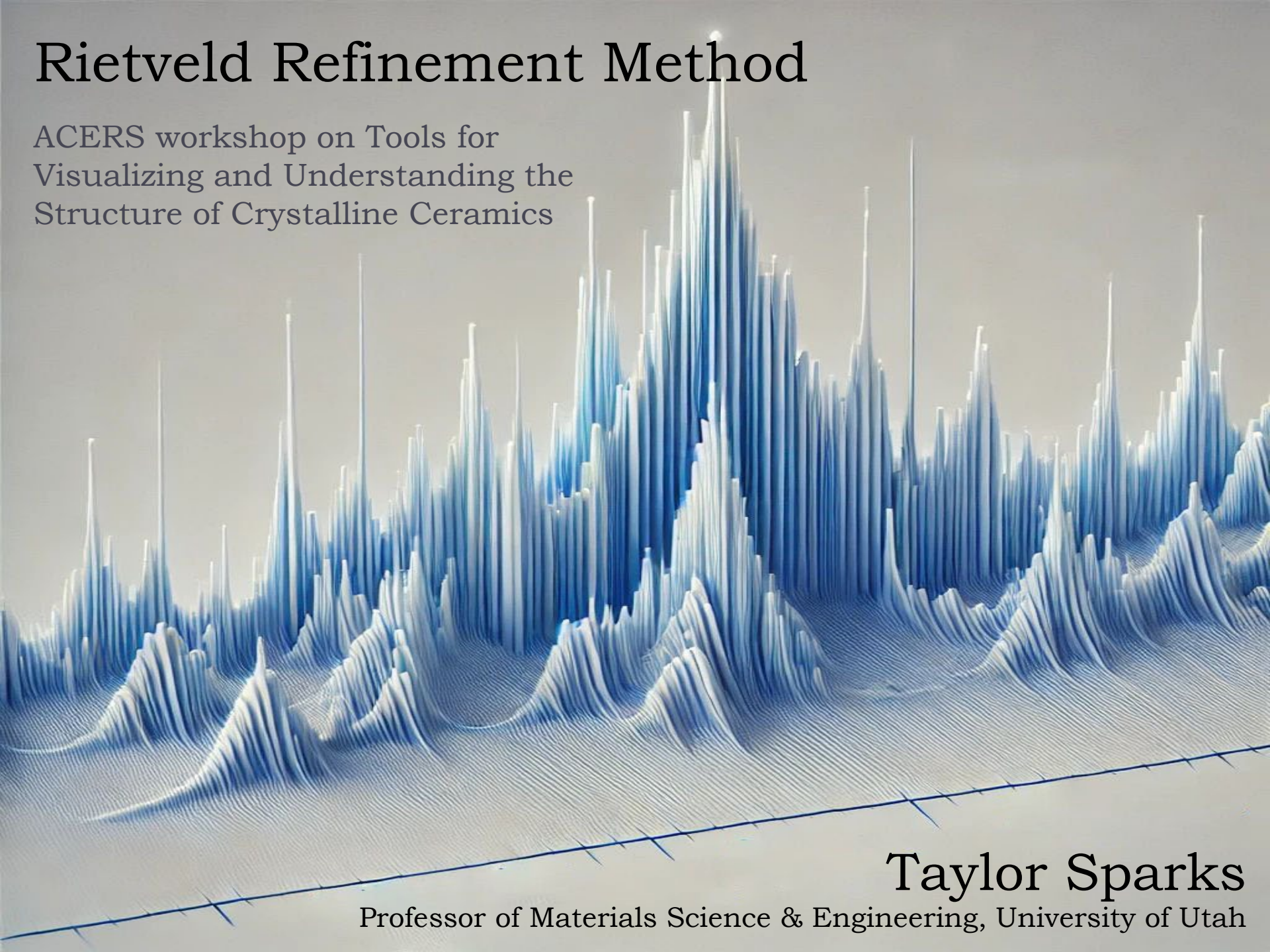
Rietveld Refinement Method

ACERS workshop on Tools for Visualizing and Understanding the Structure of Crystalline Ceramics



Taylor Sparks

Professor of Materials Science & Engineering, University of Utah

Overview

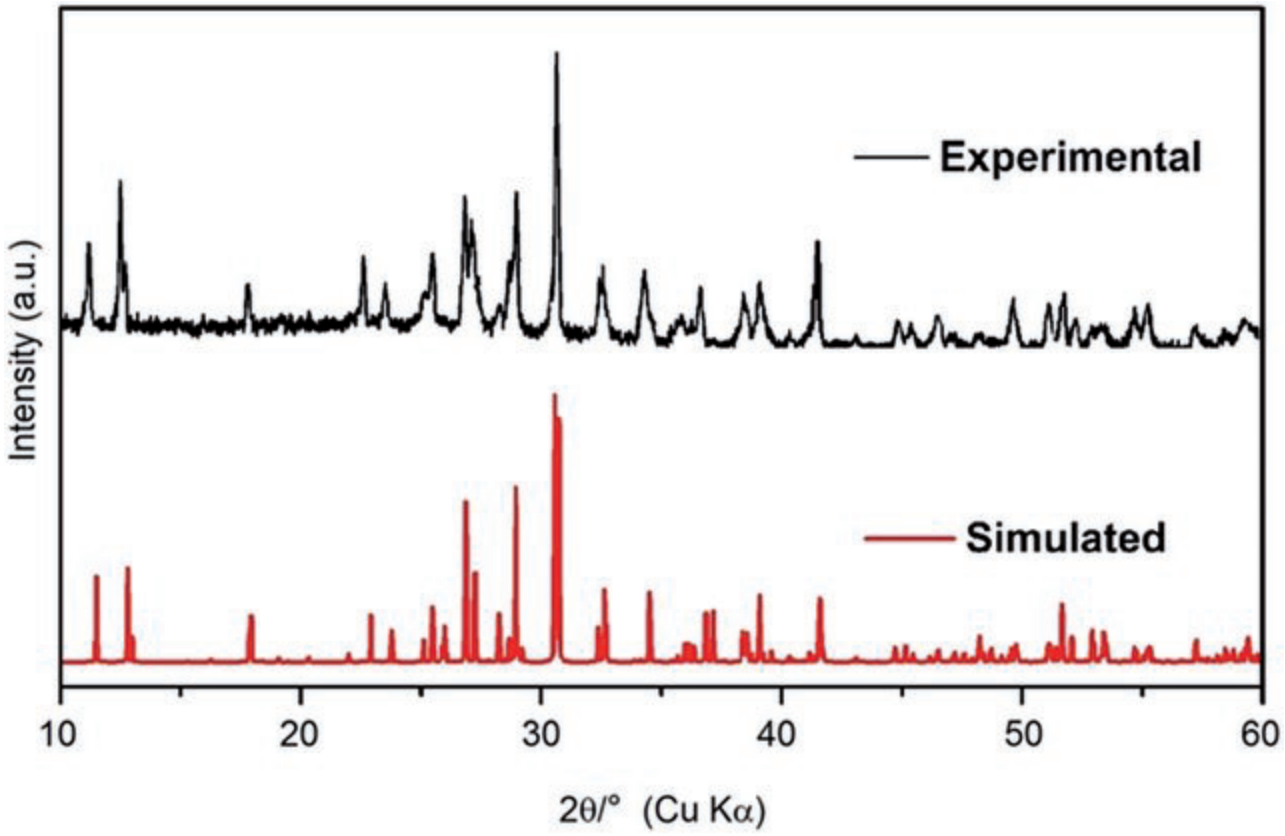
- What is it and how does it work?
- Quantitative analysis of multiple phases mixture
  - Amorphous content
- Atomic position & site occupancy
- Thermal displacement parameters
- Preferred orientation
- Crystallite size/strain

What is Rietveld refinement?

- Hugo Rietveld (1969)
- Quantitative refinement tool
  - Calculated pattern vs measured pattern
  - Variable model parameters
  - Least-squares refinement
  - Account for errors during measurement (shift, zero)
- Different from LeBail or Pawley (Profile) fitting
  - *Ab initio* crystal structure determination

http://www.ccp14.ac.uk/poster-talks/rietveld-csiro-axaa-99/rietveld/index.htm

We can simulate patterns pretty well!

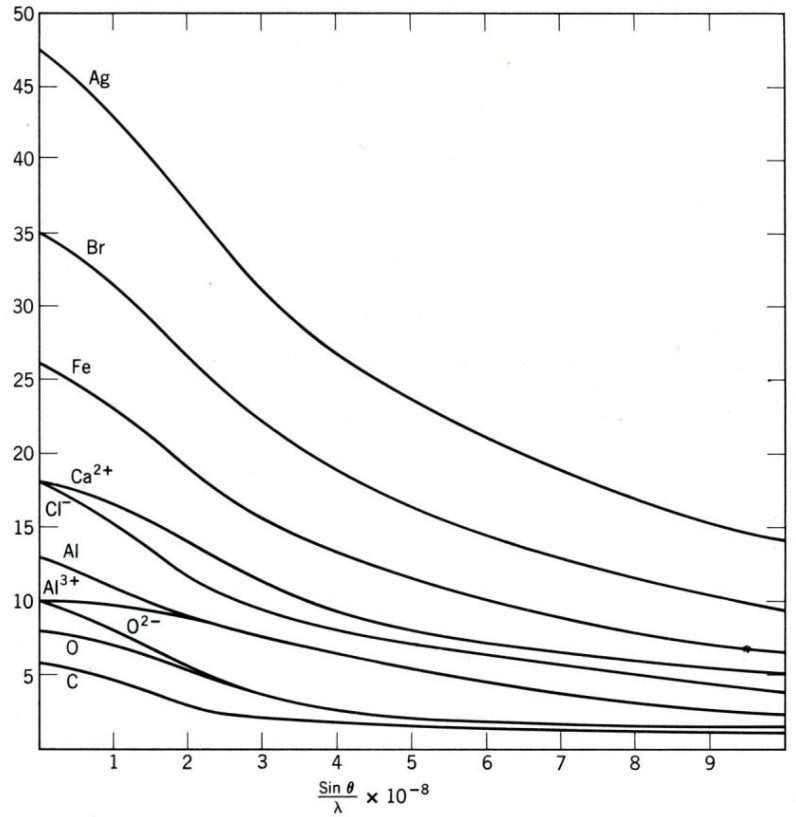


Intensity of a diffracted peak depends on many parameters!

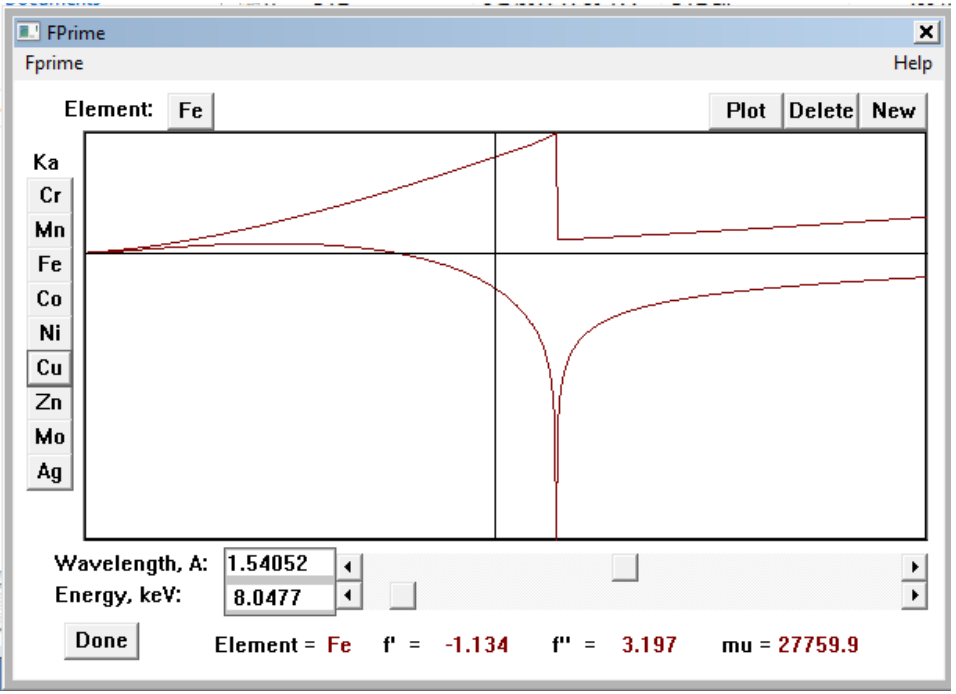
$$I_{(hkl)\alpha} = \frac{I_0 \lambda^3}{64\pi r}\left(\frac{e^2}{m_e c^2}\right)^2 \frac{M_{(hkl)}}{V_\alpha^2}\left|F_{(hkl)\alpha}\right|^2 \left(\frac{1+\cos^2(2\theta)\cos^2(2\theta_m)}{\sin^2\theta\cos\theta}\right)_{hkl} \frac{v_\alpha}{\mu_s}$$

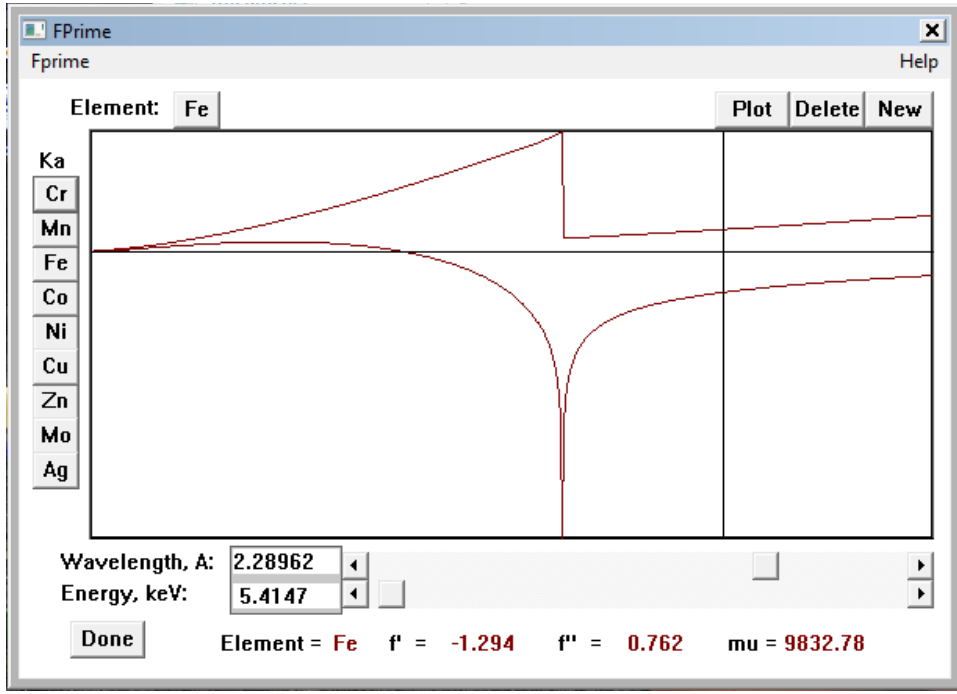
$$F_{hkl} = \sum_{j=1}^{m} N_j f_j \exp\left[2\pi i\left(hx_j + ky_j + lz_j\right)\right]$$

$$\left|f\right|^2 = \left(f_0 \exp\left[\frac{-B\sin^2\theta}{\lambda^2}\right] + \Delta f'\right)^2 + \left(\Delta f''\right)^2$$

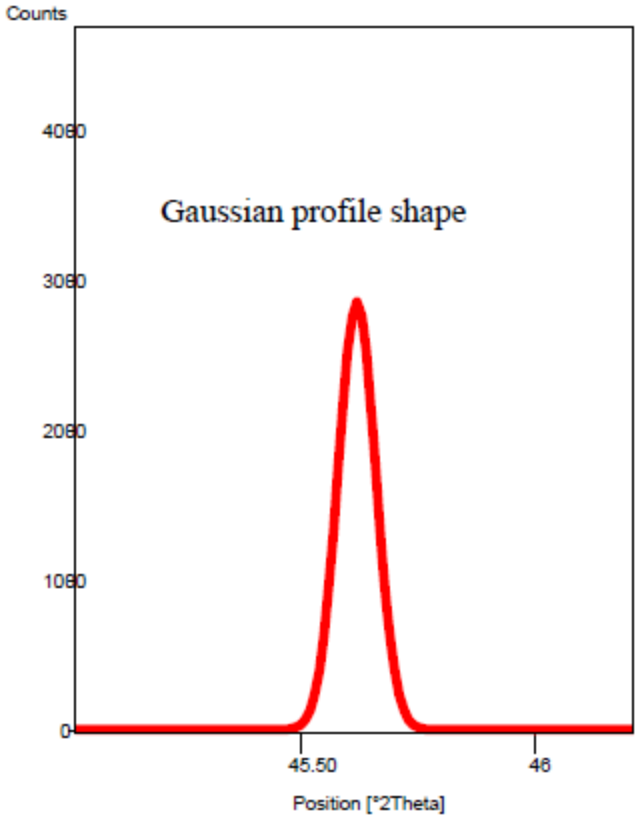


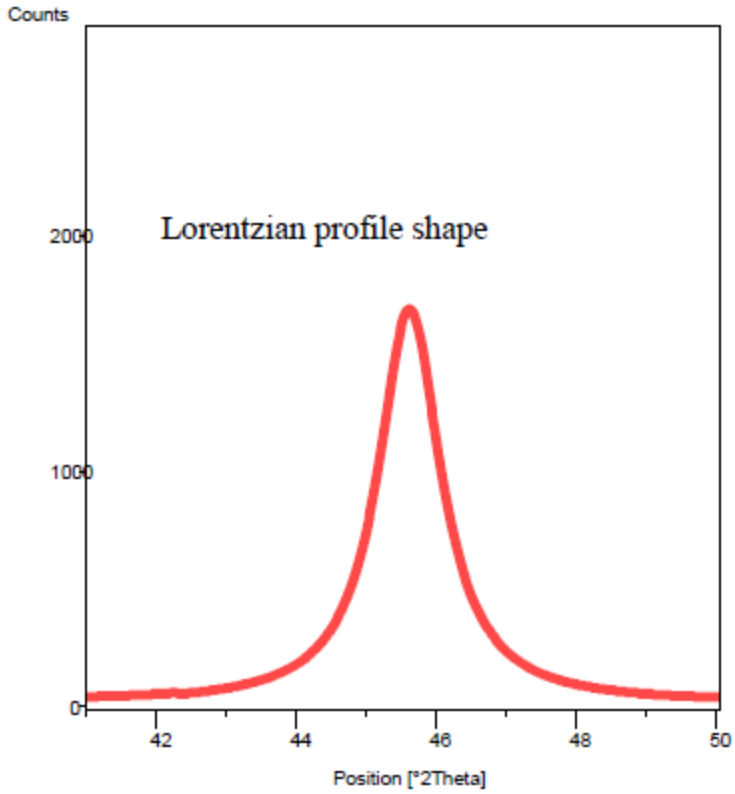
Anomalous Scattering Factors f’ & f” depends on radiation choice





Different instruments yield different peak shape





$$H_k = \left(U \tan^2 \theta + V \tan \theta + W\right)^{1/2}$$

prism.mit.edu/xray/Rietveld_XRDSimulation.pdf

Quality of the Fit

- R_p is the difference between the observed and the calculated value
- R_{wp} weights the residual so the higher intensity peaks are more important than low intensity ones

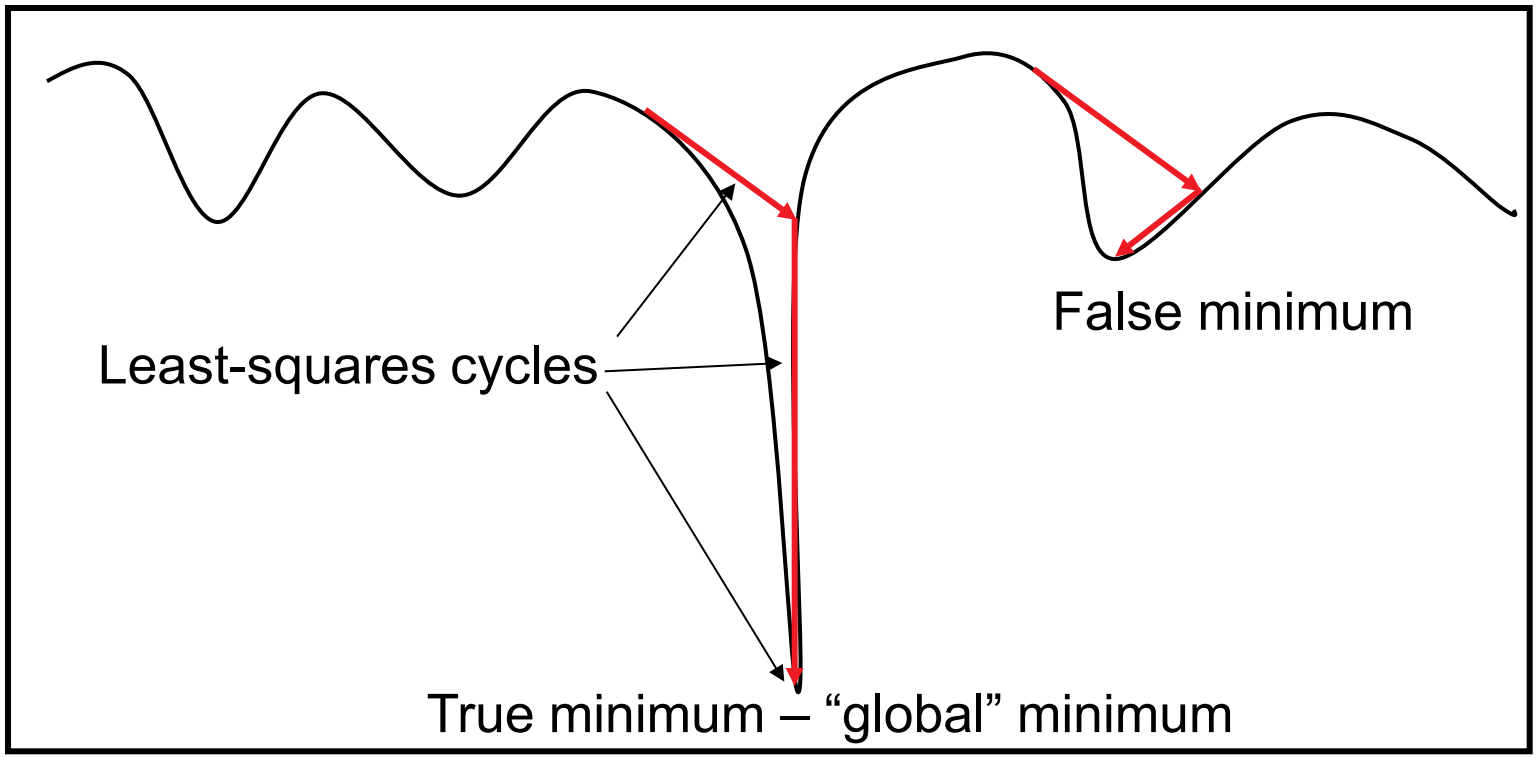
$$R_P = \frac{\sum |y_{io} - y_{ic}|}{\sum y_{io}} \qquad R_{wp} = \left[\frac{\sum w_i (y_{io} - y_{ic})^2}{\sum w_i y_{io}^2} \right]^{1/2}$$

$$GOF = \chi^2 = \left[\frac{R_{wp}}{R_{\exp}} \right]^2$$

- R_p or R_{wp} should be < 10% or $\chi^2 < 4$ for a good fit

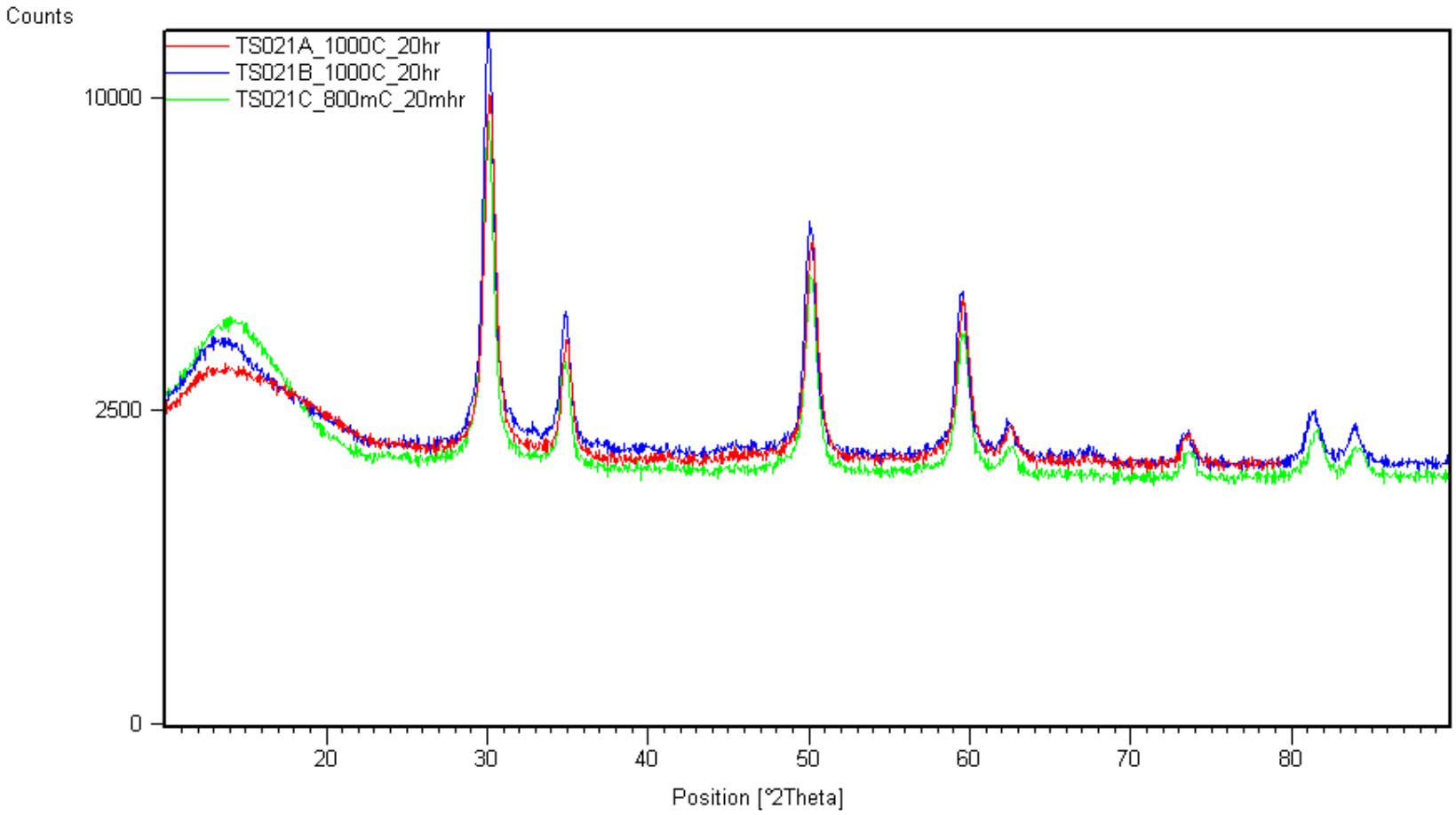
prism.mit.edu/xray/RietveldGOF.pdf

Multiple cycles required to find the true global minimum in error

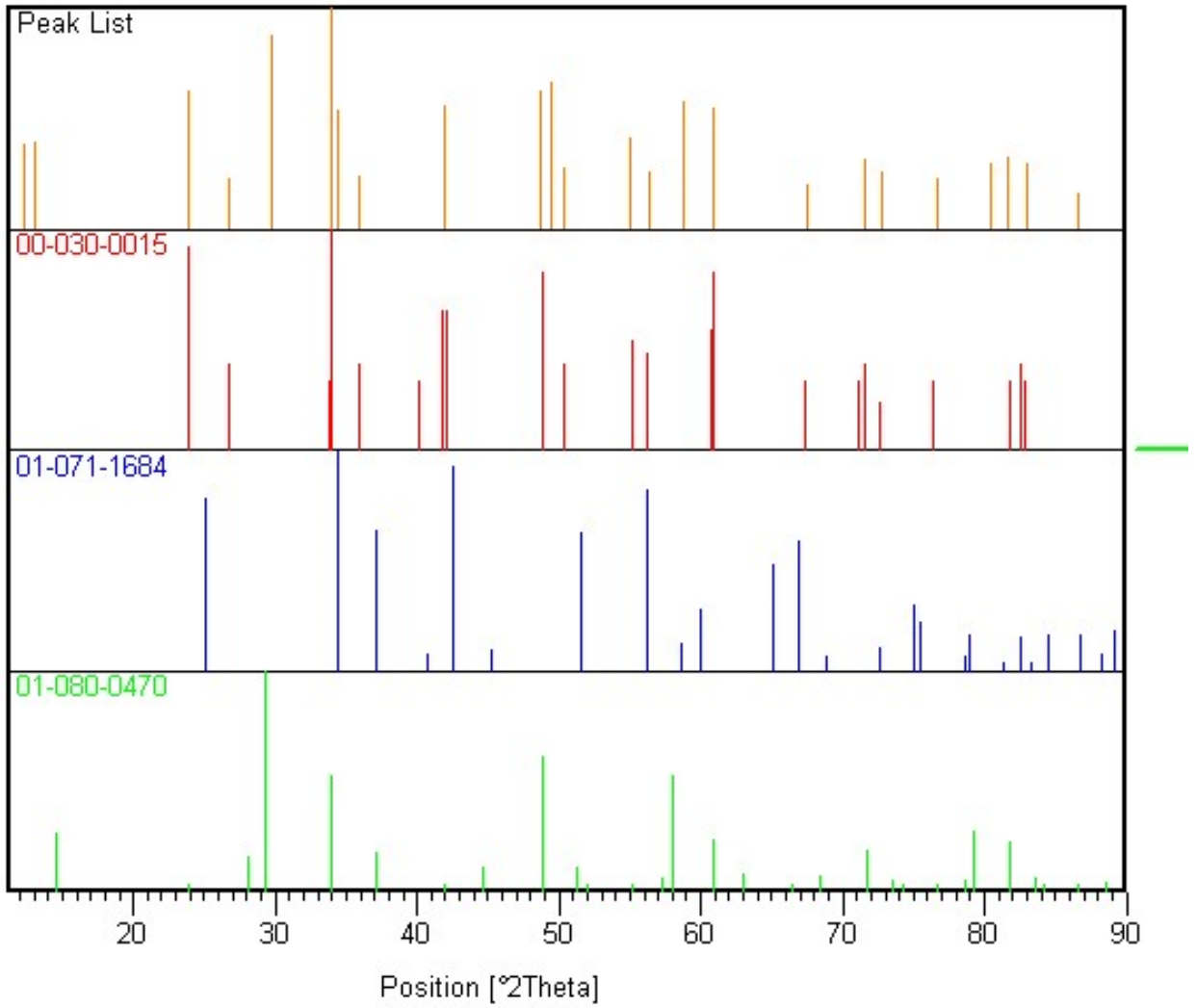


"A Rietveld refinement is never finished, only abandoned"
- P.W. Stephens

Quantitative Analysis of Multiple Phases Mixture



Quantitative Analysis of Multiple Phases Mixture

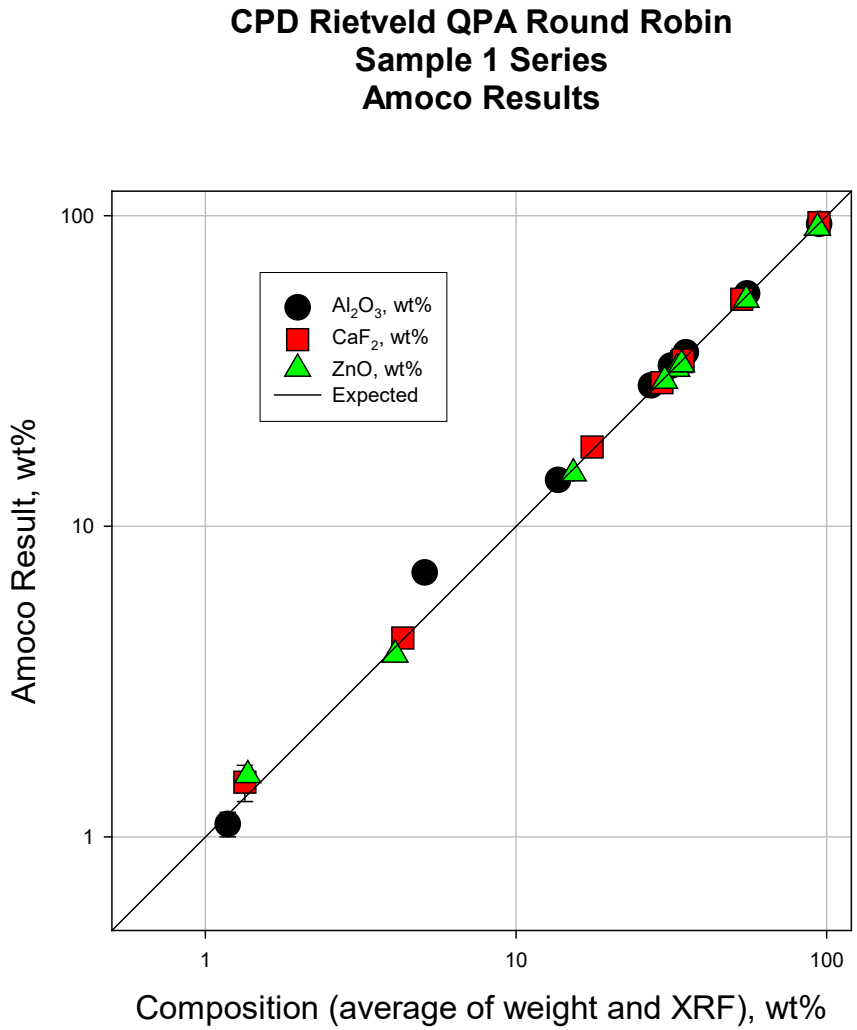


Weight Fraction: "SMZ" Method

- S is phase fraction, proportional to number of unit cells measured
- M is the molecular weight
- Z is the number of formula units per unit cell
- SMZ is proportional to the concentration

$$X_\alpha = \frac{S_\alpha M_\alpha Z_\alpha}{\sum SMZ}$$

How Good is the Quantitive Analysis?



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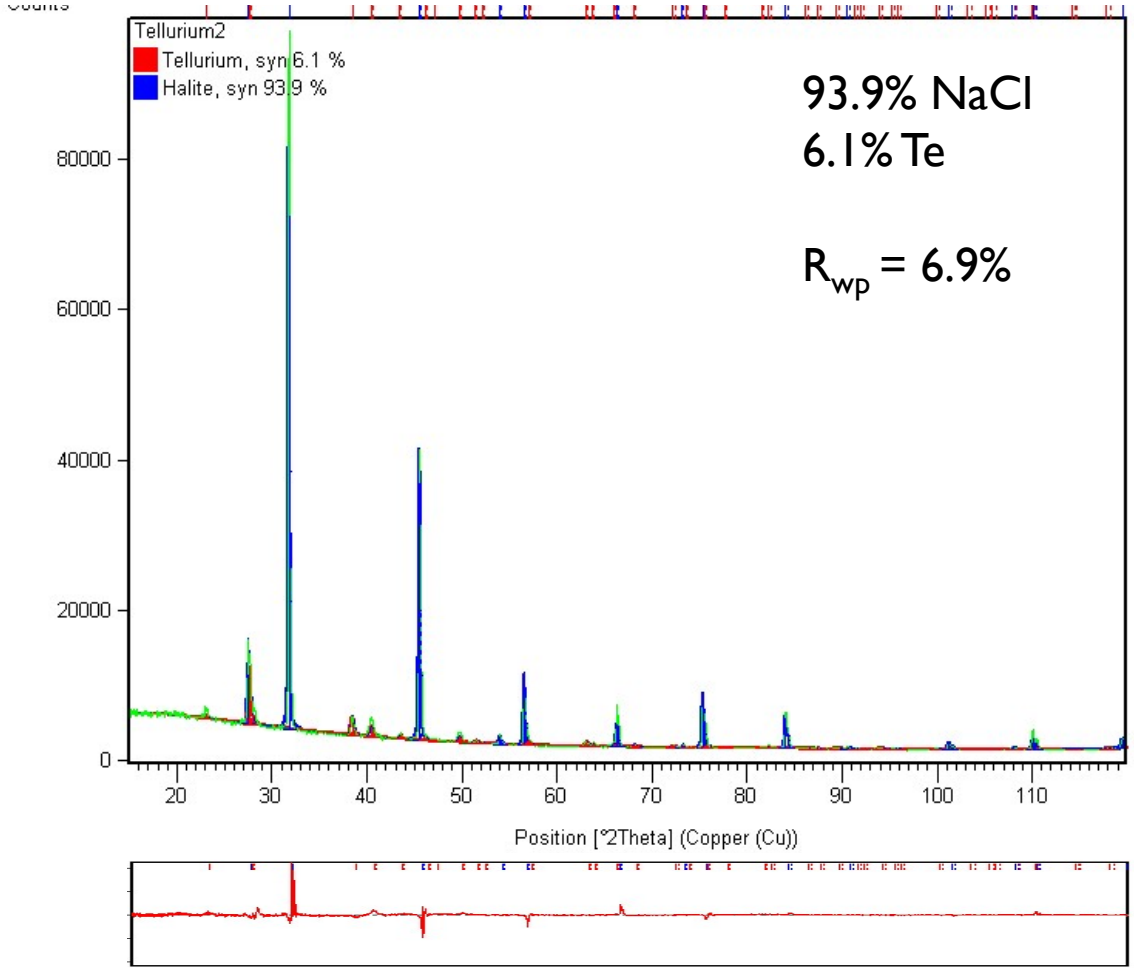
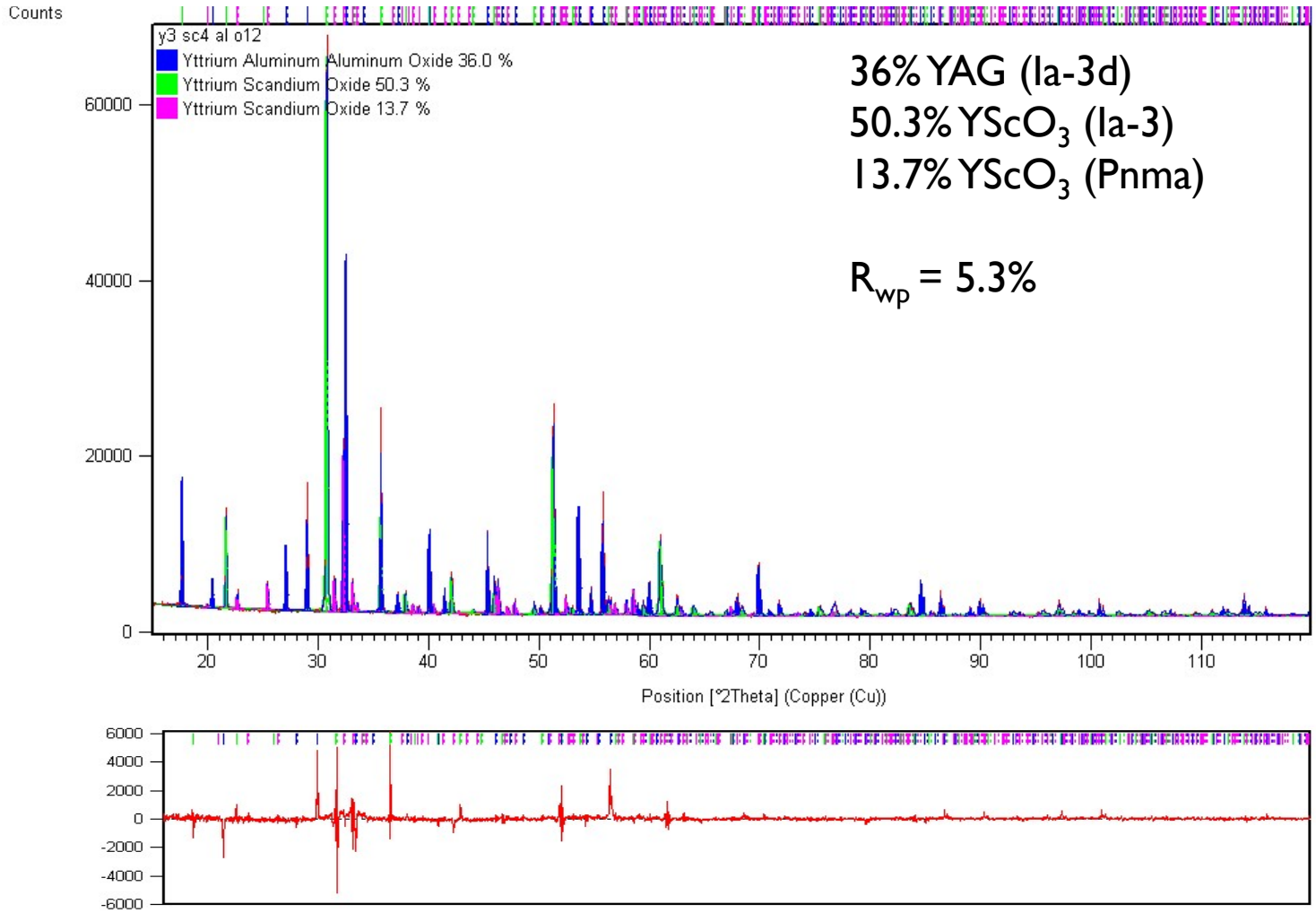
Te Fraction in Seawater Medium



Errors: absorption (transparency), sample volume (more powder)

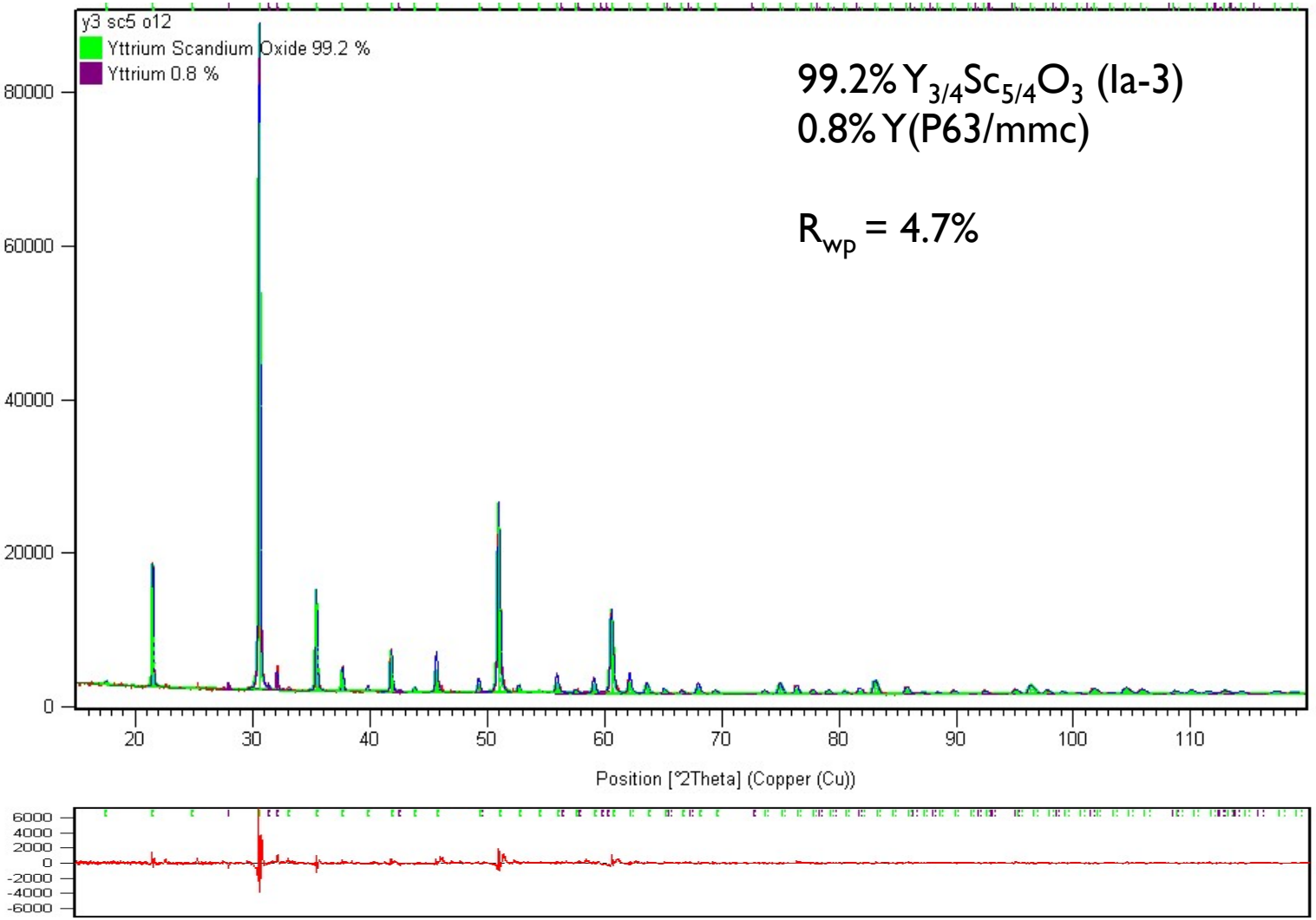
$Y_3Sc_4AlO_{12}$ Intended Composition



36% YAG (Ia-3d)
50.3% $YScO_3$ (Ia-3)
13.7% $YScO_3$ (Pnma)

R_{wp} = 5.3%

$Y_3Sc_5O_{12}$ Intended Composition



99.2% $Y_{3/4}Sc_{5/4}O_3$ (Ia-3)
0.8% Y(P63/mmc)

R_{wp} = 4.7%

Debye Equation for Amorphous Materials

Possible to determine percent amorphous material if standard is added in known amount.

$$I(\theta) = \sum_n f_n^2(\theta) + 2\sum_i \sum_j f_i(\theta) f_j(\theta) \left[\frac{\sin\left(\frac{4\pi r_{ij} \sin\theta}{\lambda} \right)}{\frac{4\pi r_{ij} \sin\theta}{\lambda}} \right]$$

$$A_i \frac{\sin(QR_i)}{QR_i} \exp(-\frac{1}{2} B_i Q^2)$$

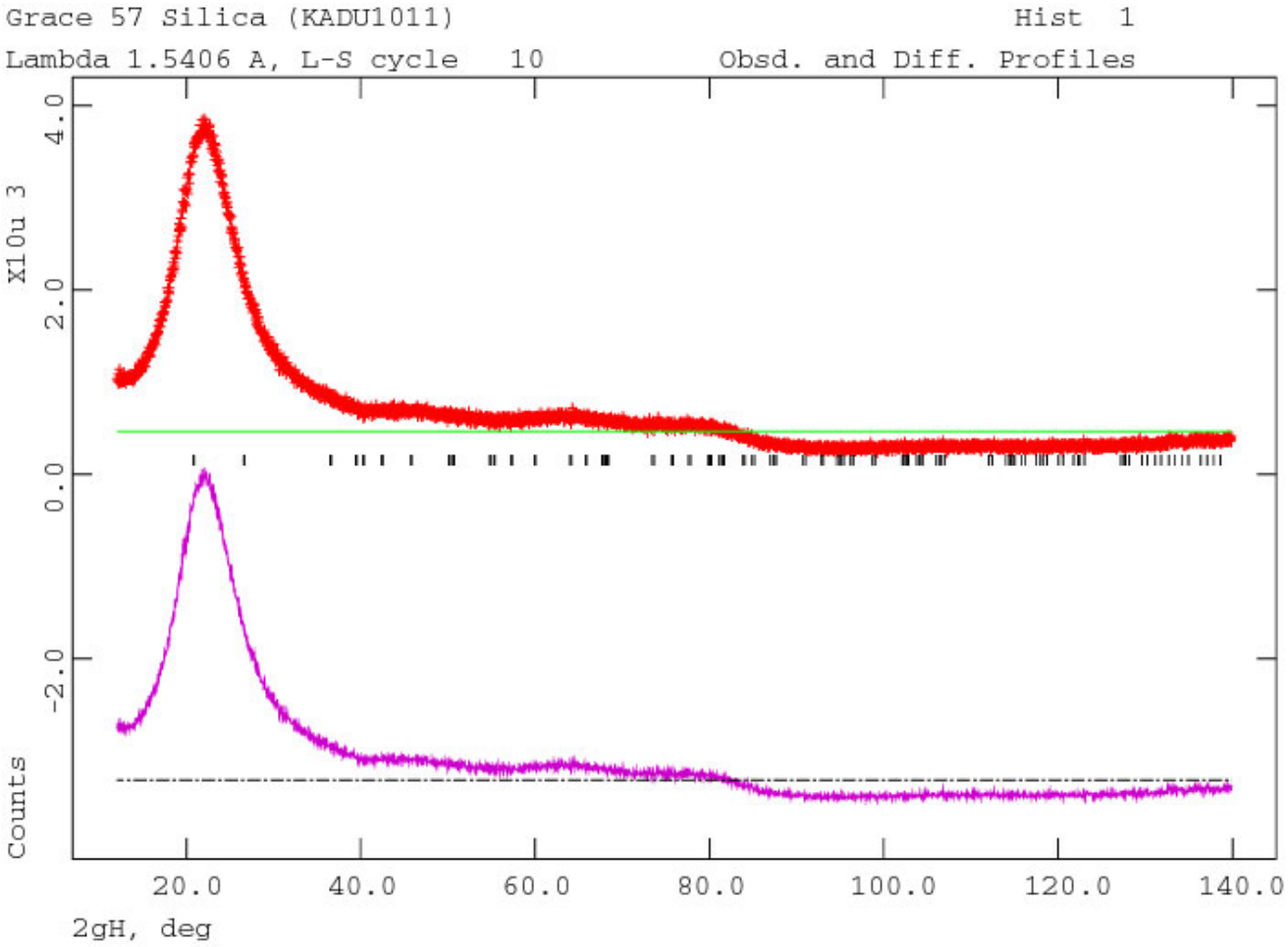
amplitude

distance

vibration

Need radial distribution function to determine bond distances for analysis

Diffuse Scattering



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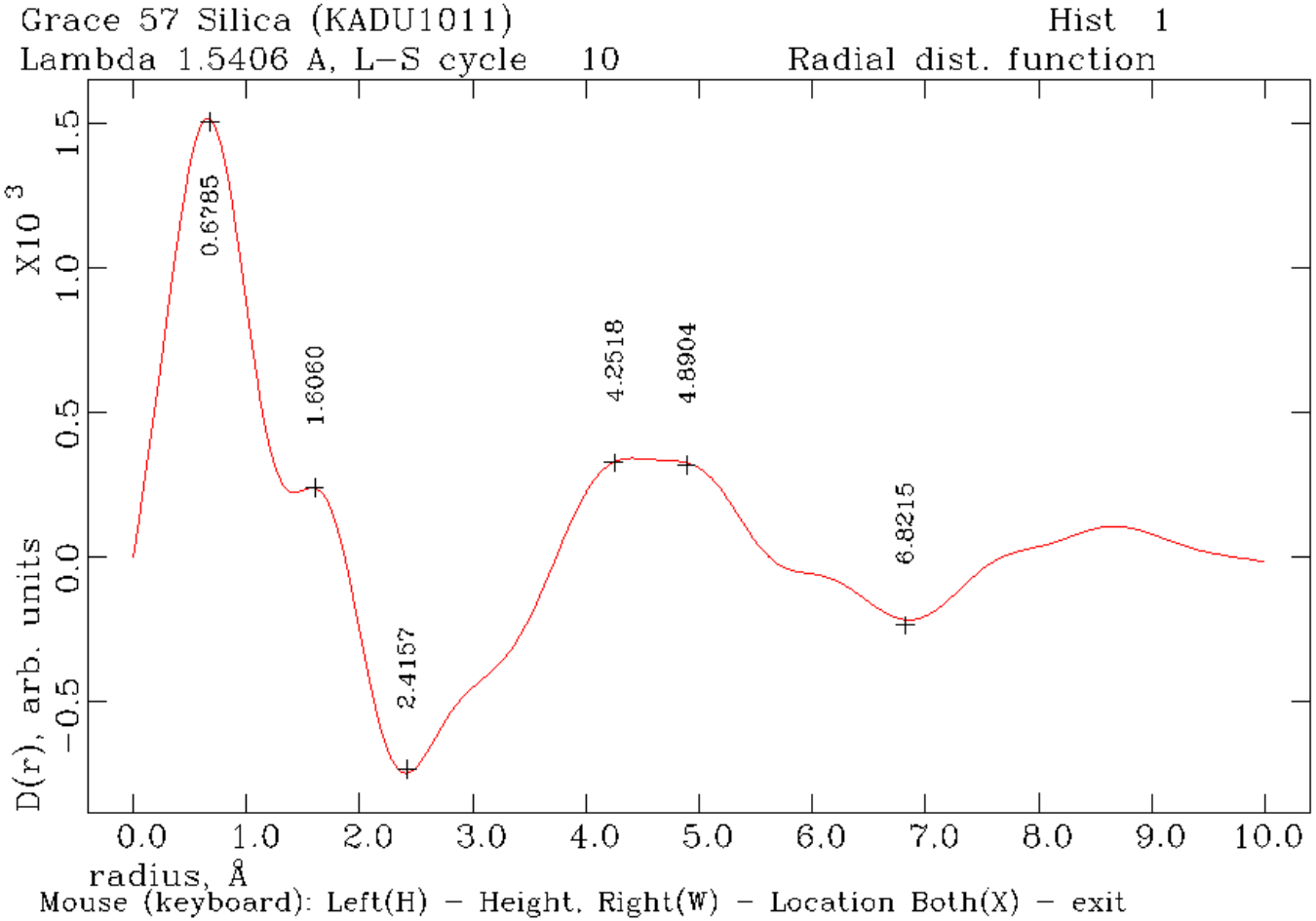
Diffuse Scattering



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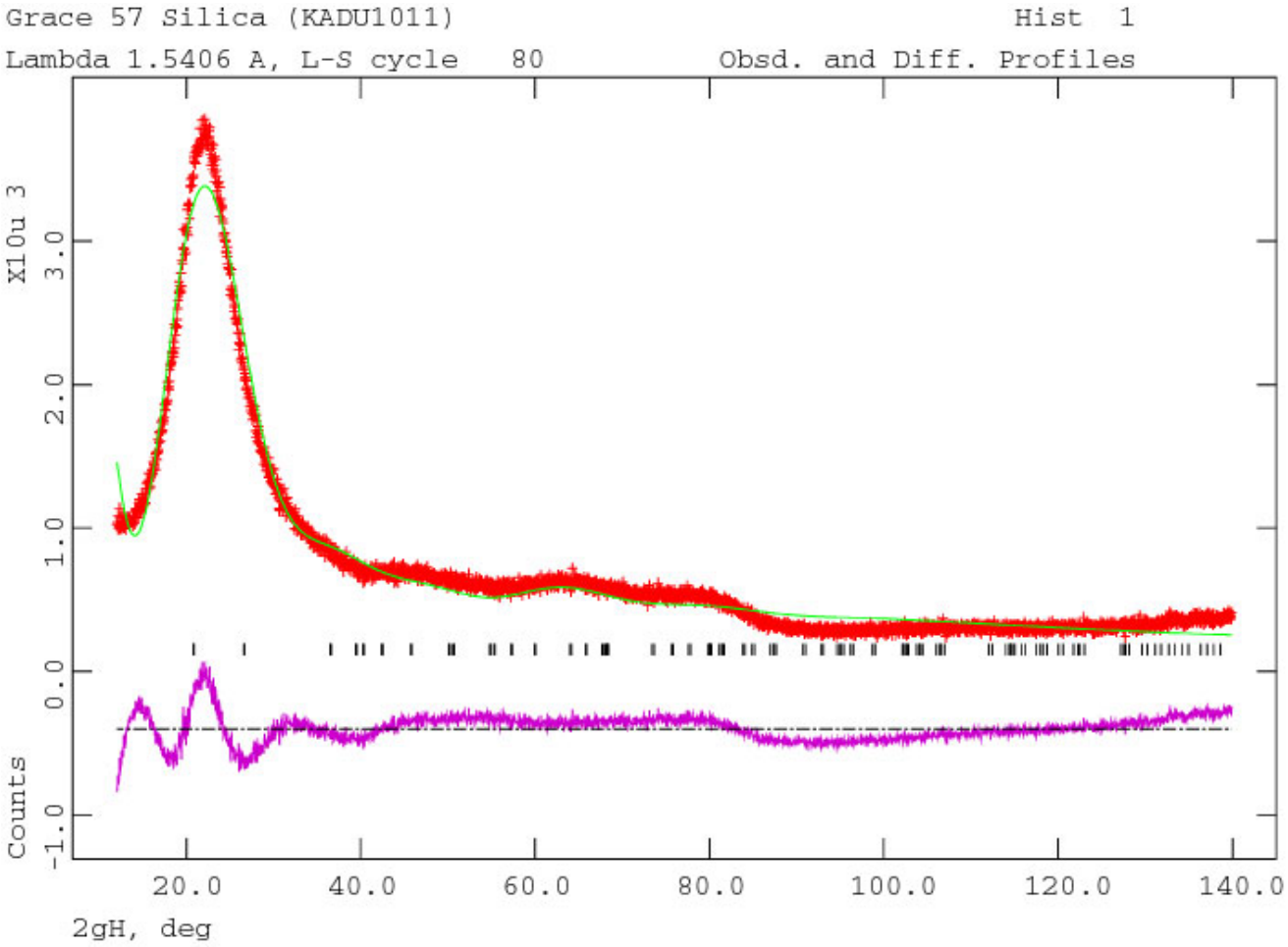

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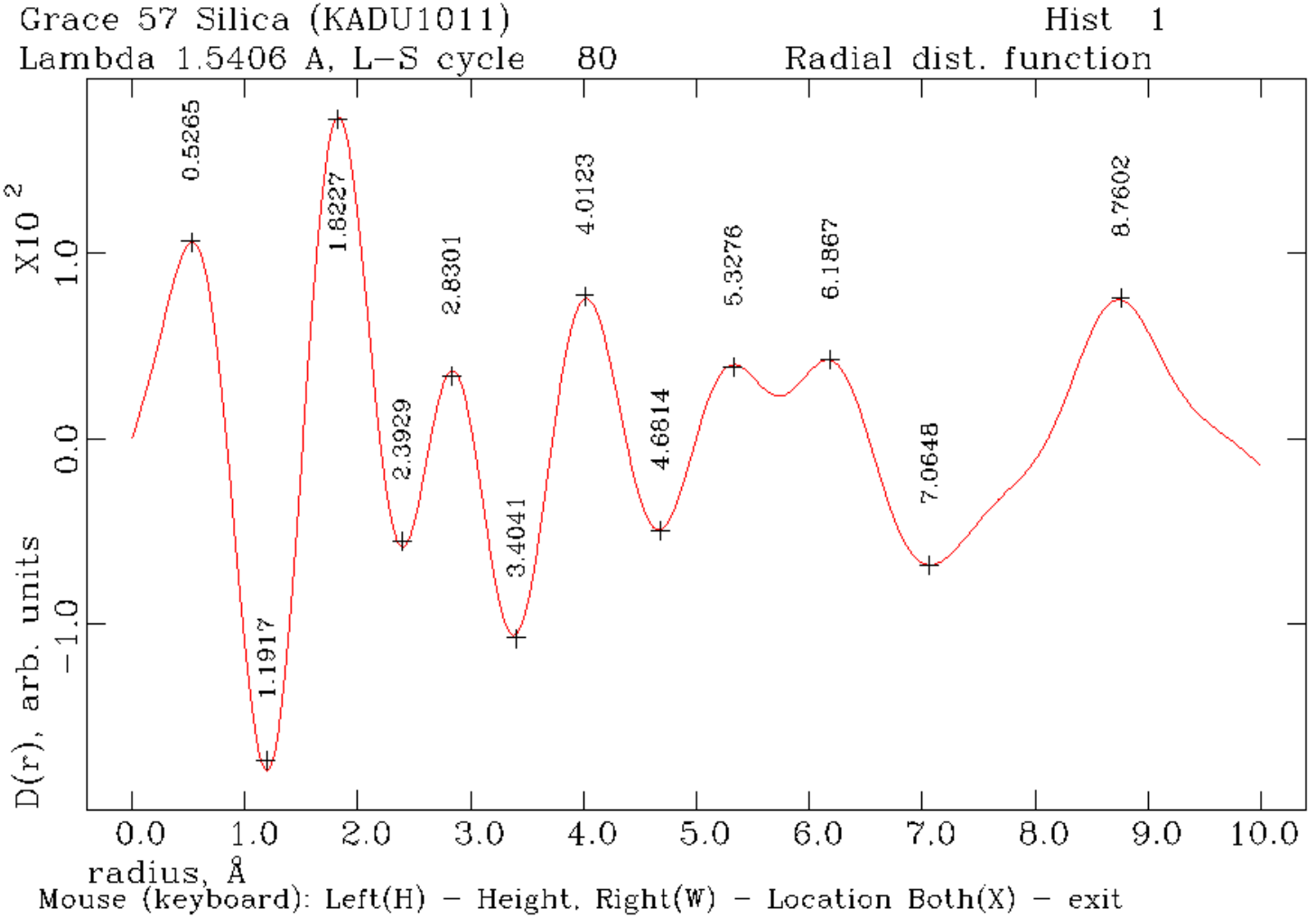
Diffuse Scattering



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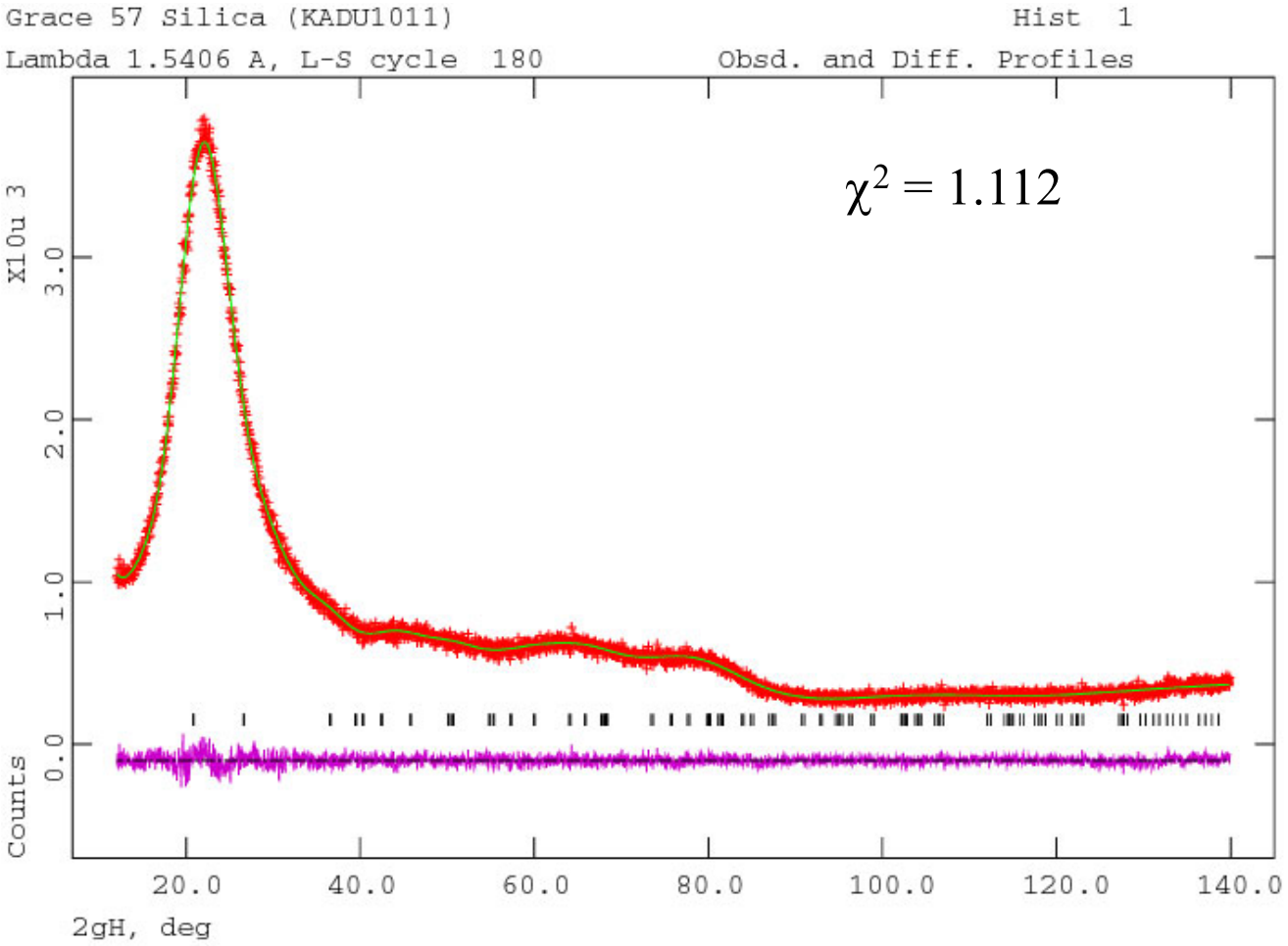
Diffuse Scattering



Atomic Position & Site Occupancy

- $Gd_{8+x}Ca_{2+y}(SiO_4)_6O_{2+3x/2+y}$ system
  - Anion/cation vacancies

- Lab XRD insufficient
  - Impurity wt%?
  - Volume change?
  - Cation site preference?
  - Meta-prism twist?

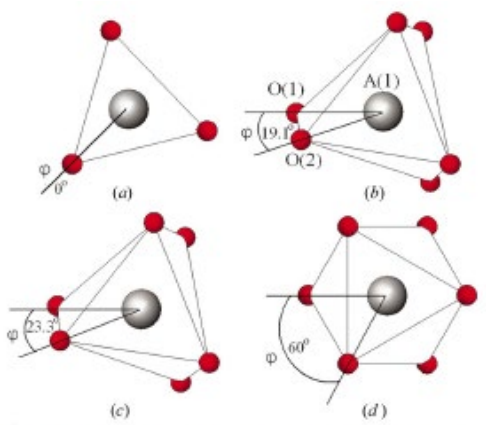
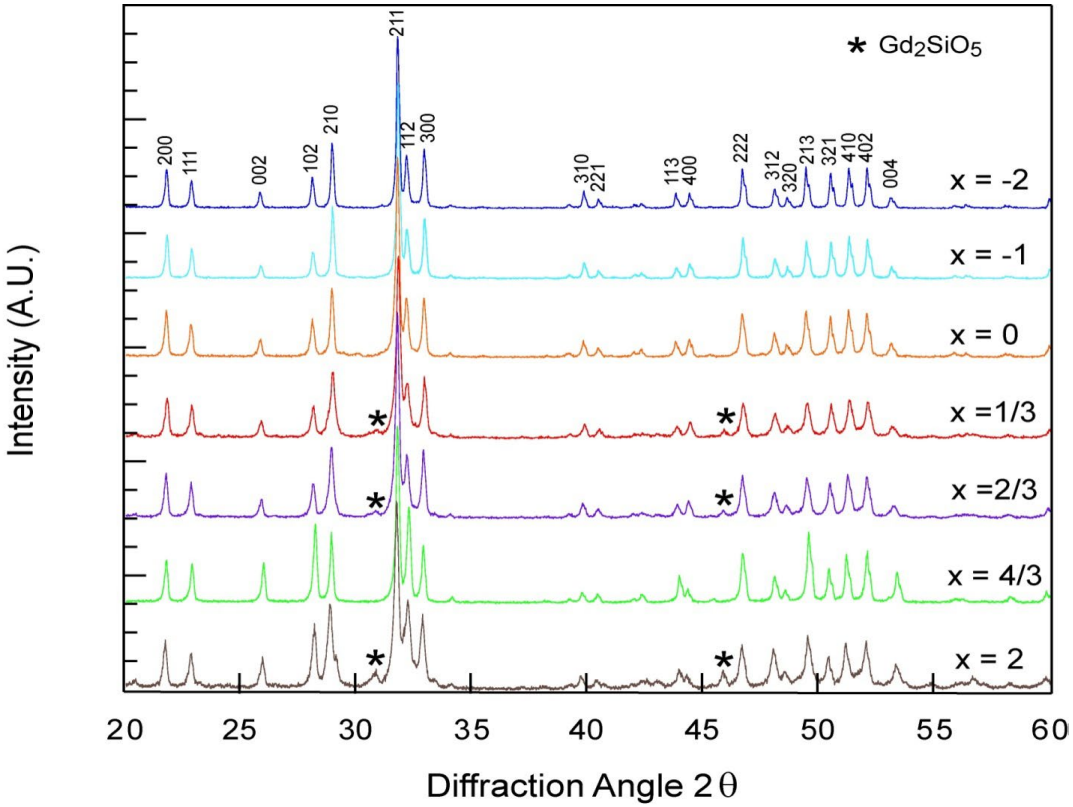


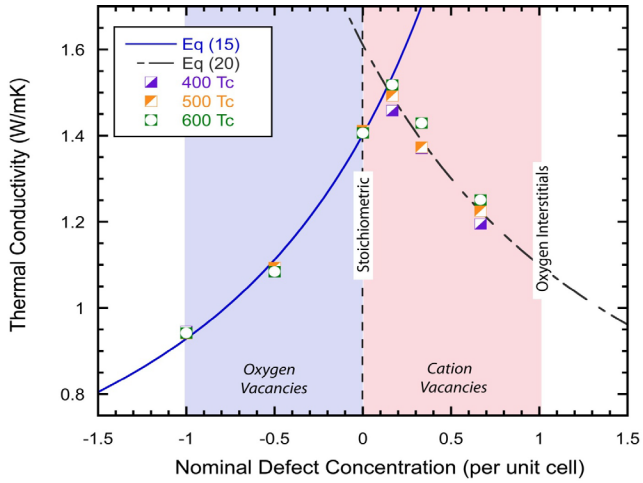
Figure 6
Twist angles of $A(1)O_6$ polyhedra in (*a*) models I and II, (*b*) chlorapatite, (*c*) fluorapatite, and (*d*) model III (as found in glaserite).



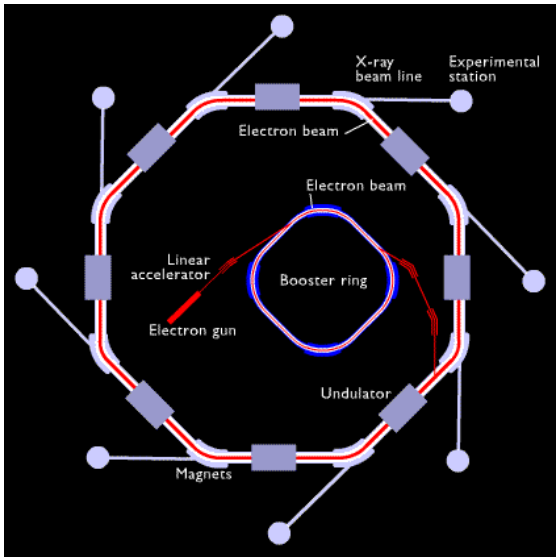
White et al, Structural derivation and crystal chemistry of apatites, Acta Cryst. B, **B59** 1-16 2003

Atomic Position & Site Occupancy

- Stoichiometric composition should have highest thermal conductivity
  - Phase separation?

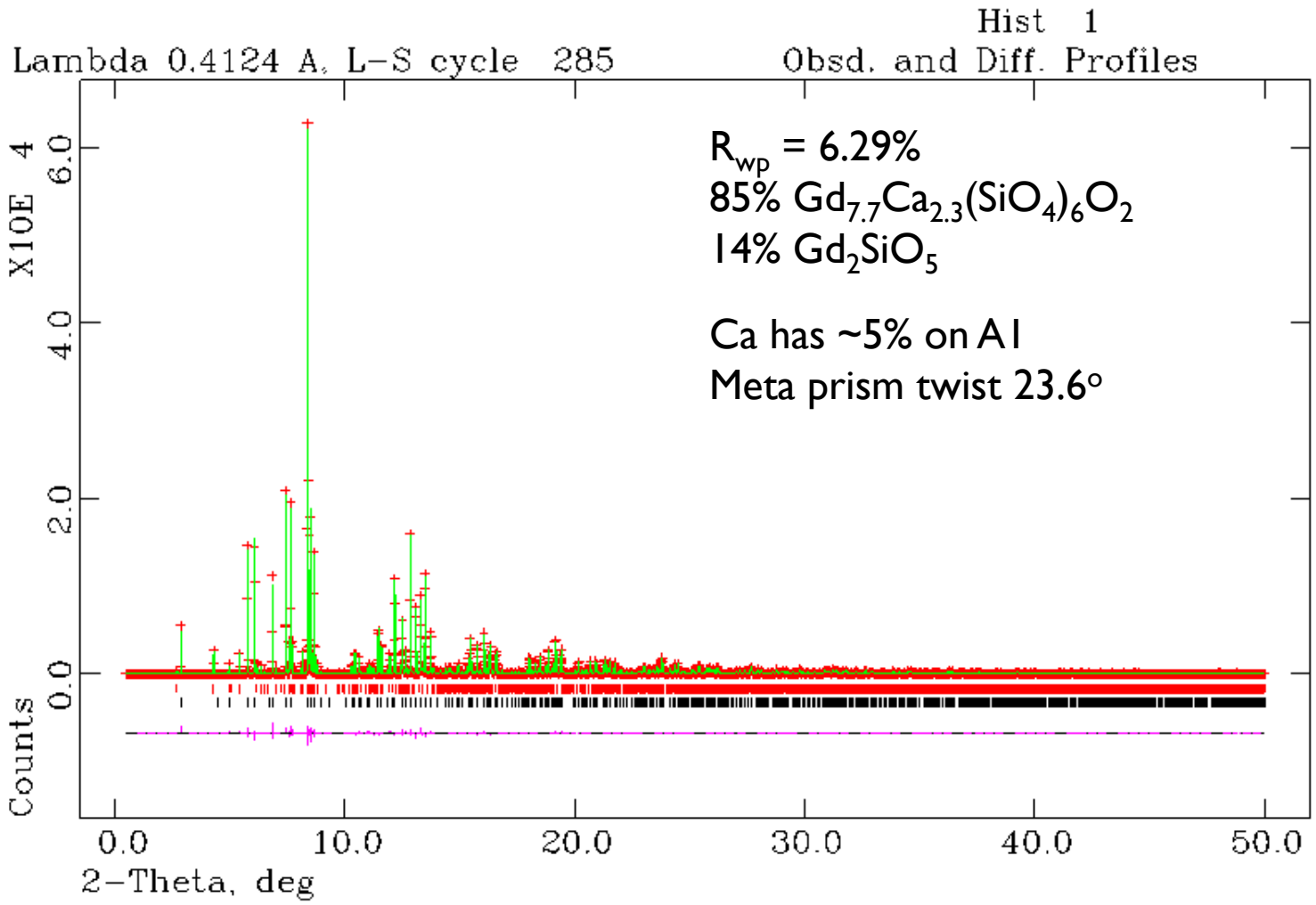


- Synchrotron diffraction
  - Improved signal to noise ratio
  - Improved resolution
  - Minimize anomalous scattering



http://www.odec.ca/projects/2005/shar5a0/public_html/mainpage.htm

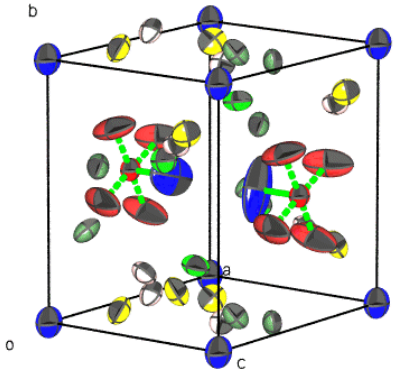
Atomic Position & Site Occupancy

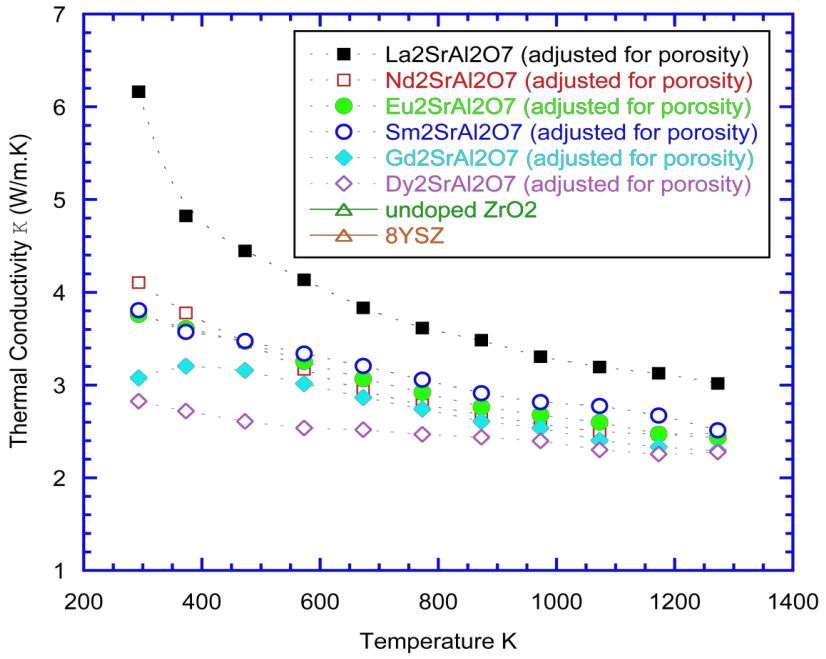


- Initial composition $Gd_{8.333}Ca_{1.5}(SiO_4)_6O_2$

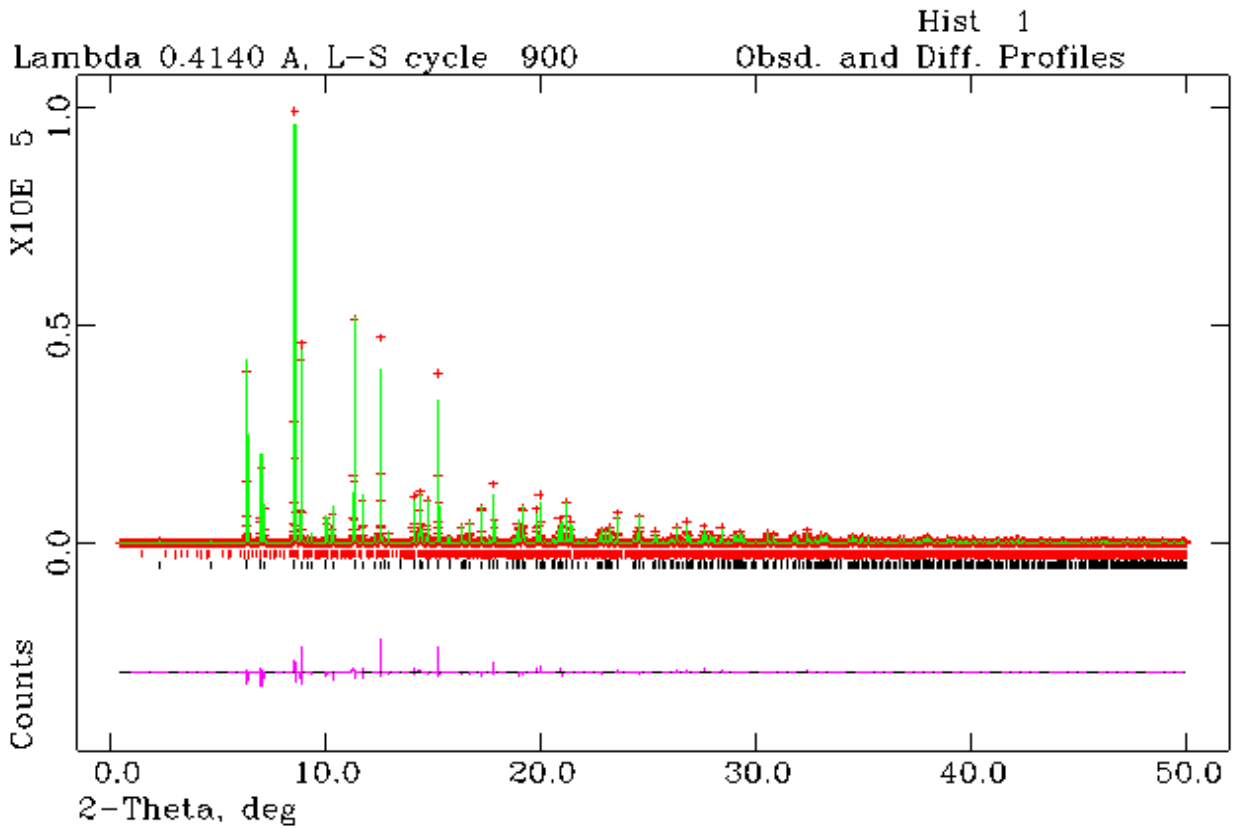
Thermal Displacement Parameters

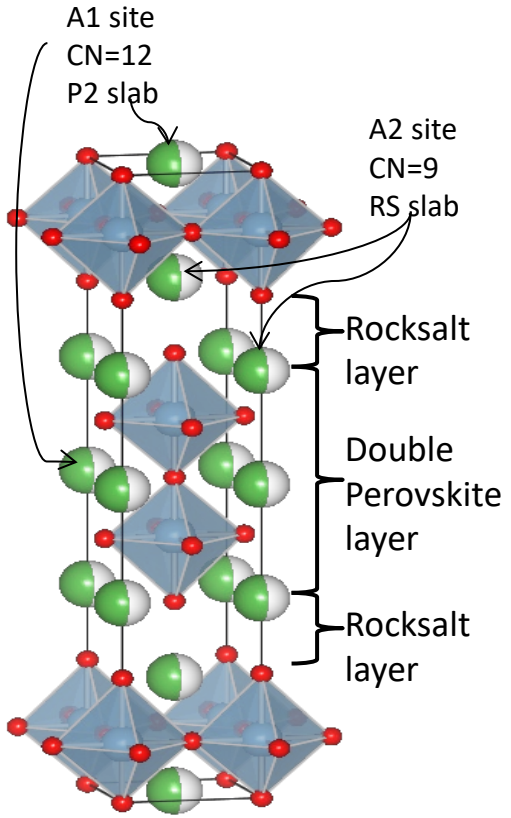
- Thermal vibrations quantitatively studied in Rietveld refinement
  - U_{iso} or U_{ij} for anisotropic vibration
- Large U values could be due to rattling
  - Explanation of $RE_2SrAl_2O_7$ thermal conductivity?





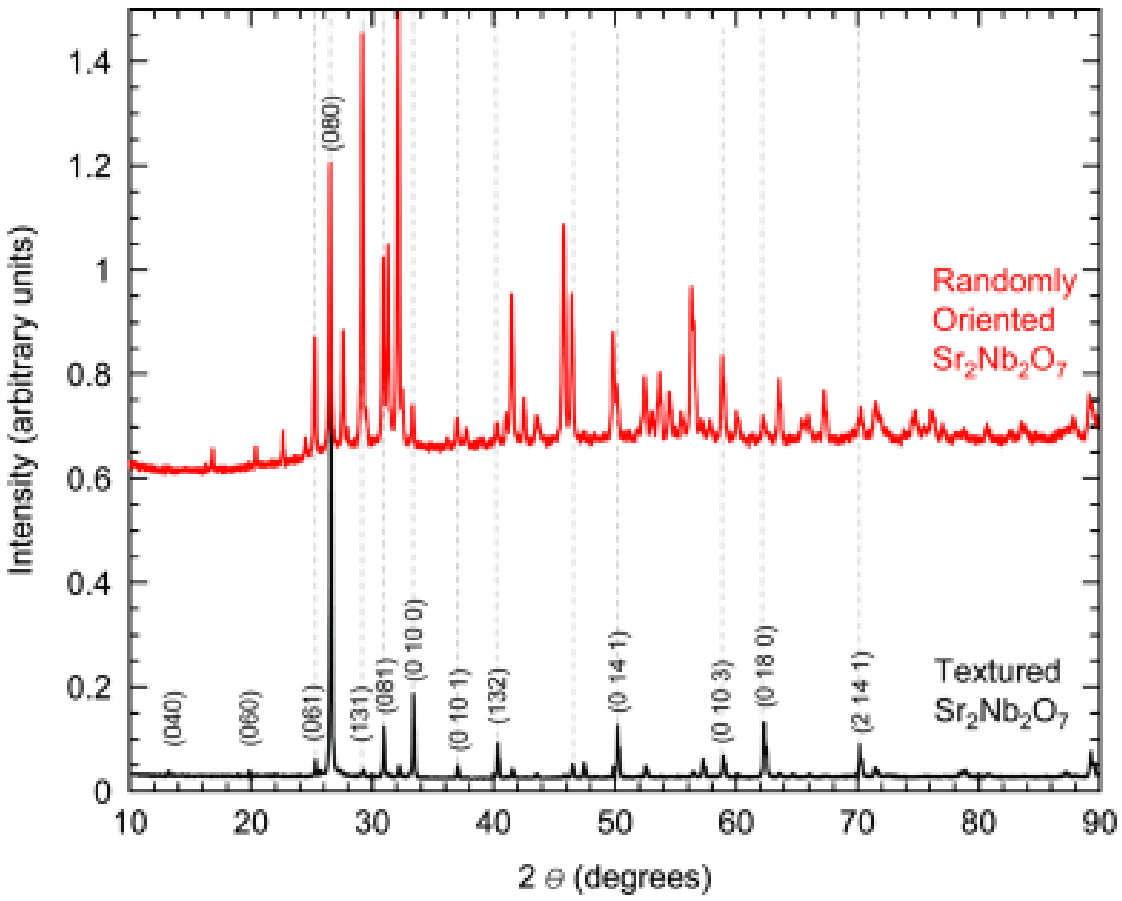
Thermal Displacement Parameters





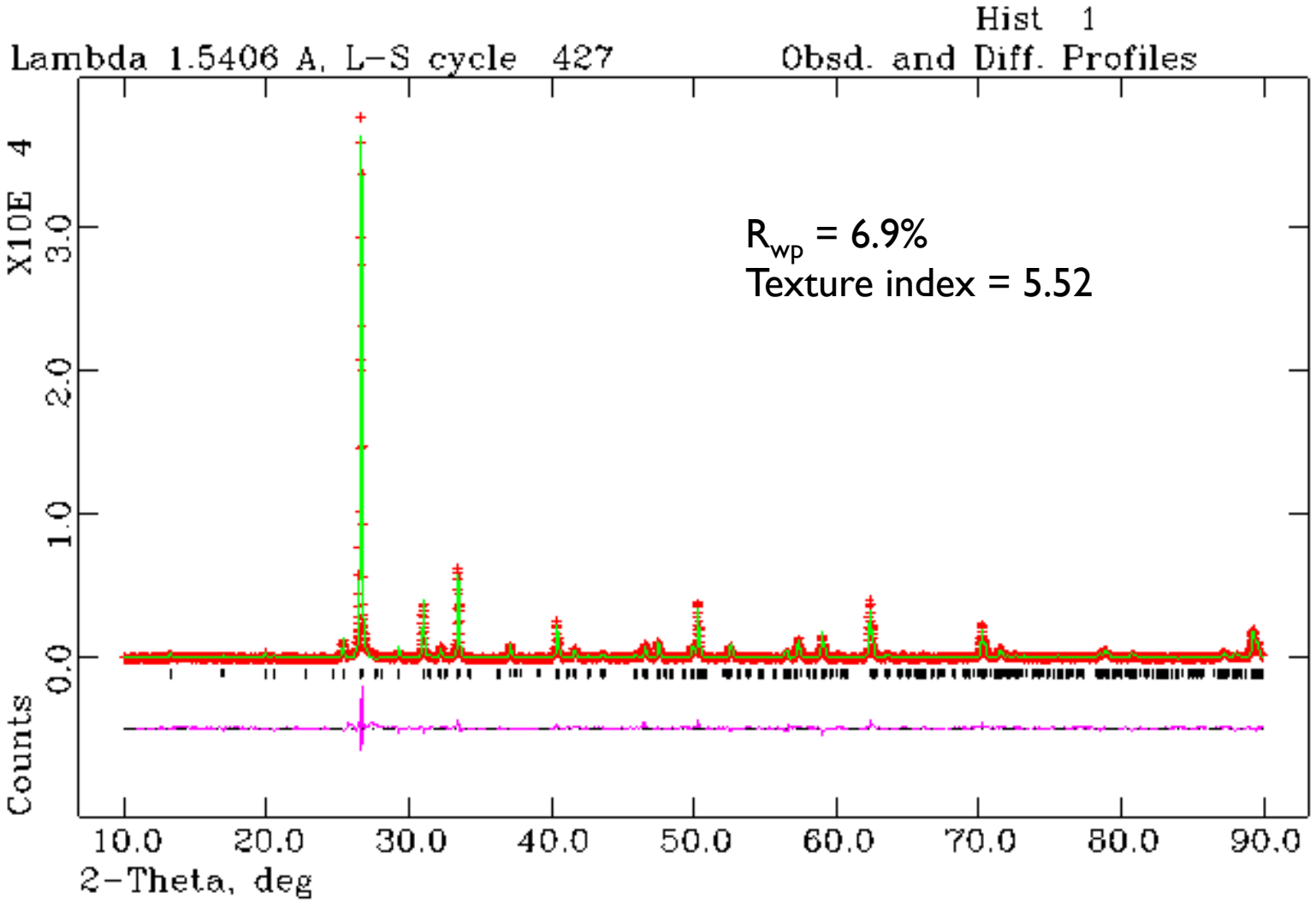
Compostion	$La_2SrAl_2O_7$	$Nd_2SrAl_2O_7$	$Sm_2SrAl_2O_7$	$Eu_2SrAl_2O_7$	$Gd_2SrAl_2O_7$	$Dy_2SrAl_2O_7$
Uiso A1	0.11(2)	0.21(5)	0.40(3)	0.20(1)	0.37(3)	0.96(2)
A1 (P2) occupancy	.73	.54	.43	.32	.25	.21
A2 (RS) occupancy	.27	.46	.56	.67	.72	.79

Preferential Orientation: $Sr_2Nb_2O_7$



Clearly textured to b-axis, but what is preferred orientation factor?

Preferential Orientation $Sr_2Nb_2O_7$



- Note: Actual compound had small amount of La^{3+} doped on Sr^{2+} site

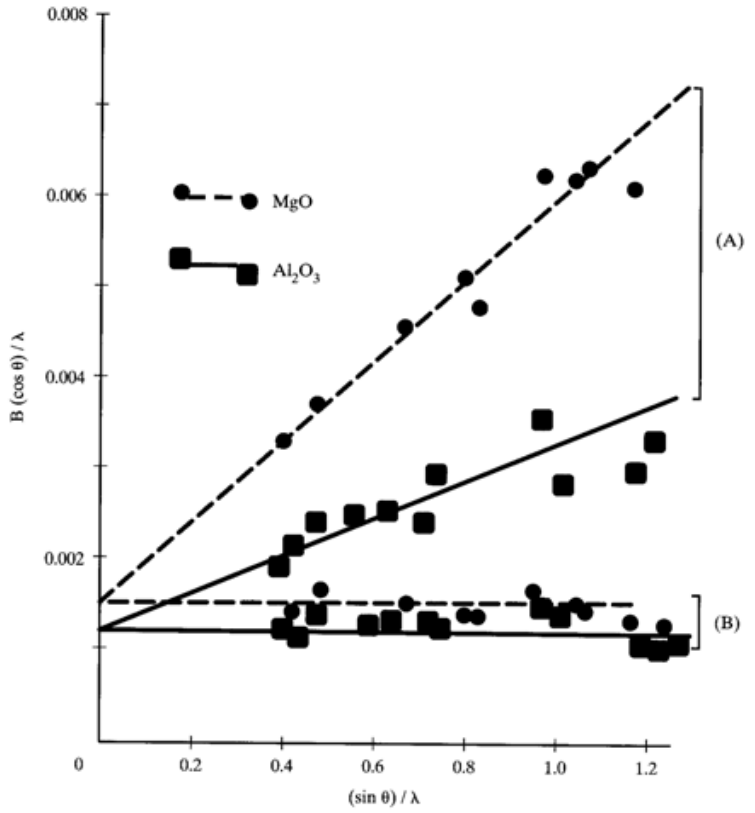
Size & Strain

First need to characterize the instrument shape parameters using a standard.
Then use U,V,W to obtain integral breadth for Scherrer's & Stokes' equation.

$D_v = K\lambda/\{\beta \cos \theta\}$ $\varepsilon = \beta/\{4 \tan \theta\}$

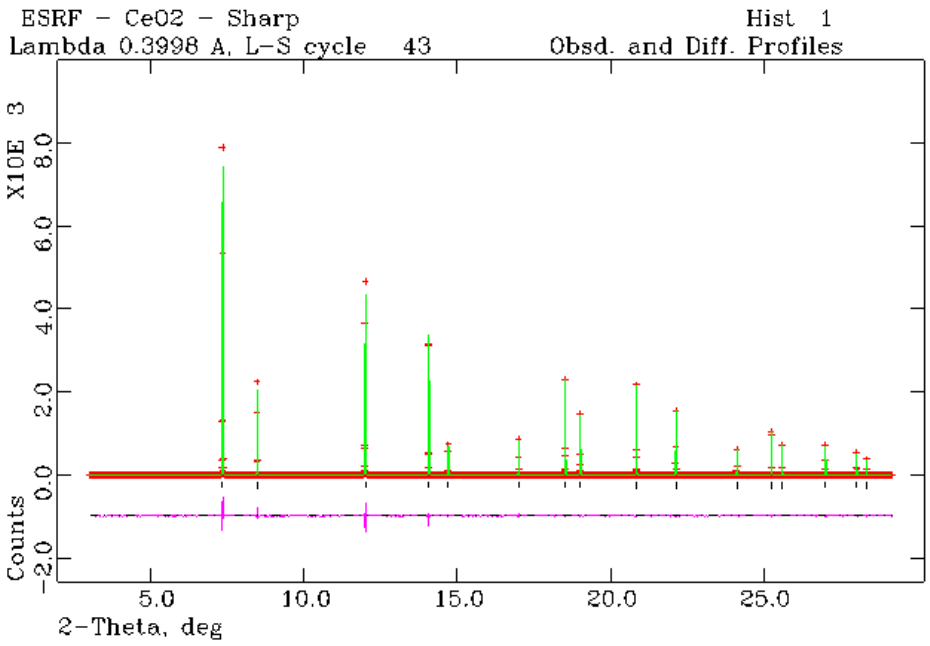
$\{\beta_{obs} - \beta_{inst}\}\cos \theta = \lambda/D_v + 4\,\varepsilon\{\sin \theta\}$

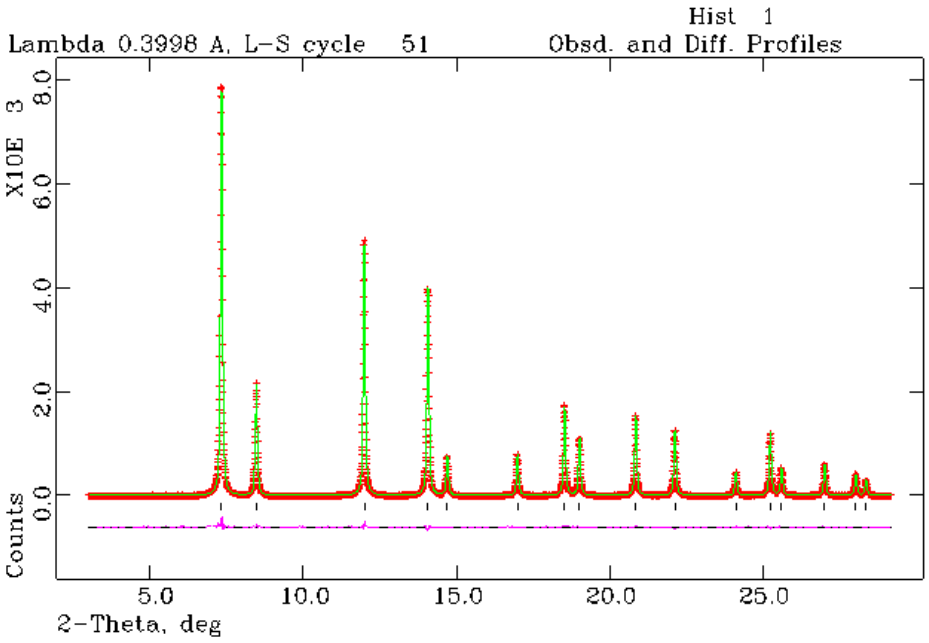
Williamson-Hall plot
-Plot $\beta\cos(\theta)/\lambda$ against $4 \sin(\theta)$
-Slope & intercept give size and strain



Size & Strain

CeO_2 before and after micronizing





Volume weighted domain size, D_v, of broadened CeO_2 is 226 Å and maximum strain, e is 0.011%

Summary

- Rietveld refinement a valuable quantitative analysis tool for determining…
  - Crystal structure information
    - atomic positions, thermal displacement parameters, occupancy
  - Other information
    - Preferred orientation, size, strain, quantitative analysis (including amorphous material)