiO₂ diffracts X-rays more efficiently

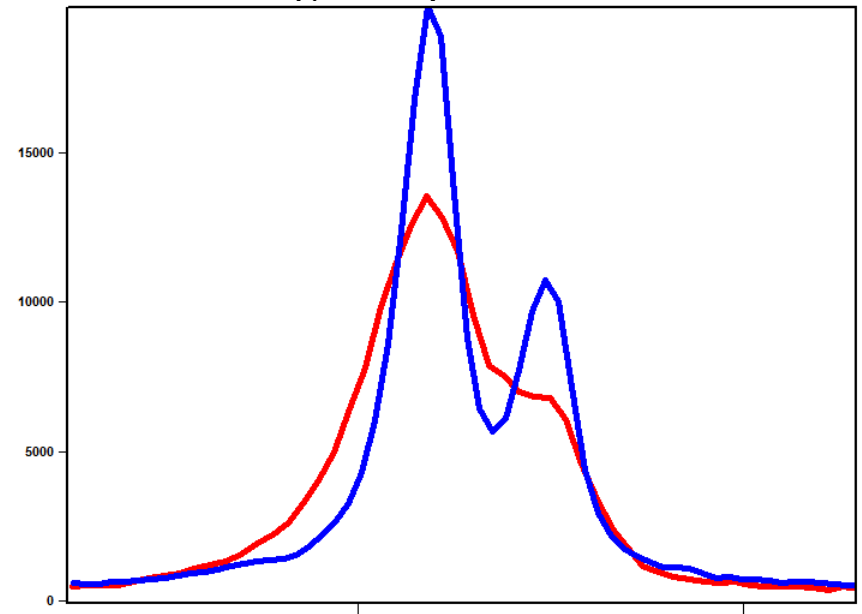
With proper calibration, you can calculate the amount of each phase present in the sample

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)**

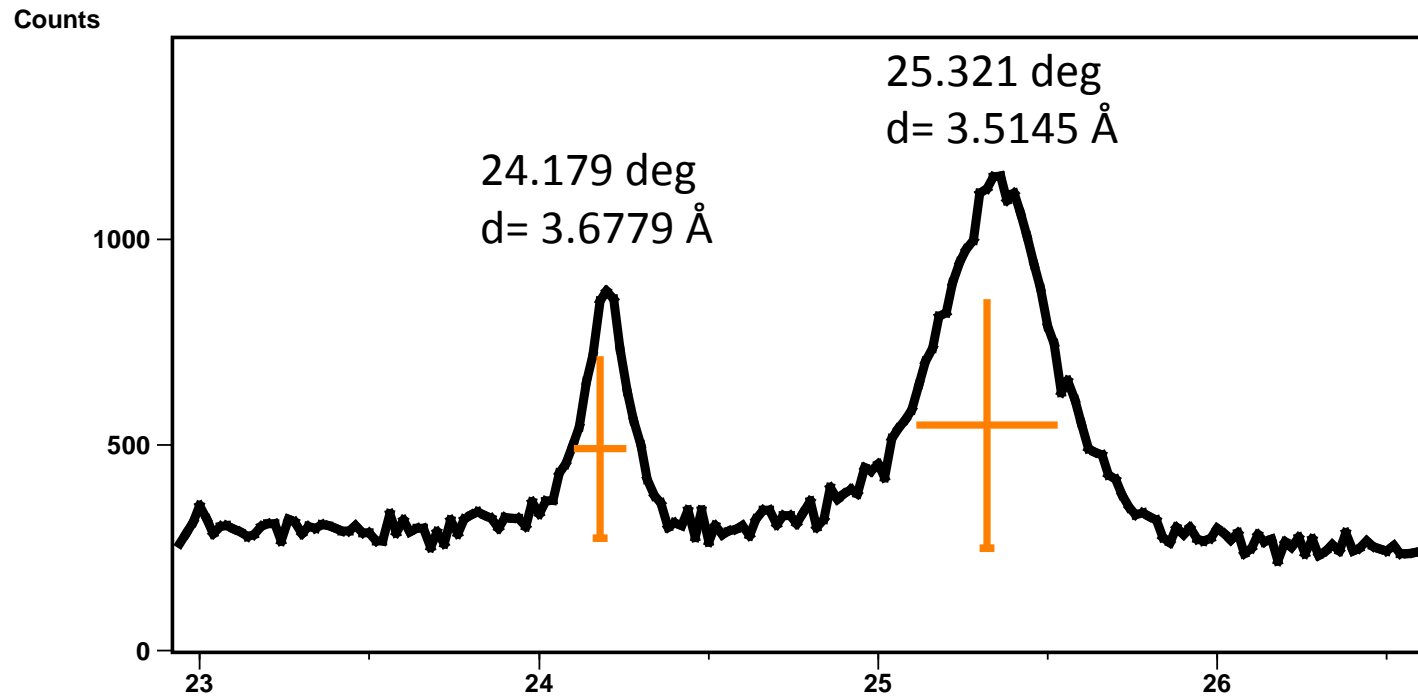


These patterns show the difference between the exact same sample run on two different instruments.

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

Quantitative Analysis of XRD Data

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

To calculate unit cell lattice parameters from the diffraction peak positions

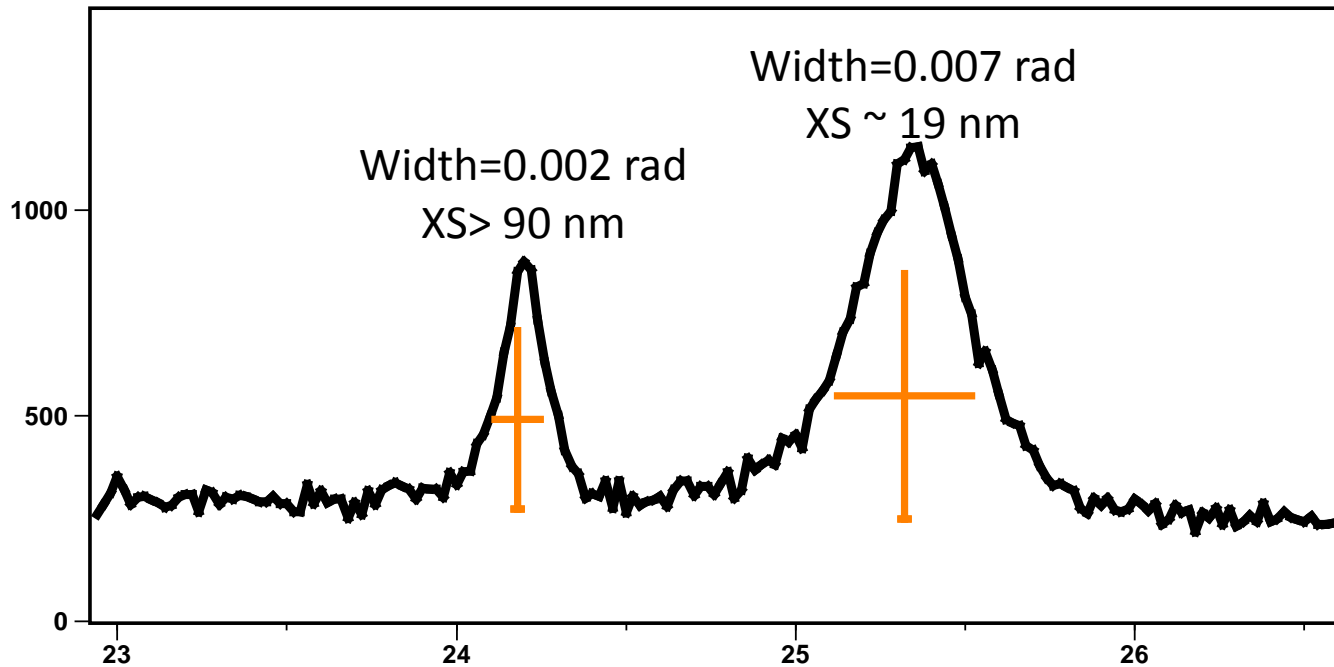
- Convert the observed peak positions, 2θ , into d_{hkl} values using Bragg's Law:

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

- 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

$$d_{hkl}^2 = h^2 a^2 + k^2 b^2 + l^2 c^2 + 2hka^* b^* \cos \gamma^* + 2hla^* c^* \cos \beta^* + 2klb^* c^* \cos \alpha^*$$

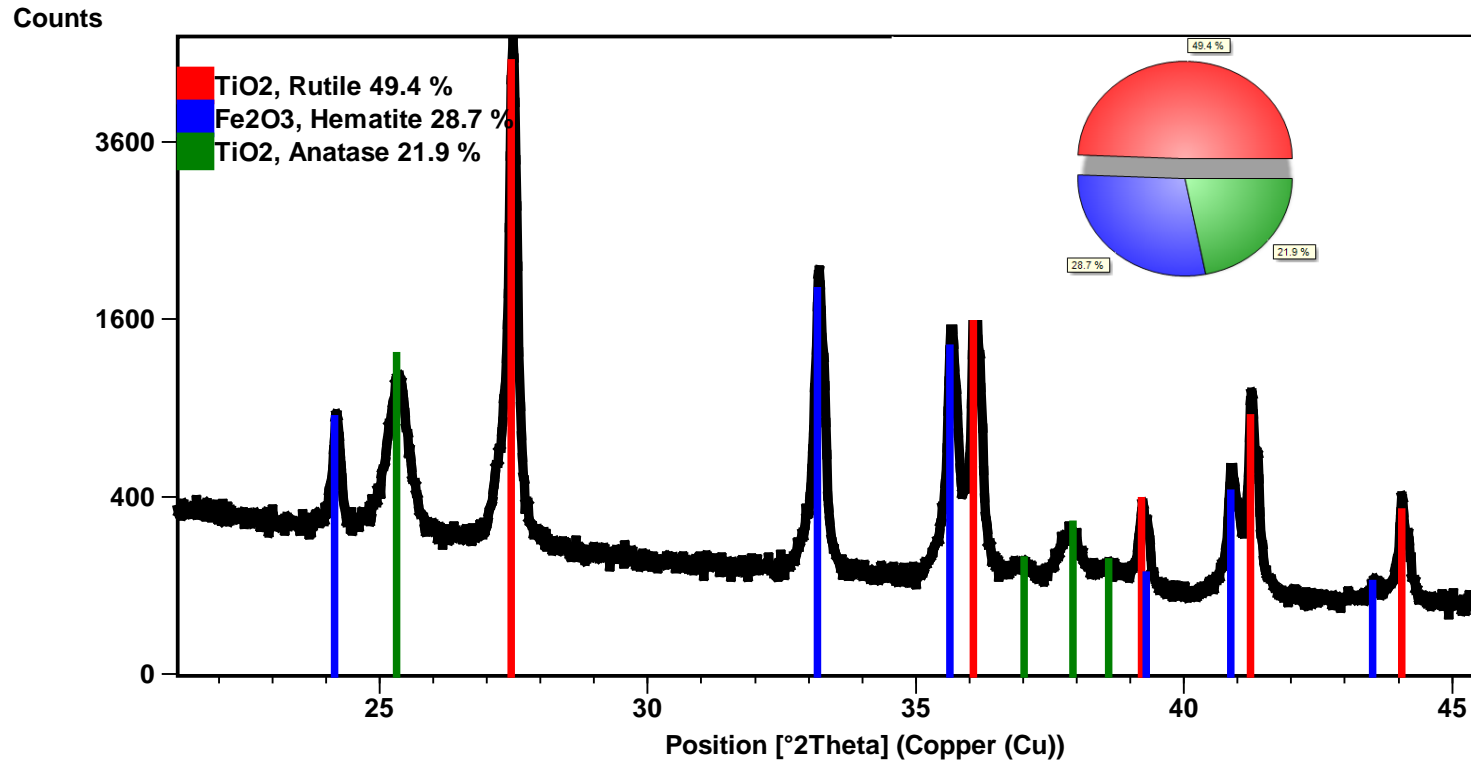
The diffraction peak width may contain microstructural information



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

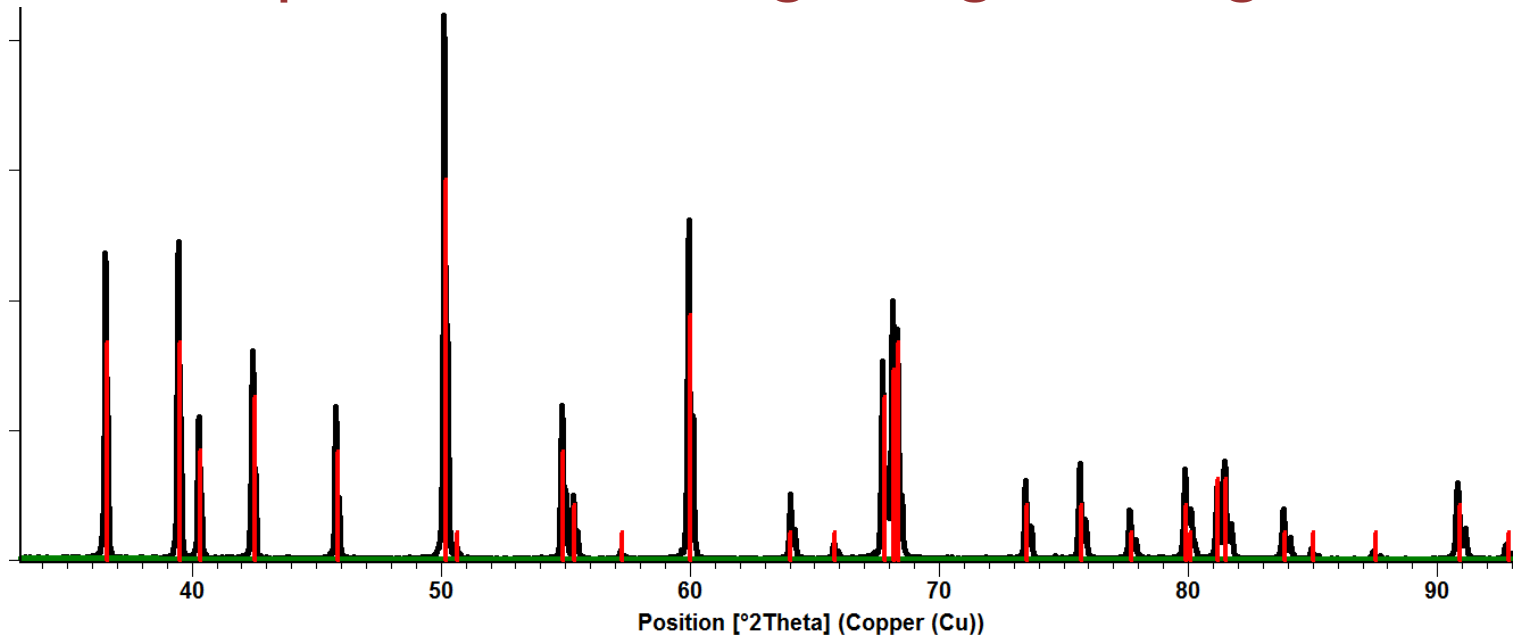
- Nanocrystallite size will produce peak broadening that can be quantified
 - Once the crystallite size is larger than a maximum limit, the peak broadening cannot be quantified. This creates an upper limit to the crystallite size that can be calculated.
 - The upper limit depends on the resolution of 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

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

All calculations are more accurate if you use more peaks over a longer angular range



- If you use one or two peaks, you must assume:
 - That there is no specimen displacement error when calculating lattice parameters
 - That there is no microstrain broadening when calculating crystallite size
- If you use many peaks over a long angular range (for example, 7+ peaks over a 60° 2theta range), you can:
 - Calculate and correct for specimen displacement when solving lattice parameters
 - Calculate and account for microstrain broadening when calculating crystallite size
 - Improve precision by one or two orders of magnitude

There are different ways to extract peak information for quantitative analysis

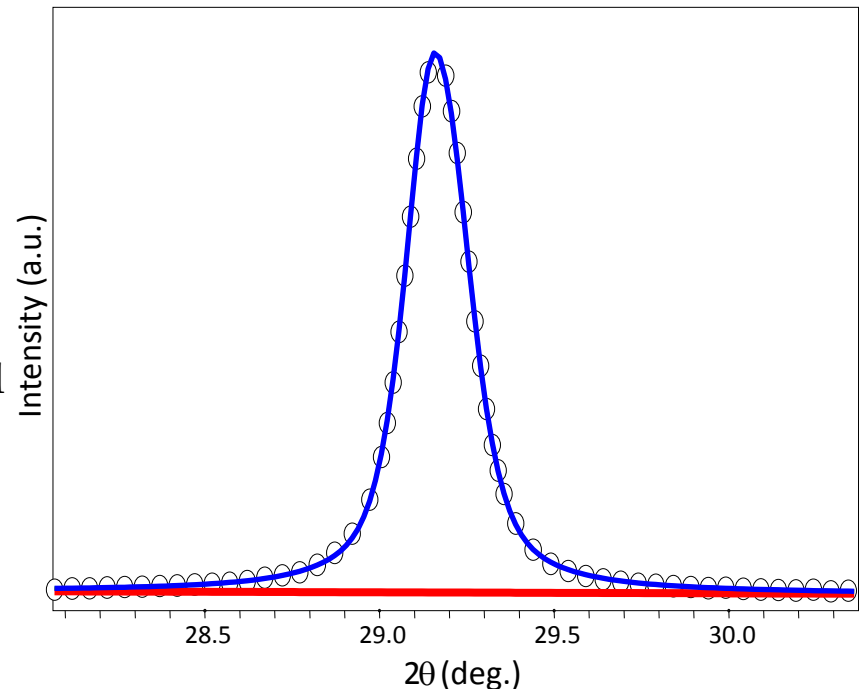
- Numerical methods reduce the diffraction data to a list of discrete diffraction peaks
 - The peak list records the position, intensity, width and shape of each diffraction peak
 - Calculations must be executed based on the peak list to produce information about the sample
- Full pattern fitting methods 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

A peak list for empirical analysis can be generated in different ways

- The diffraction data are reduced to a list of diffraction peaks
- Peak search
 - Analysis of the second derivative of diffraction data is used to identify likely diffraction peaks
 - Peak information is extracted by fitting a parabola around a minimum in the second derivative
 - *This method is fast but the peak information lacks precision*
- Profile fitting
 - Each diffraction peak is fit independently with an equation
 - The sum of the profile fits recreates the experimental data
 - Peak information is extracted from the profile fit equation
 - *This method provides the most precise peak information*

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



Diffraction peak lists are best reported using d_{hkl} and relative intensity rather than 2θ and absolute intensity.

- The peak position as 2θ 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 2θ 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

Full pattern fitting methods use different models to produce a calculated pattern

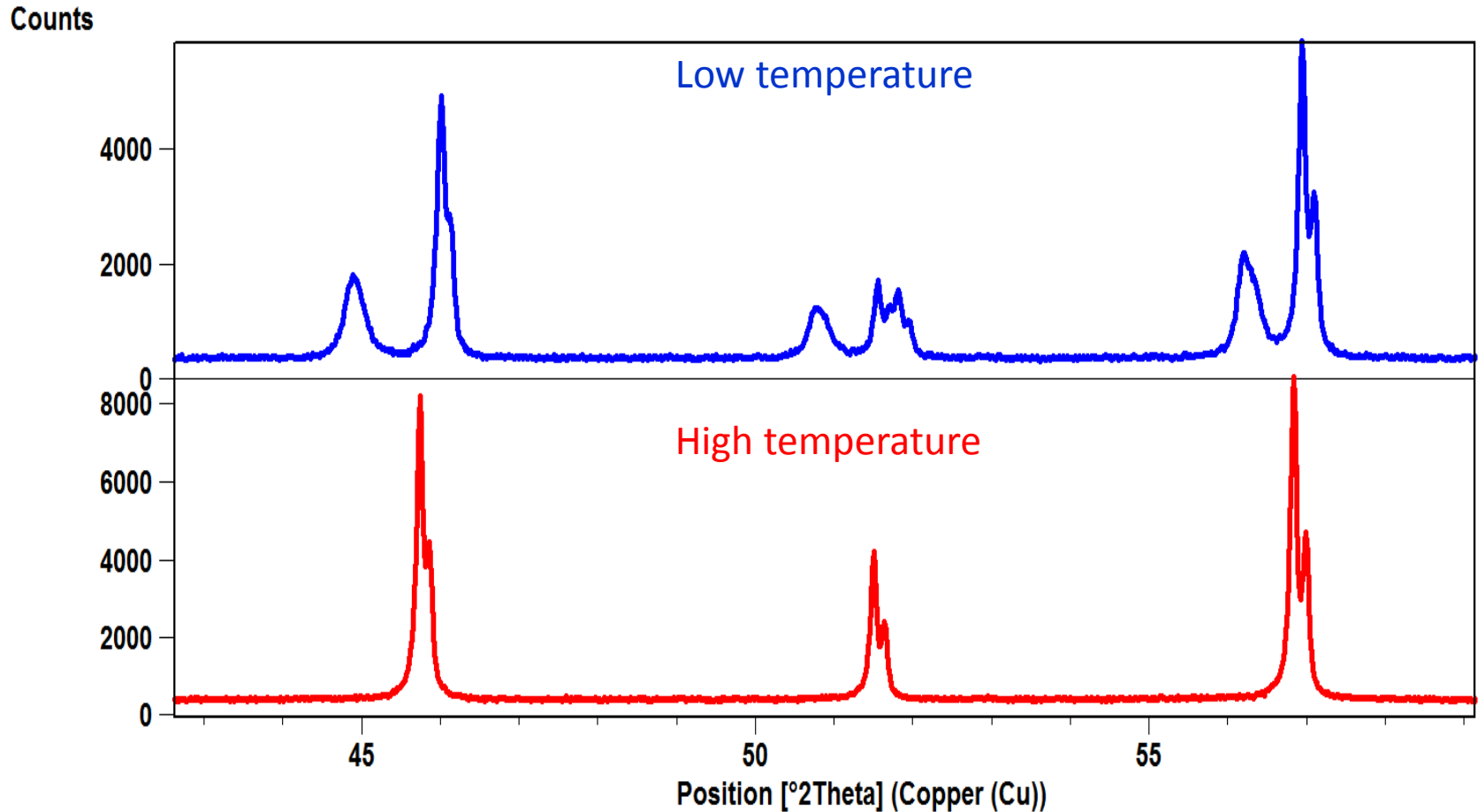
- The Rietveld method uses fundamental calculations from crystal structure models to produce the calculated diffraction pattern
 - Analysis produces a refined crystal structure model for all phases in the sample
 - Peak positions and intensities are constrained by the crystal structure model
 - Crystallite size, microstrain, and preferred orientation can be extracted from empirical models included in the refinement
- Le-Bail and Pawley fitting methods use unit cell models combined with empirical fitting of peak intensities
 - Analysis produces a refined unit cell model but does not immediately yield information about parameters related to peak intensities

Other analytical methods

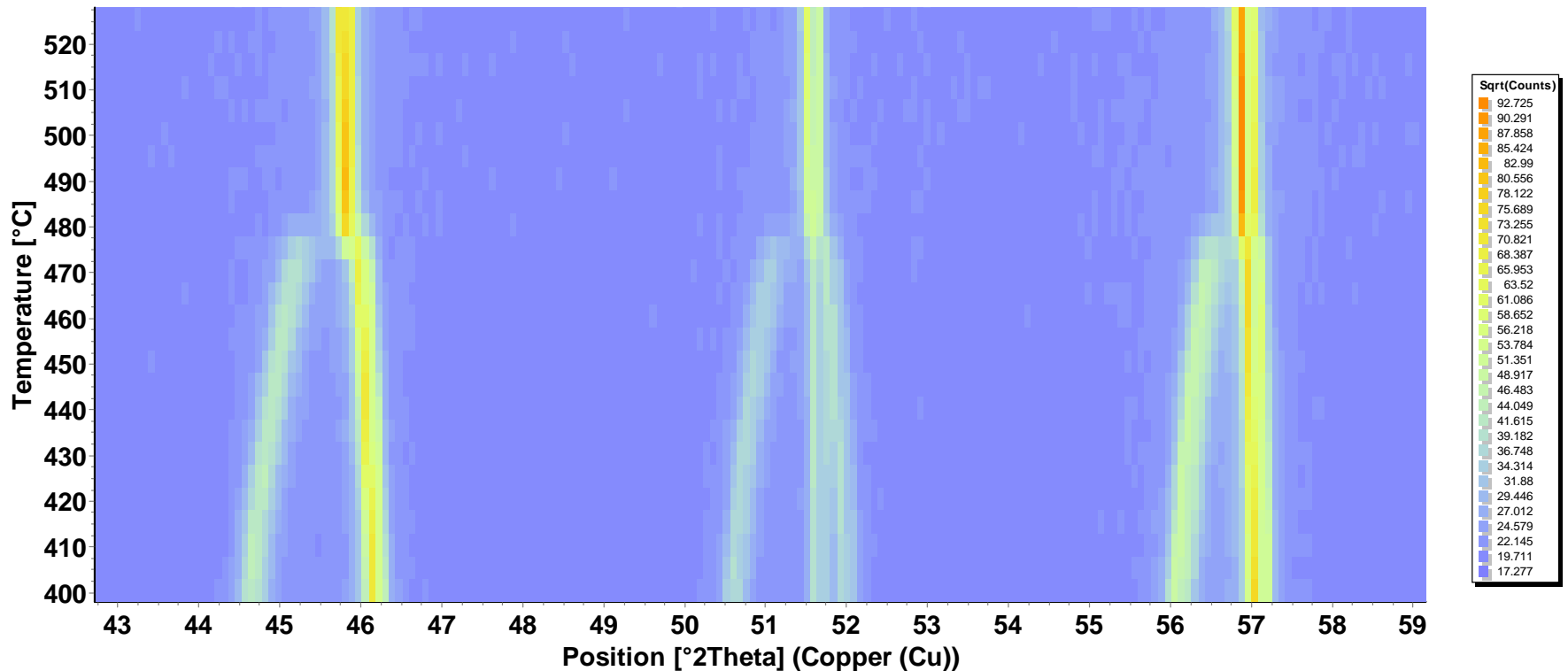
- Total scattering methods (whole pattern fitting) attempts to model the entire diffraction pattern from first principal calculations
 - Calculations include
 - Bragg diffraction peaks,
 - diffuse scatter contributions to background,
 - peak shapes based on diffractometer optics,
 - peak shapes based on crystallite size, shape, defects, and microstrain
- Pair distribution functional analysis uses Fourier analysis to produce an atomic pair density map
 - Can yield atomic structure information about non-crystalline, semi-crystalline, and highly disordered materials

Examples of Data Analysis

PbTiO₃ transforms from tetragonal to cubic crystal systems at elevated temperatures



In situ XRD identifies the PbTiO_3 transformation from tetragonal to cubic between 475 and 480 °C



XRD data can be used to calculate the lattice parameters and solve the crystal structure at each temperature.

In situ X-Ray Studies of Ti-doped Sodium Alanate

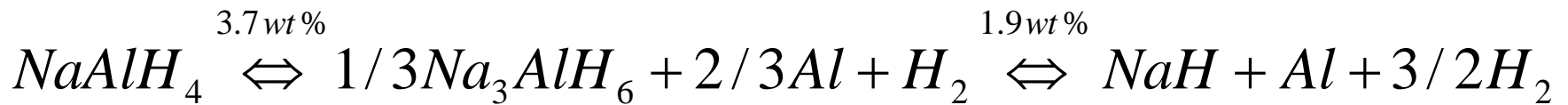
Scott A Speakman, MIT

Joachim H Schneibel, Dewey S Easton, ORNL

Tabbatha A Dobbins, Louisiana Tech Univeristy

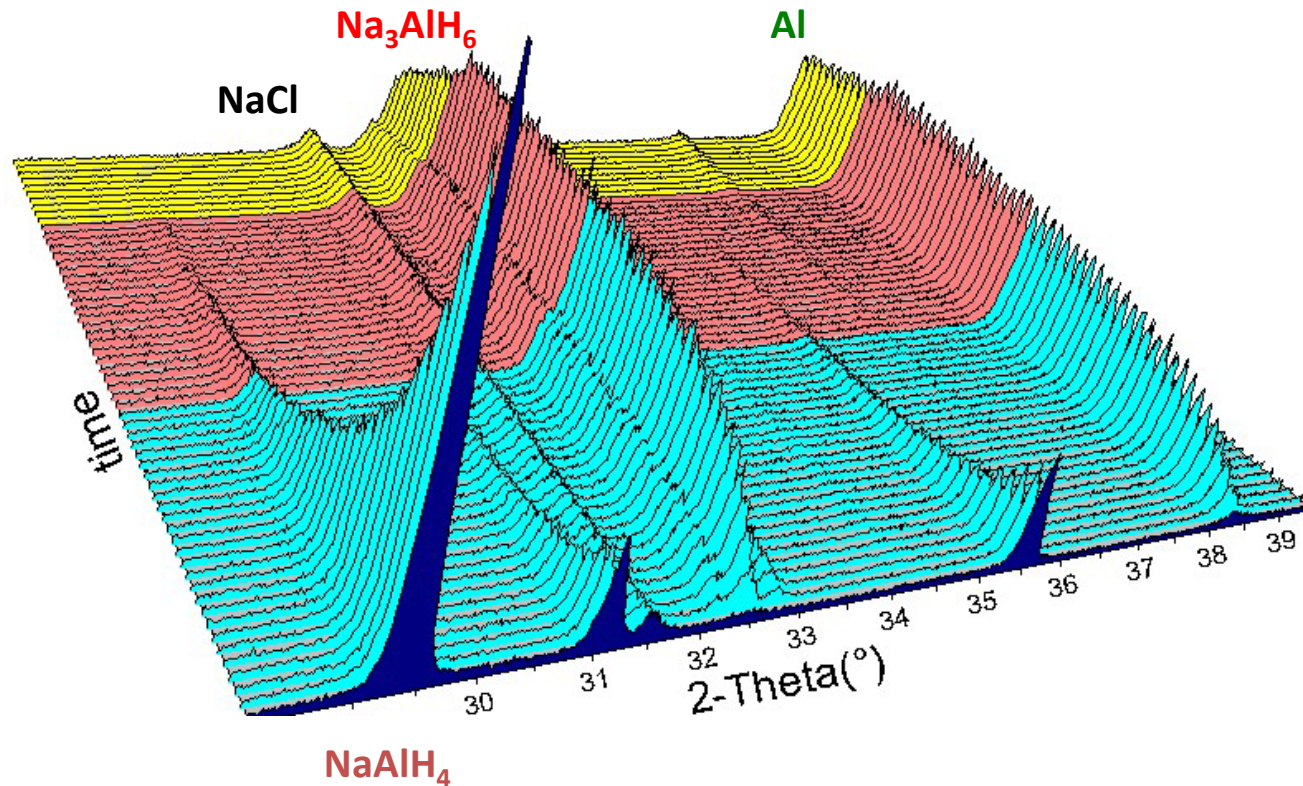
Roland Tittsworth, CAMD

Sodium alanate was one of the first complex hydrides with reversible desorption/resorption of H₂



- Sodium alanate (NaAlH₄) is doped with 2 wt% TiCl₃
 - Enhances desorption kinetics
 - Produces reversible absorption
- NaAlH₄ cannot meet requirements for a hydrogen storage material
 - Acceptable energy density
 - Poor specific energy (5.6 wt% H₂ not including system weight)
 - Has some problems with maintaining reversibility after repeated cycling

XRD data were collected quickly to quantify the change in phase composition with time

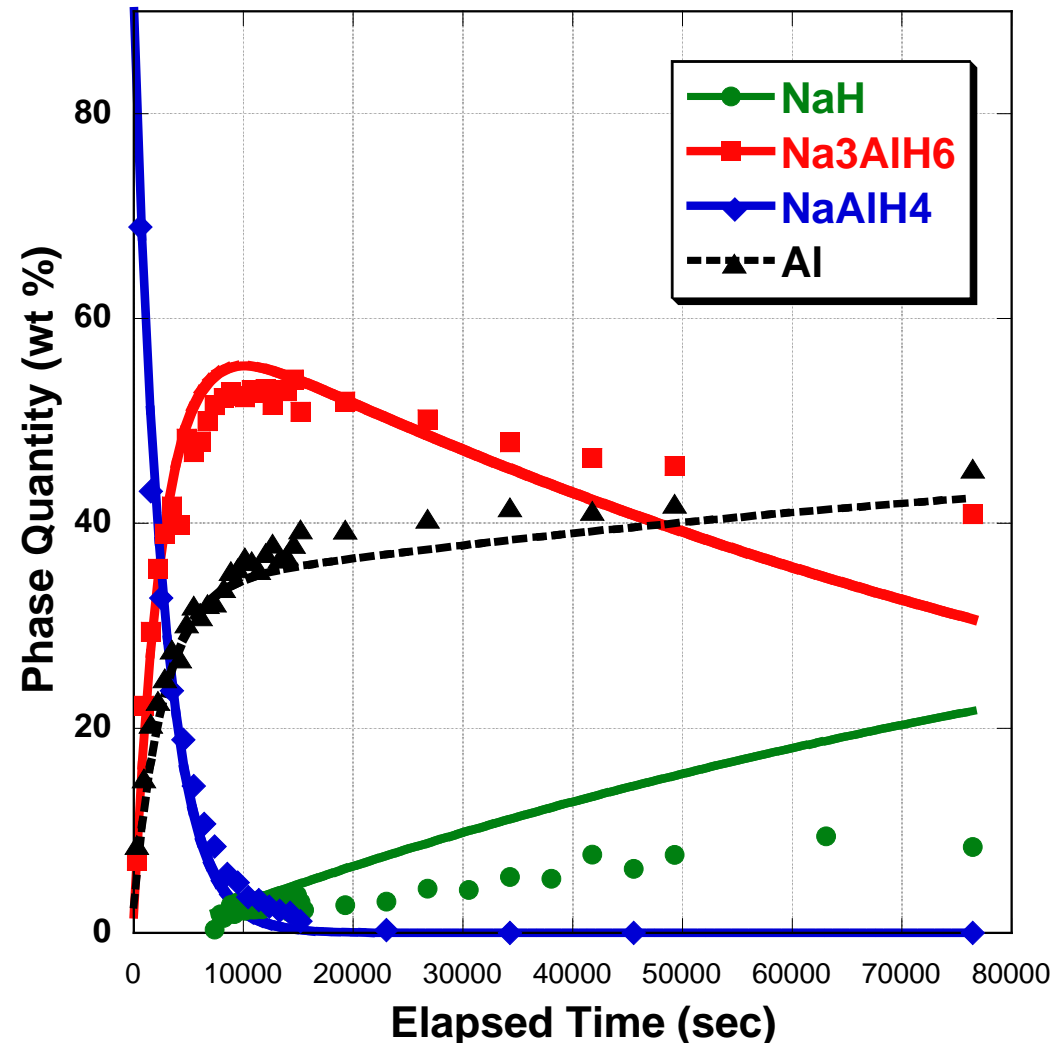


- Data over a $60^\circ 2\theta$ range collected in 5 min increments
- Over 100 patterns per experiment
- Phase quantities were calculated using batched Rietveld analysis

The change in phase fractions with time were used to calculate the reaction rate constants

- from PCI
 - $k_1 = 44 \times 10^{-4} \text{ s}^{-1}$
 - $k_2 = 21 \times 10^{-5} \text{ s}^{-1}$

	k_1 (10^{-4} s^{-1})	k_2 (10^{-5} s^{-1})
XRD		
Avg.	3.8	0.94
NaAlH_4	3.7	-
Na_3AlH_6	3.2	0.76
Al	4.4	1.6
NaH	-	0.41



Coarsening of CeO₂ nanoparticles

Brian Neltner, Brian Peddie, Alex Xu, William Doenlen, Keith Durand, Dong Soo Yun, Scott Speakman, Andrew Peterson, Angela Belcher, “Production of Hydrogen Using Nanocrystalline Protein-Templated Catalysts on M13 Phage,” ACS Nano 4 [6] 2010.

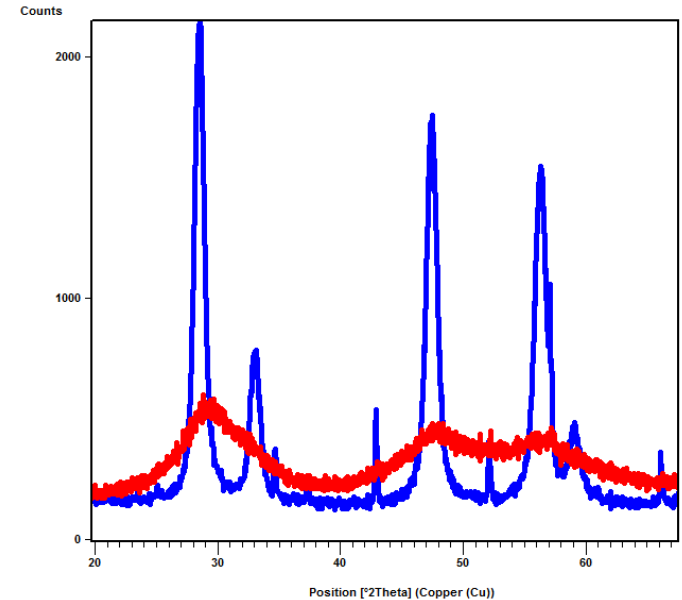
Brian Neltner, Scott Speakman, Dong Soo Yun, Angela Belcher, “Time resolved nanocrystalline growth of cerium oxide and lanthanum-doped cerium oxide using X-Ray diffraction– unusually low nanocrystalline growth” *pending publication*

Ceria nanoparticles used as catalysts are limited by their tendency to coarsen at high temperatures

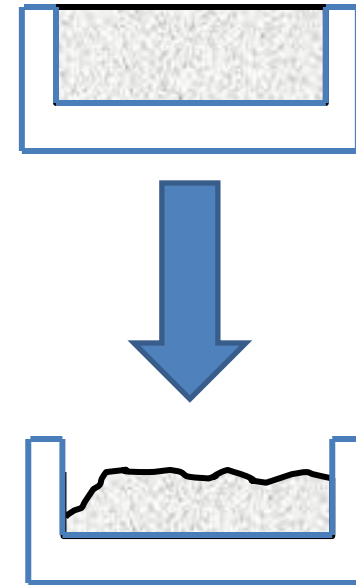
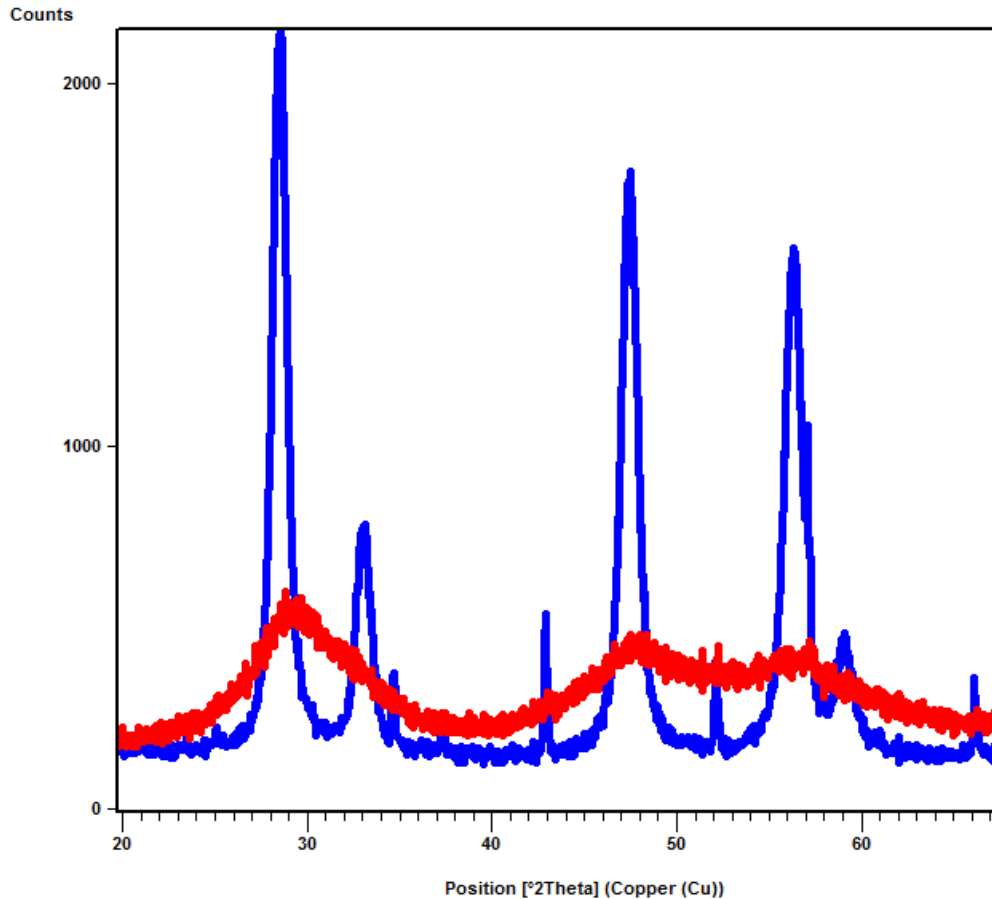
- Ceria is used as a catalyst for steam reforming of ethanol-water mixtures to produce H_2
 - Rh with Ni on CeO_2 is used to enhance the conversion at low temperatures
- By using very small nanocrystalline CeO_2 , 100% conversion could be achieved at 300 °C.
- Biological templating on M13 bacteriophage was demonstrated to improve the resistance of the catalyst to deactivation.
- This is one example of how Prof Belcher is using biological templating and surface treatments to improve the stability of nanocrystalline catalysts
- *The examples shown within actual combine a few different studies, including some using a different stabilization technique. Some data have been 'enhanced' for teaching purposes- see cited publications for authentic findings.*

Ex-situ XRD can be used to determine what samples will show the most and least amount of grain growth

- When screening techniques to inhibit grain growth of nanocrystalline catalysts:
 - Take 20 prospective samples plus a few control samples
 - Heat in a furnace at the target temperature for a few hours
 - Use XRD data collected at normal (standard temperature) conditions to determine how much the grain size changed for each sample
- In-situ XRD is most useful to determine the kinetics and mechanism of grain growth by using time-resolved data collection at various different temperatures



First HTXRD experiments revealed that nanoparticles tend to sinter, creating large displacement errors



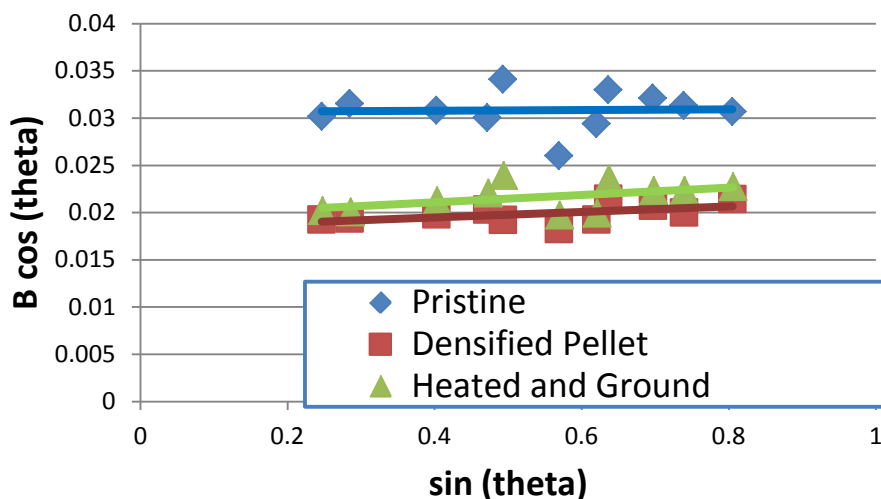
Nanopowder was pressed into a pellet to provide a more dense starting piece that densified less



- Pellets pressed with excessive pressure had a tendency to warp during data collection
- Lightly pressed pellets still densified but created less displacement error
- Analysis of densified pellets determined that the displacement error did not affect crystallite size analysis

Careful analysis of a sample before and after was used to optimize data collection

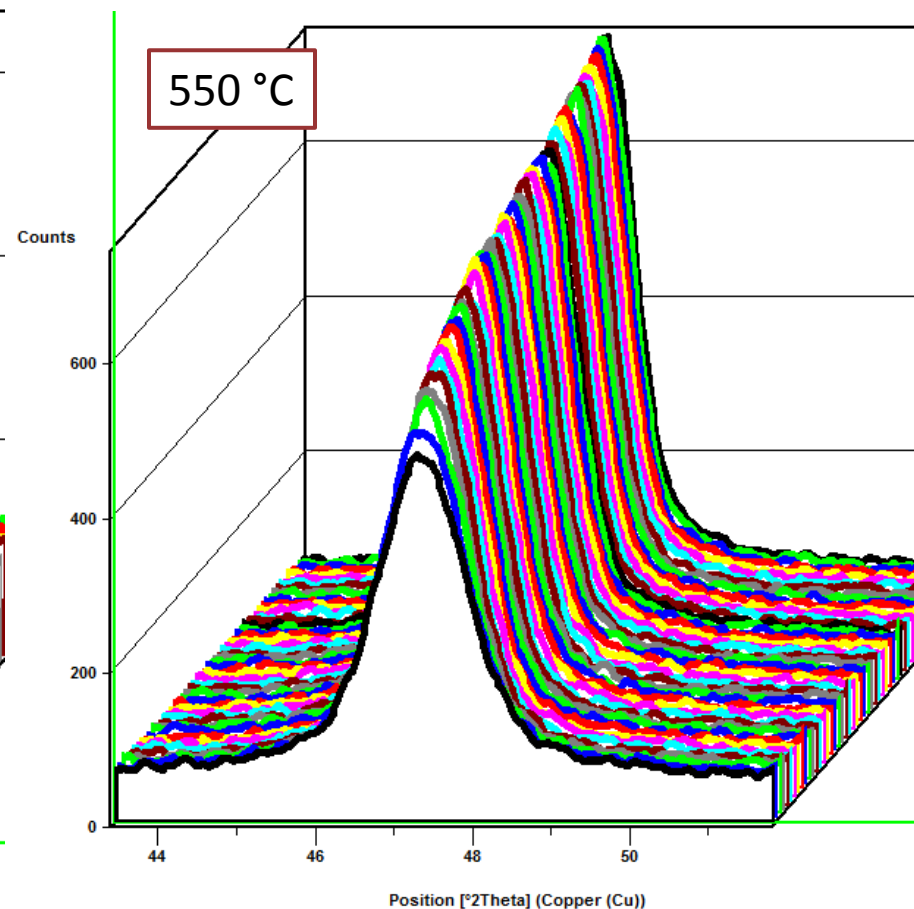
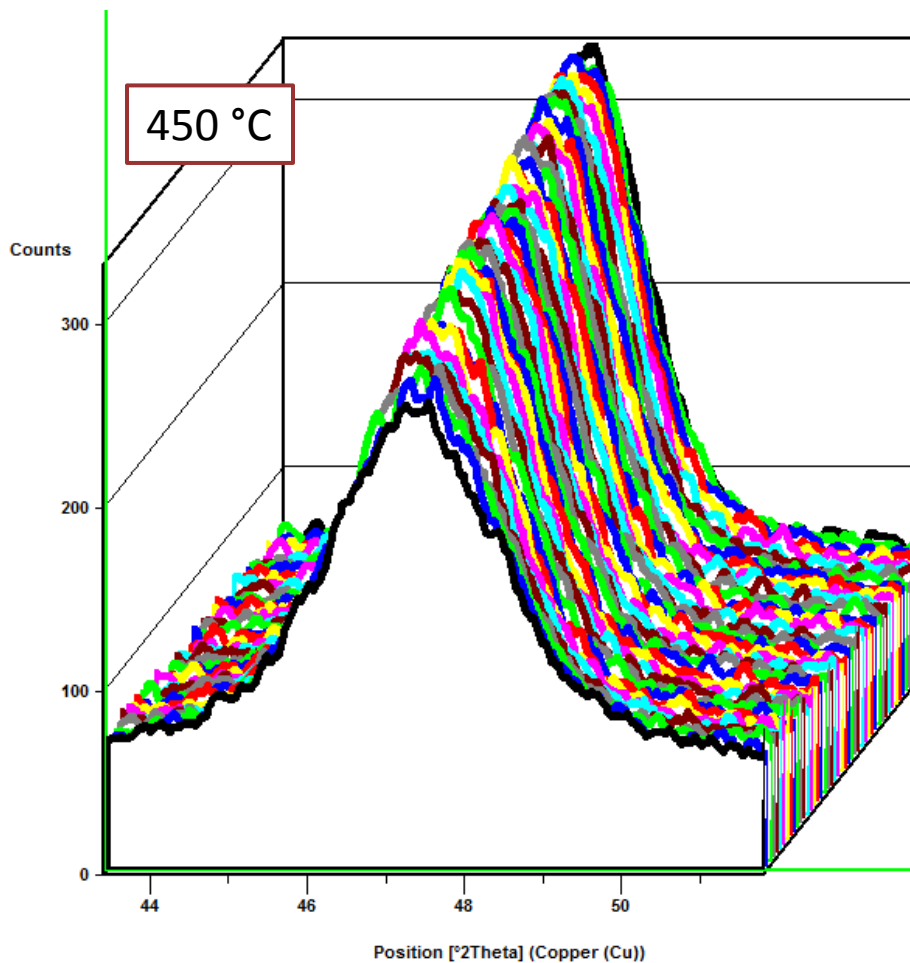
- Williamson-Hall analysis of a sample before and after heat treatment indicated that there was no microstrain
- After heat treatment, size analysis was done on the densified pellet with specimen displacement error. The same sample was ground and prepared as an 'ideal' powder sample.
 - Both data sets produced the same crystallite size



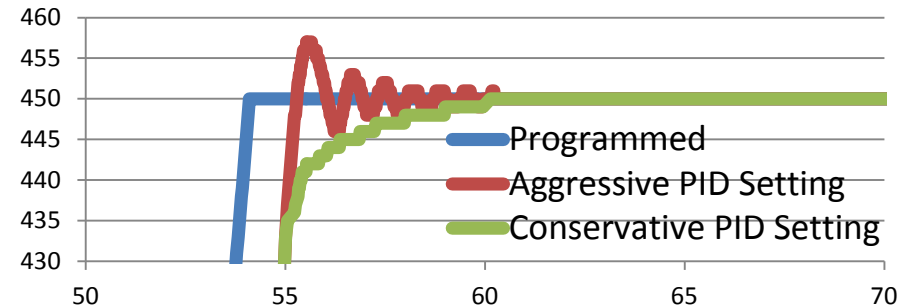
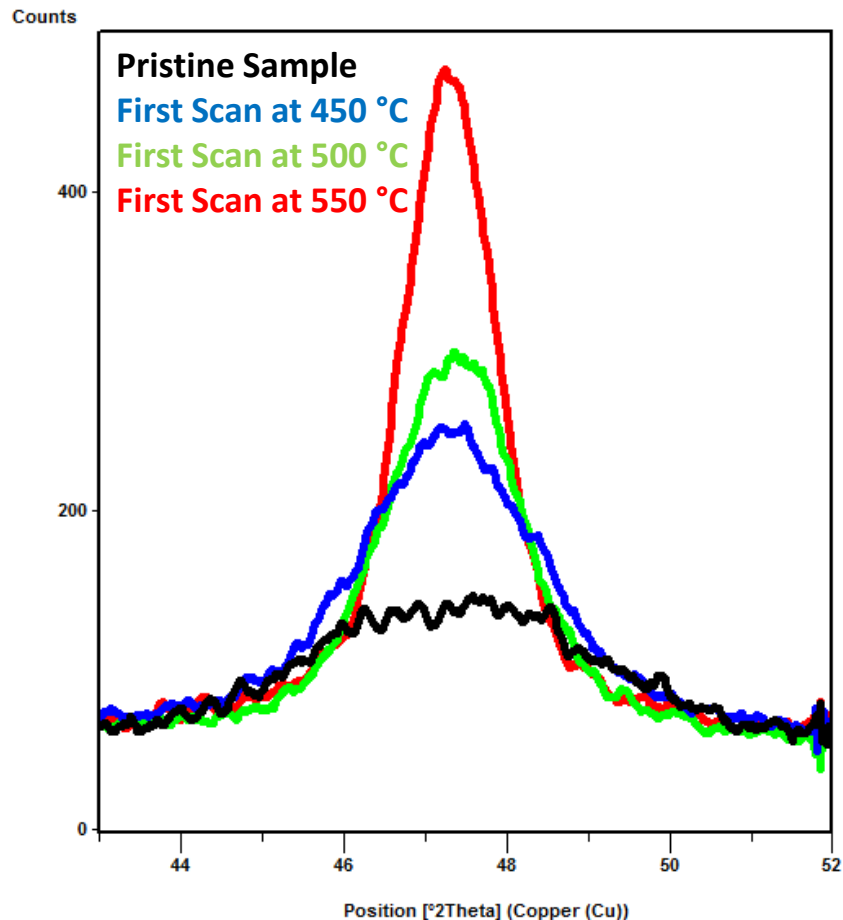
	Williamson-Hall	(220) Peak
Pristine	50	50
Densified Pellet	79	78
Heated then Ground	84	73

This optimization and validation allowed us to reduce scan times to 1 minute.

Scans were collected in 1 minute intervals at 450, 500, and 550 °C for ~2 hours

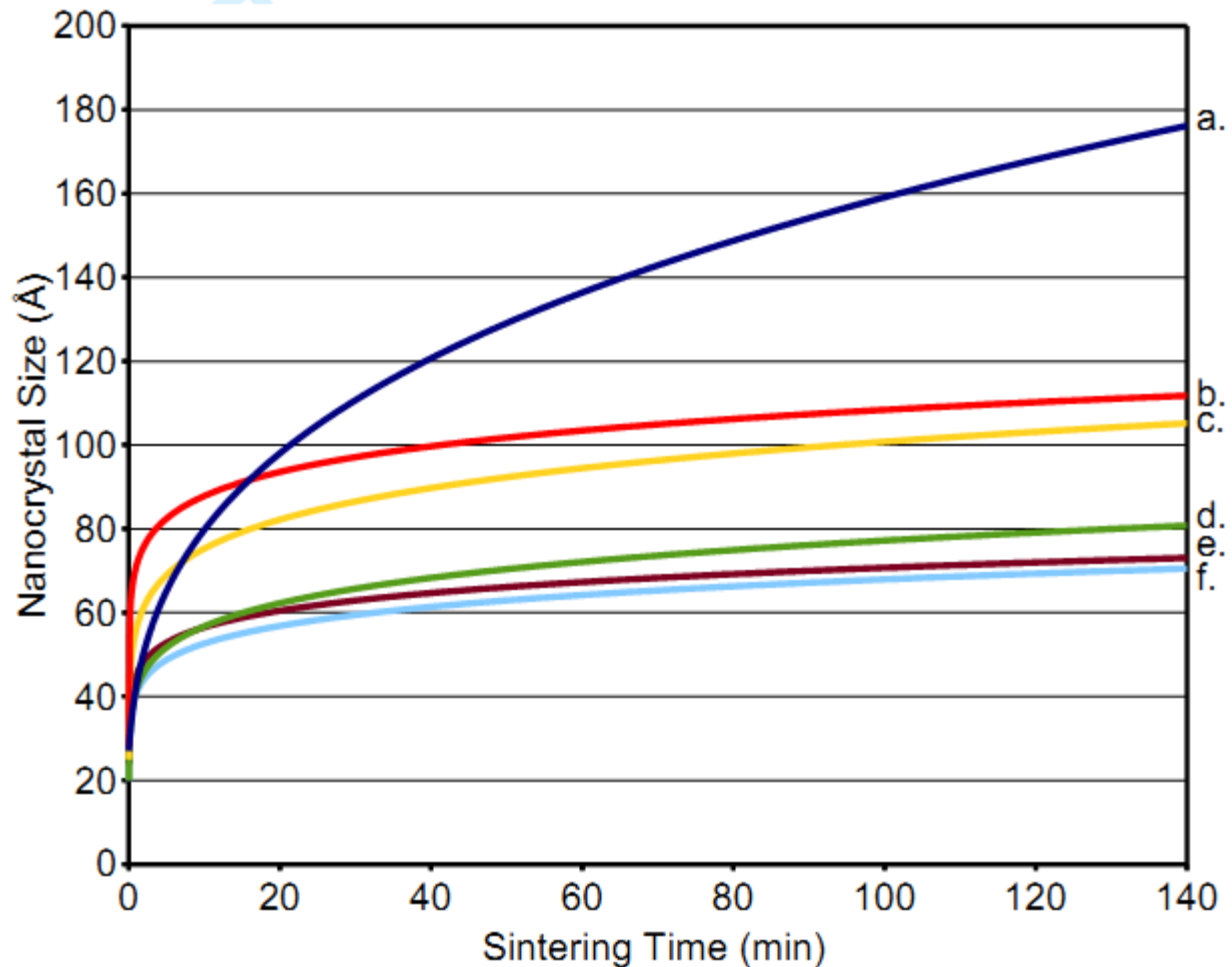


The first scan at different temperatures was different because of grain growth that occurred during heating

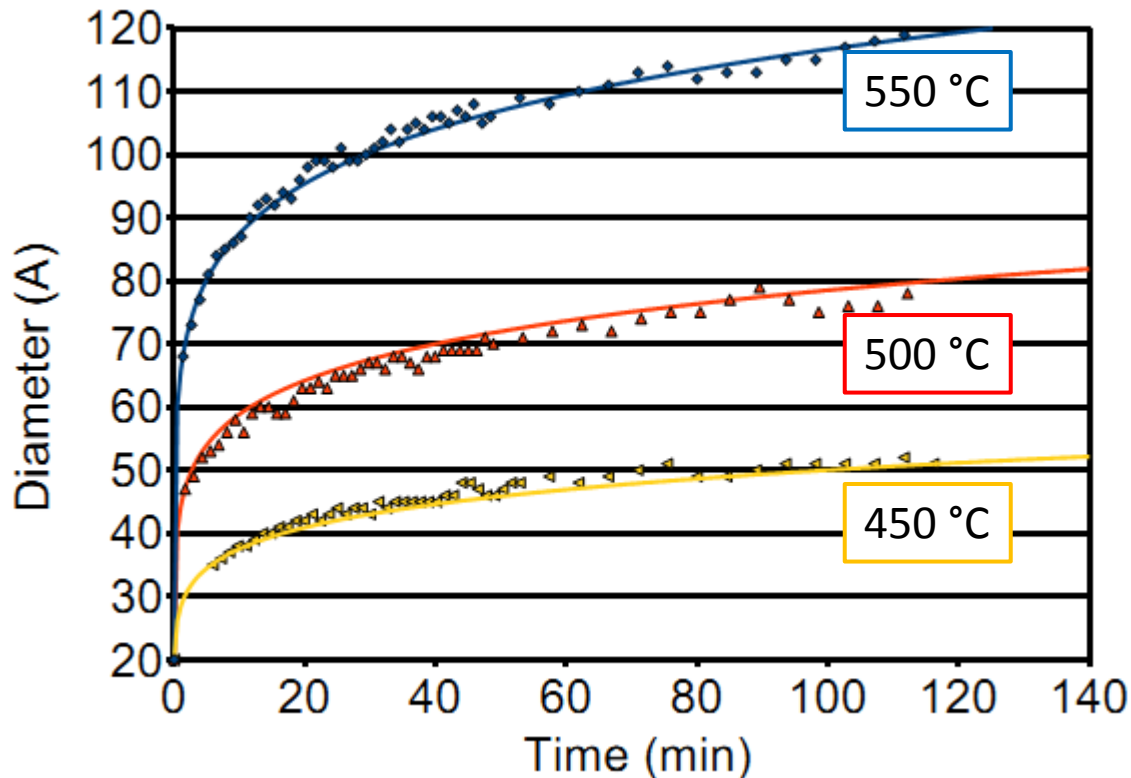


- The furnace ramp rate slows as it approaches the setpoint.
- We changed the software configuration so that the first scan began when the temperature was within 10 °C of the setpoint
- Since we know the starting size and the rate of change at temperature, the grain growth during heating is only a small source of error.

In-situ XRD was used to evaluate the effectiveness of different ways to hinder crystallite growth



Observed crystal growth at different temperatures were used to model the kinetics



- The rate of crystal growth was calculated for each temperature using a power-law equation:
- $D(t)^m - D(0)^m = k \cdot t$
- The rate constants at different temperatures were used to determine activation energy and prefactor in an Arrhenius model:
- $k = C \cdot \exp\left(\frac{-Q}{k_B T}\right)$

This analysis allowed the identification of the most efficient ways to passivate the Ceria surface and hinder grain growth

	Untreated CeO ₂	Most effective treatment
Growth exponent	3.3	11
Final crystallite size	18 nm	7 nm

- The starting crystallite size was 2 nm
 - In 2+ hours at 550 C, the treated sample grew much less than the untreated sample.
- A typical growth exponent is 3
- Results of in-situ XRD, combined with XPS and TEM, indicated that oxygen vacancies created in the surface of nanoparticles was one mechanism that reduced crystallite growth at high temperatures

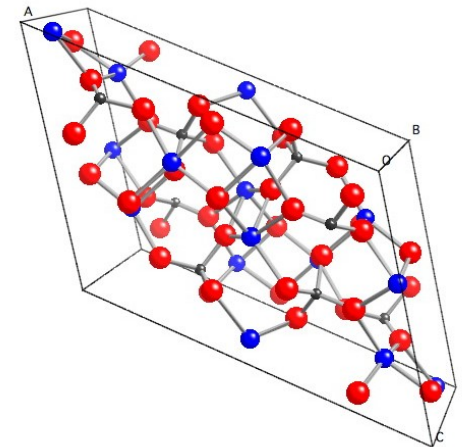
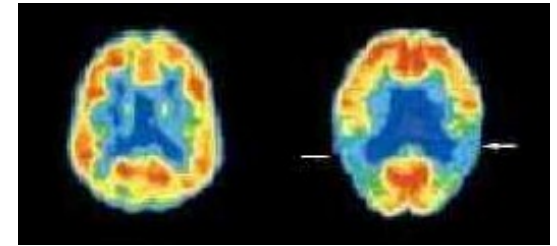
Scintillator Materials for Medical Imaging: Thermal expansion and stability of Ce:LSO

Merry A Spurrier, Chuck L Melcher
CTI Molecular Imaging Inc.

Camden R Hubbard, Larry F Allard,
Wally D Porter
Oak Ridge National Laboratory

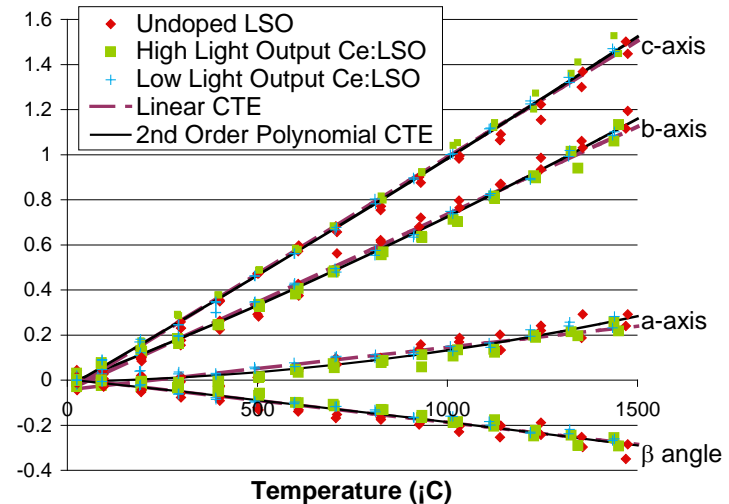
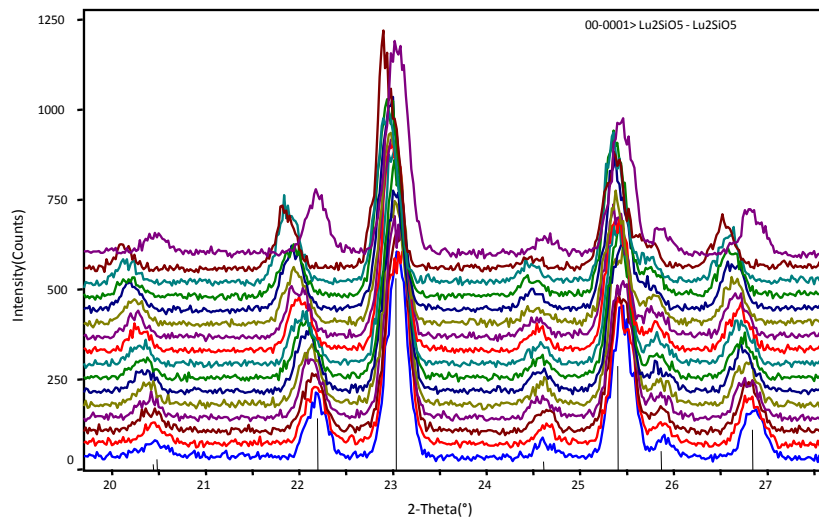
Ce-doped Lu_2SiO_5 (Ce:LSO) is the current state-of-the-art scintillator crystal in PET scanners

- Ce:LSO is a good scintillator crystal
 - good detection efficiency, high light output, short decay time, high density and atomic number
 - These lead to faster measurements and greater resolution.
- Boules of LSO single crystals are grown using the Czochralski method.
 - N_2 gas environment to prevent oxidation of Ir crucible.
- Some as-grown crystals have low light output.
 - This can often be remedied with an annealing procedure.
- Some crystals crack as they cool from the melt.



The thermal expansion of LSO is highly anisotropic.

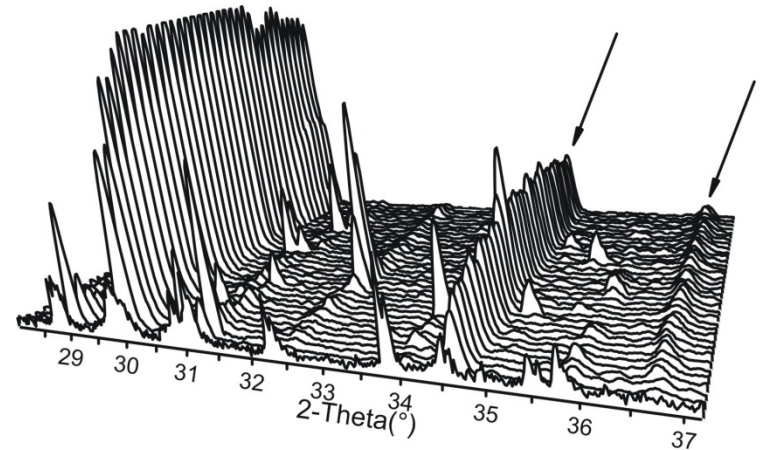
- In-situ XRD and push-rod dilatometry were used to measure the thermal expansion of several different LSO samples.



- Thermal expansion along the b and c axes are 4 to 5 times greater than that along the a axis.
- The thermal expansion of each axis is well fit by a 2nd order polynomial.
- No difference in crystal structure or CTE of high and low light output samples.

In low oxygen environments, Si volatilizes out of Lu_2SiO_5 .

- Lu_2SiO_5 decomposes into Lu_2O_3 in oxygen-poor atmospheres.
- In a vacuum or gettered Ar environment (<1 ppm O_2), Lu_2SiO_5 decomposes at a temperature between 1350 and 1420 °C.
 - As Lu_2O_3 forms, no evidence of Si or SiO_2 is observed
 - LSO is stable in air up to these temperatures
- At 1500 °C in vacuum, decomposition begins after 30 minutes.
 - The formation of Lu_2O_3 slows significantly after 9 hours.
- An oxygen level between 100 and 150 ppm O_2 stabilizes LSO up to 1760 °C.
 - Begins decomposing slowly between 1760 and 1850 °C.



On-going work

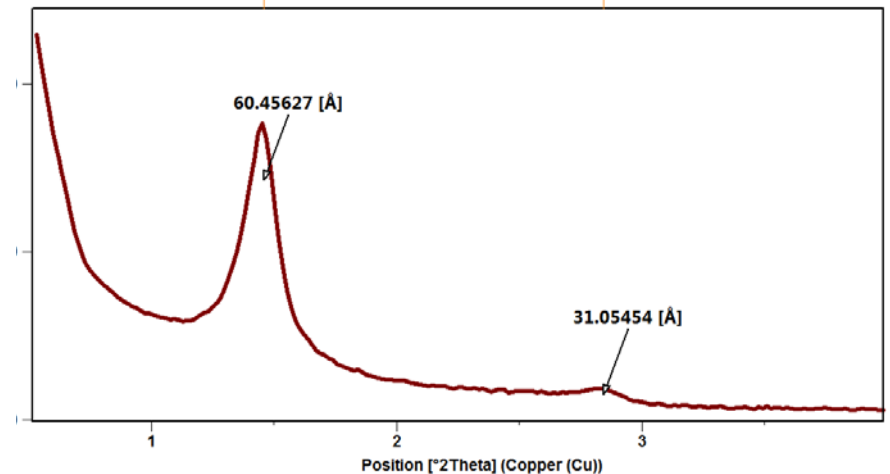
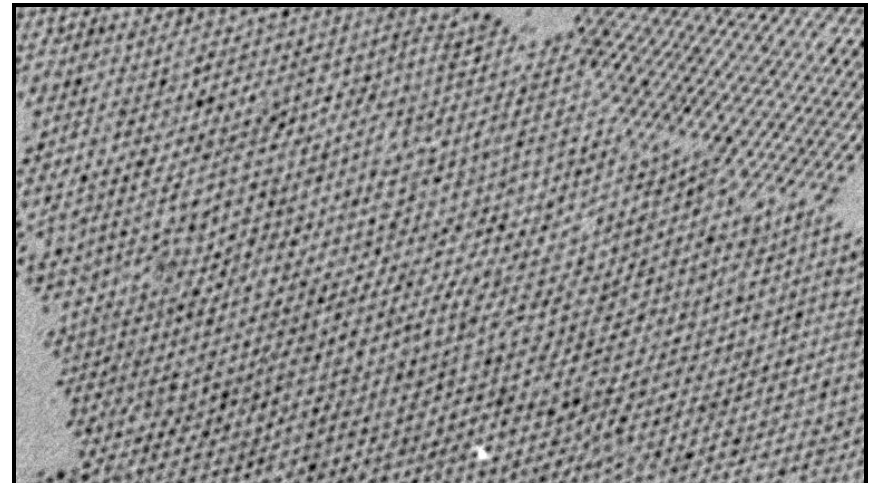
- Investigating phase transformations, or lack thereof, in $(\text{Lu}_{1-x}\text{Y}_x)_2\text{SiO}_5$
- Searching for light quenching impurities in LuAlO_3 crystals
- Explore the decomposition of LuAlO_3 into $\text{Lu}_2\text{Al}_4\text{O}_9$ during crystal growth
- Develop nanocrystalline scintillator particles in transparent ceramics

Thermal Stability of PbSe Quantum Dots

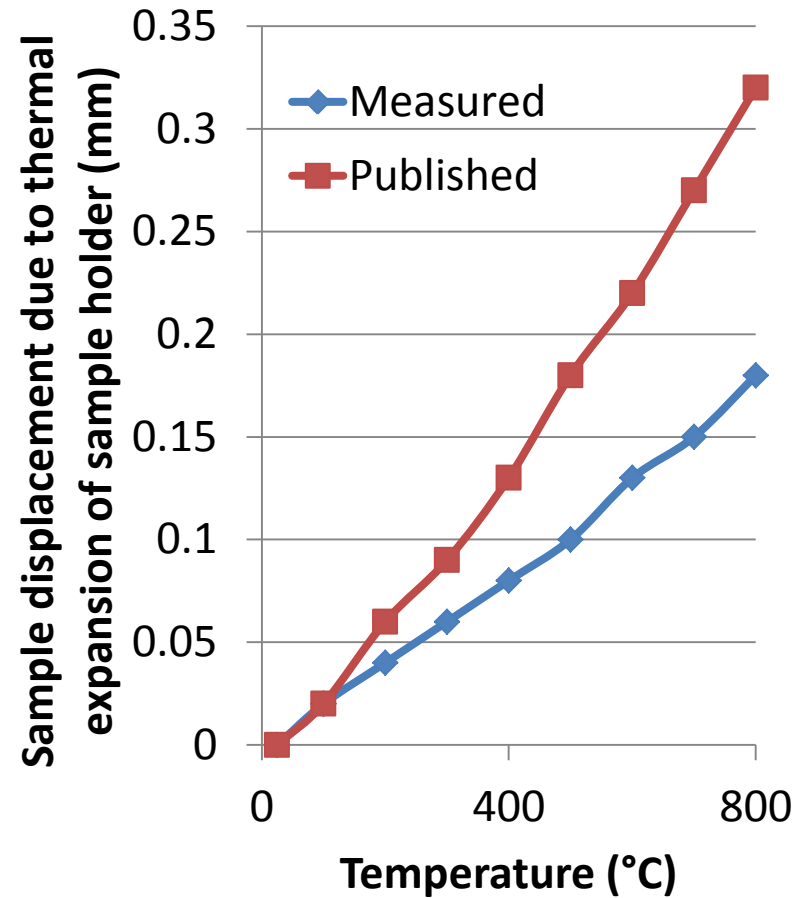
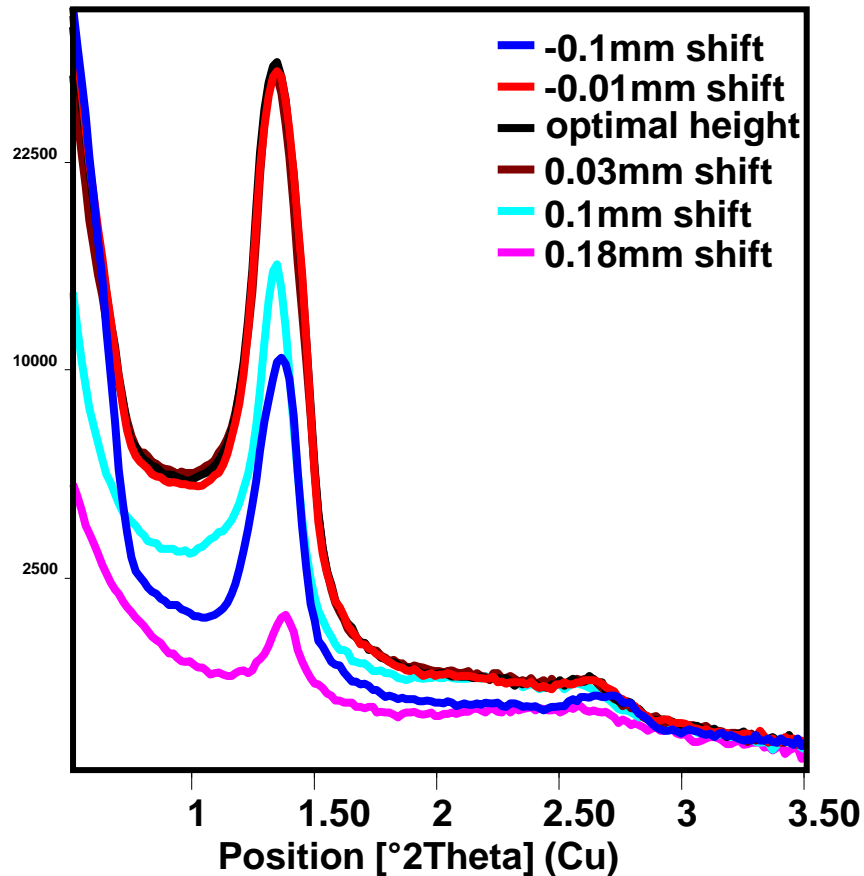
Tad Sudnick, Tamar Mentzel, Scott Speakman

HTXRD was used to evaluate the thermal stability of quantum dot nanostructures

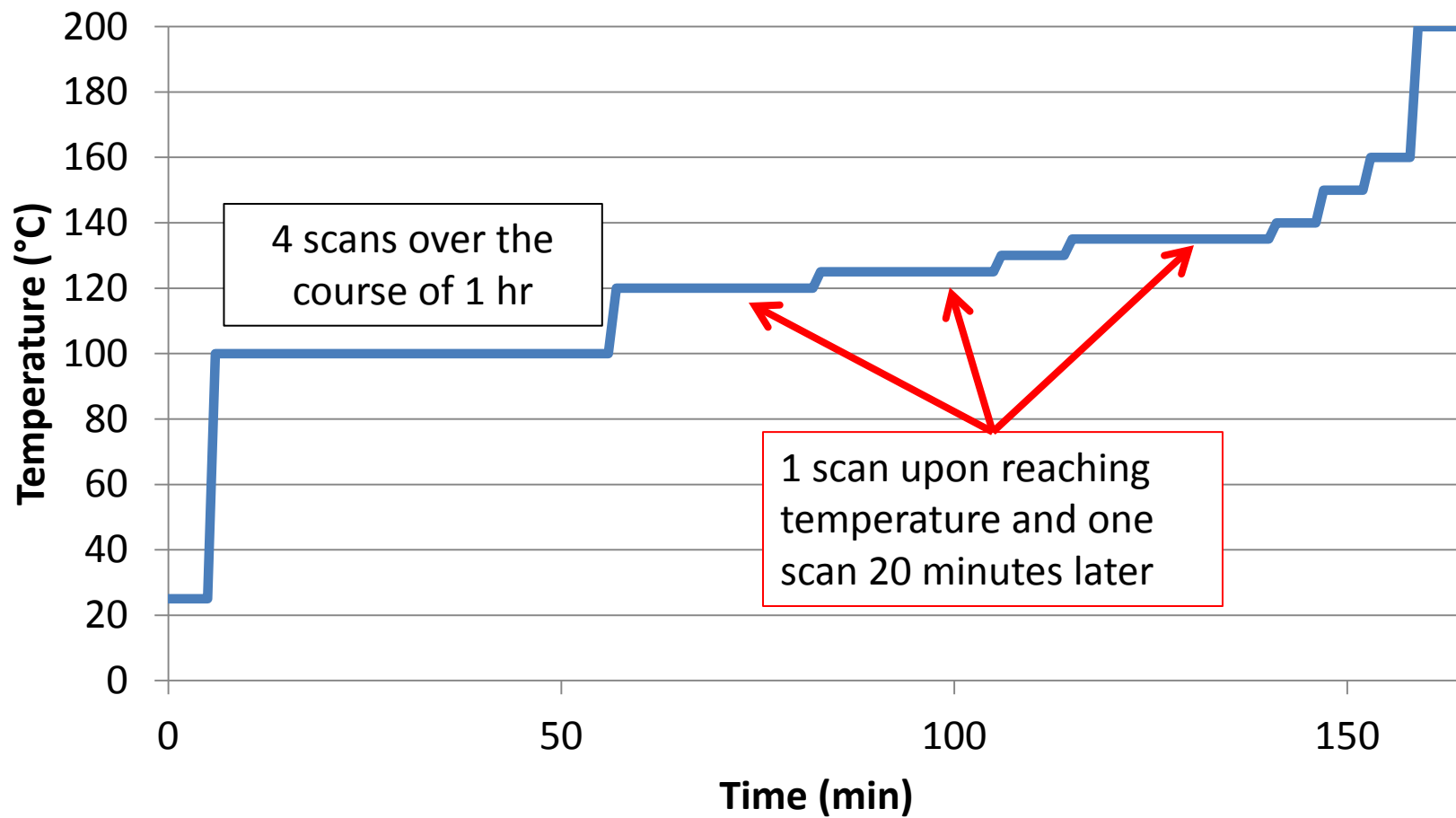
- Quantum dots were made from spherical nanoclusters of PbSe
- Ligands were used to help the quantum dots self-assemble into orderly close-packed hexagonal arrays
- The nanostructured film of quantum dots is a photoconductor with potential use as a detector or other electro-optic device
- The ordered nanostructure produces a diffraction pattern



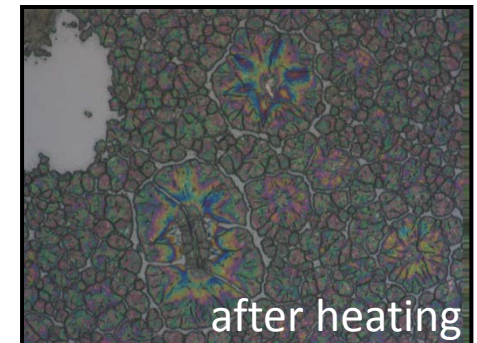
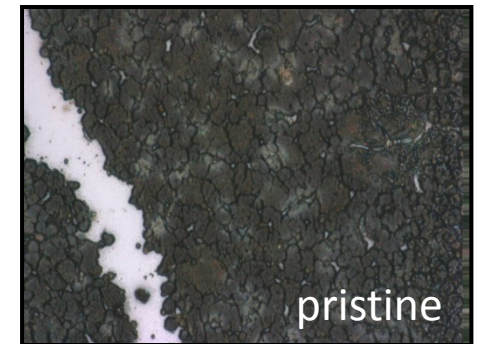
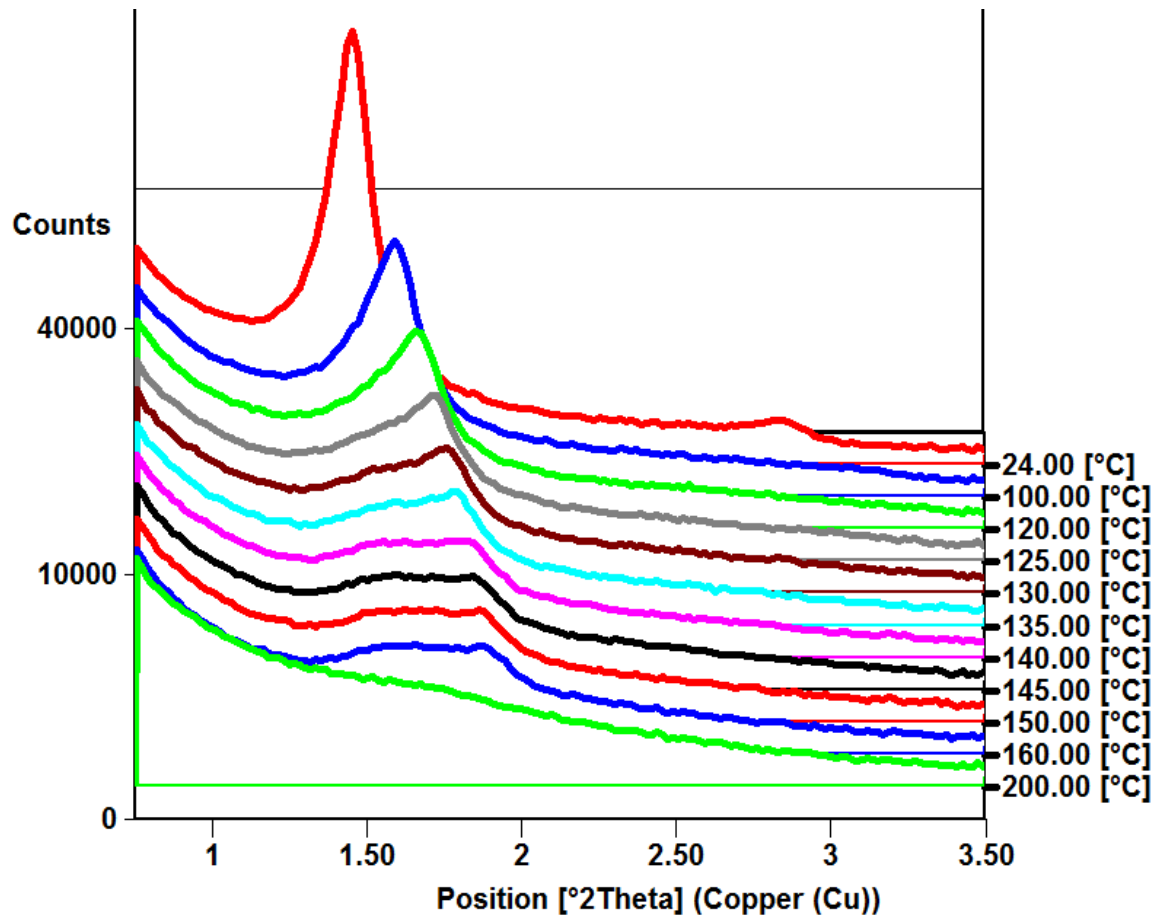
Optimizing the experiment: determining how much sample displacement will affect the data quality



The measurement was planned to study temperature stability with very limited instrument time

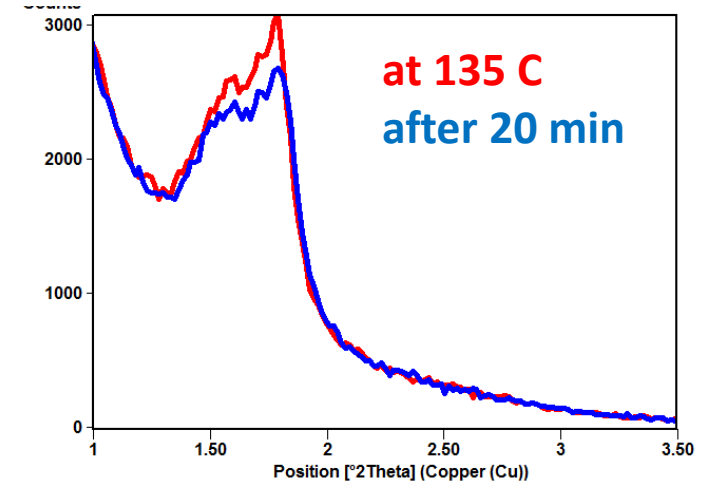
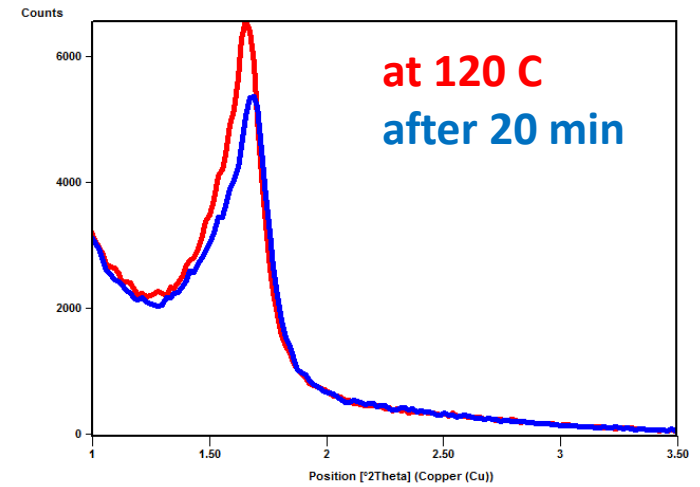
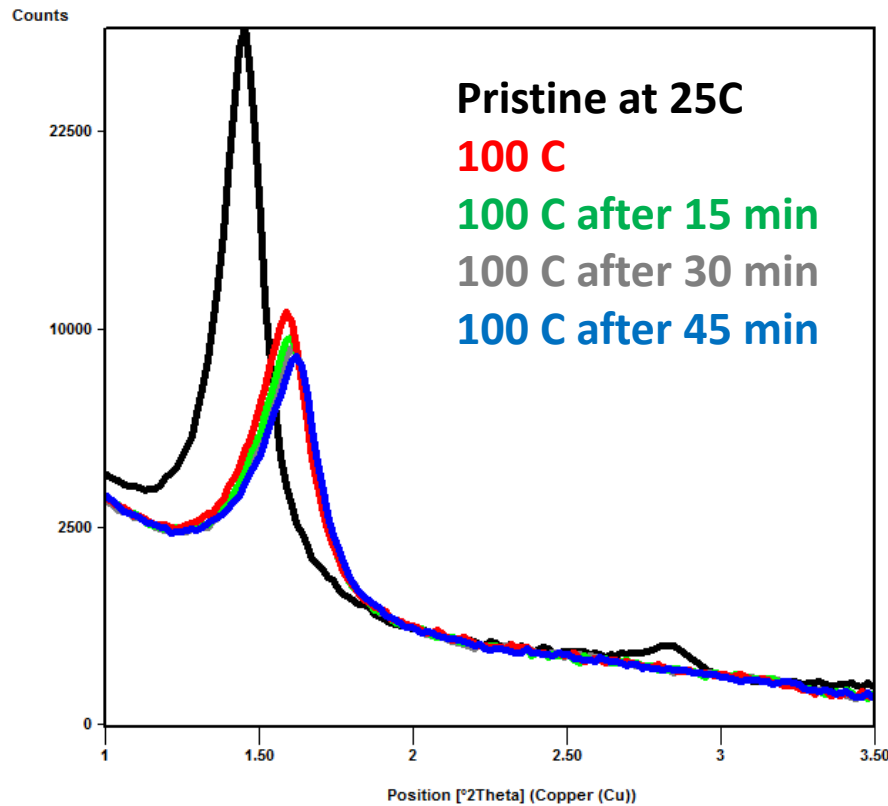


The scans collected at different temperatures show how the ordered nanostructure collapses upon heating



Confocal microscopy used to confirm XRD results.

Time resolved data shows that most changes occur very rapidly once sample reaches temperature



<http://prism.mit.edu/xray>