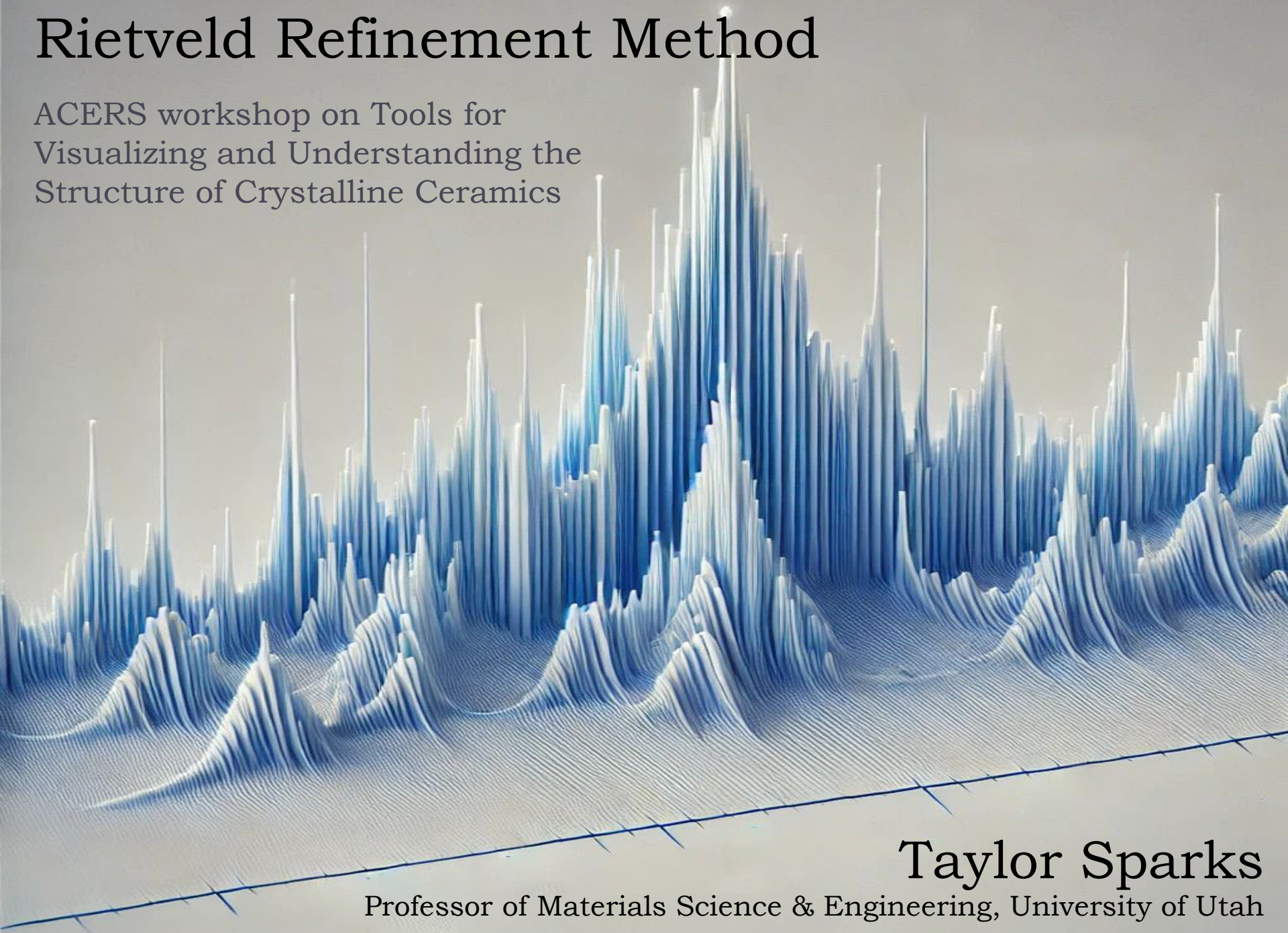


# Rietveld Refinement Method

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



Taylor Sparks

Professor of Materials Science & Engineering, University of Utah

# Overview

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- ▶ 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



# First, lets identify the software we use

## GSAS-II Home Page



### Contents

1. GSAS-II Installation Options
2. Available Documentation for GSAS-II
3. Mailing List
4. Reporting GSAS-II Bugs
5. Information for GSAS-II Developers
6. Compiling GSAS-II
7. Customized Python Installation
8. Web Proxies

Welcome to the home page for GSAS-II, a unique and comprehensive open source Python project for determination of crystal structures and diffraction-based materials characterization for crystalline solids on all scales, from perovskites through proteins, using both powder and single-crystal diffraction and with both x-ray and neutron probes. Refinements can combine measurements from laboratory and synchrotron x-rays, as well as constant wavelength or time-of-flight neutron sources. It provides structure solution and refinement, as well as extensive visualization capabilities.

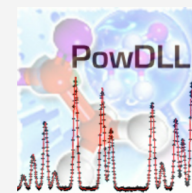
GSAS-II is made available for free use (see [license](#)) with open access to the [source code](#).

## PowDLL .NET converter for XRPD files

[Home \(Lab\)](#) [Download](#) [Hints'n'Tips](#) [Screenshots](#) [For programmers](#) [Updates](#) [Contact](#)

**PowDLL** is a .NET dynamic link library used for the interconversion procedure between variable formats of Powder X-Ray files. The DLL is capable of handling the most common file formats (binary and ASCII). The library can be used as a reusable component with any .NET language or as a **standalone utility**.

**PowDLL can run on windows OS as long as they have dotnet runtimes version 2 (or later) installed (i.e., Windows Vista SP1 or later). Linux is also supported through Wine.**



### Imports

Bruker/Siemens RAW (versions 1,2,4), Bruker BRML, STOE RAW (plus multi-range files), Scintag RAW (plus multi-range files), Rigaku RAW, Shimadzu RAW, Philips RD, Philips SD, Scintag RD, Panalytical XRDML, INEL Binary, INEL ASCII, Scintag ARD, powderCIF, Sietronics CPI, Riet7 DAT, DBWS, GSAS (CW STD), Jade MDI, Rigaku RIG, Philips UDF, UXD, XDA, XDD, CCDC Mercury XYE, XPOWDER PLV (old and new format), UDF (NEX), ProtoXRD and ASCII XY Files.

### Exports

Bruker/Siemens RAW (versions 1,2), Philips RD, Scintag ARD, Sietronics CPI, Riet7 DAT, DBWS, GSAS (CW STD), Jade MDI, Rigaku RIG, Philips UDF, UXD, XDA, XDD, Panalytical XRDML, ASCII XY Files, MS-Excel Multiple XY, Xpowder PLV files.

### Citation

Please cite if you find PowDLL useful:

PowDLL, a reusable .NET component for interconverting powder diffraction data: Recent developments, N. Kourkoumelis, ICDD Annual Spring Meetings (ed. Lisa O'Neill), Powder Diffraction, 28 (2013) 137-48.

# What is Rietveld refinement?

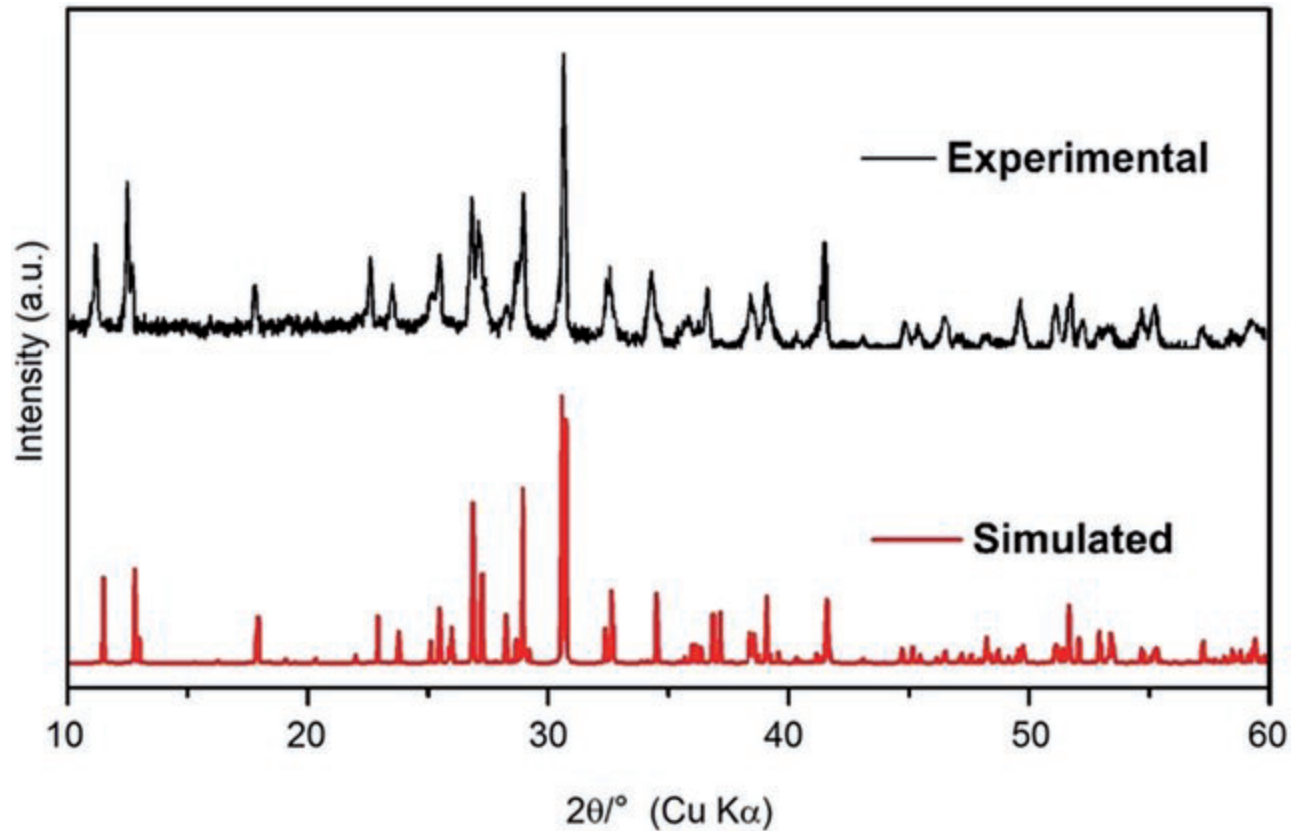
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- ▶ Hugo Rietveld (1969)
- ▶ Quantitative refinement tool
  - ▶ Calculated pattern vs measured pattern
  - ▶ Variable model parameters
  - ▶ Least-squares refinement
  - ▶ Account for errors during measurement (shift, zero)
- ▶ Different from LeBail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



# We can simulate patterns pretty well!

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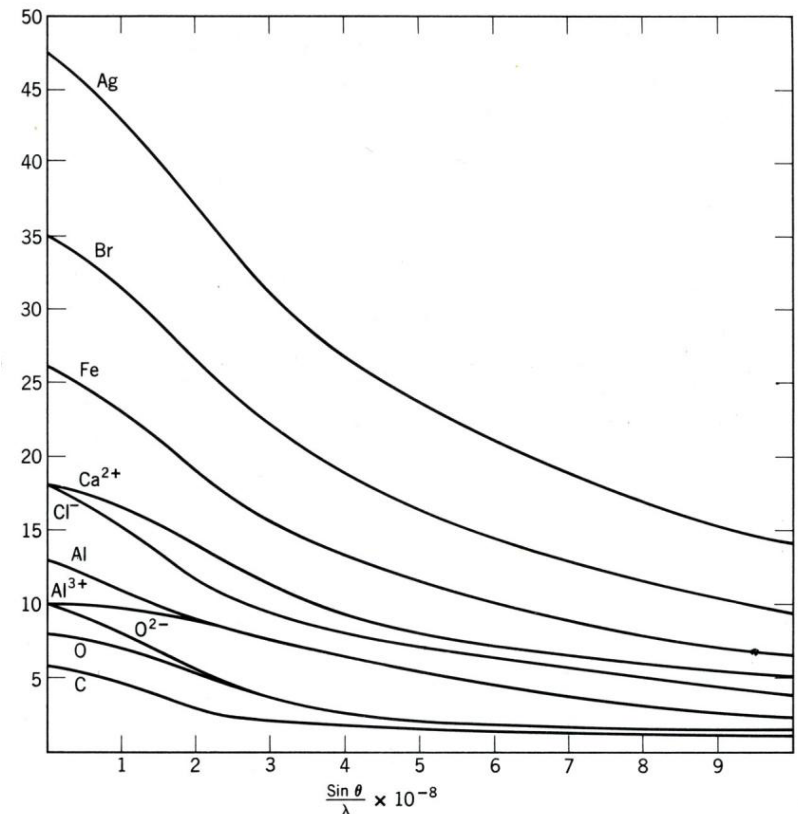


Intensity of a diffracted peak depends on many parameters!

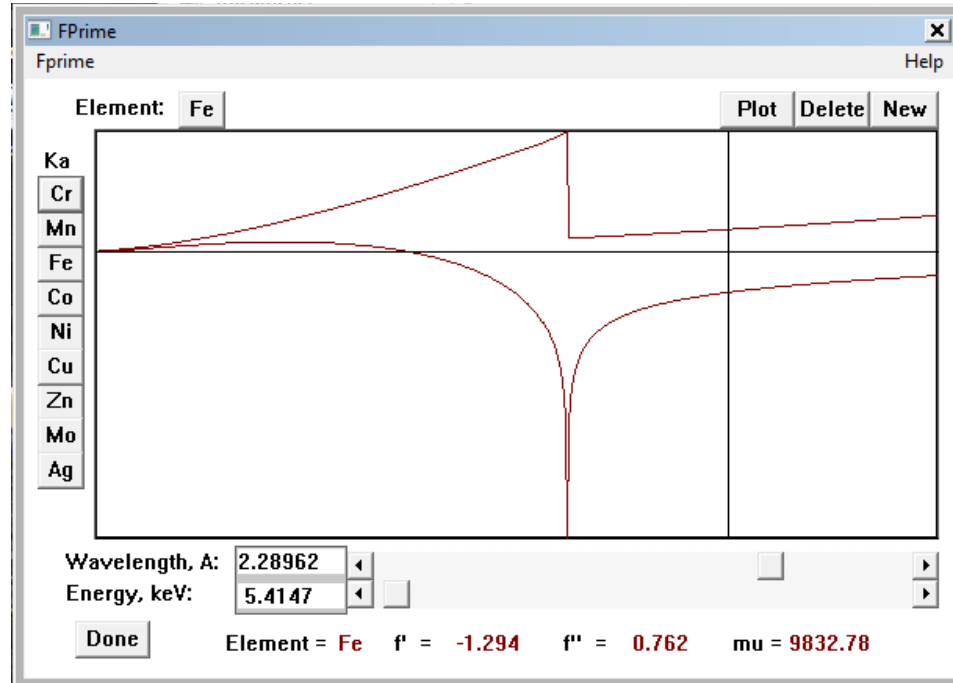
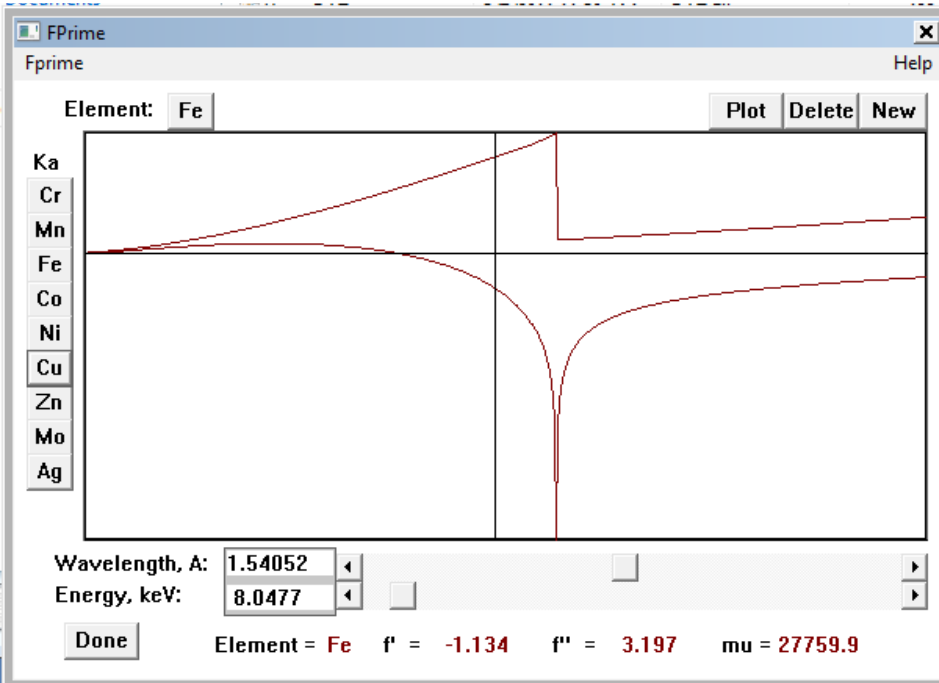
$$I_{(hkl)\alpha} = \frac{I_0 \lambda^3}{64\pi r} \left( \frac{e^2}{m_e c^2} \right)^2 \frac{M_{(hkl)}}{V_\alpha^2} |F_{(hkl)\alpha}|^2 \left( \frac{1 + \cos^2(2\theta) \cos^2(2\theta_m)}{\sin^2 \theta \cos \theta} \right)_{hkl} \frac{v_\alpha}{\mu_s}$$

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

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

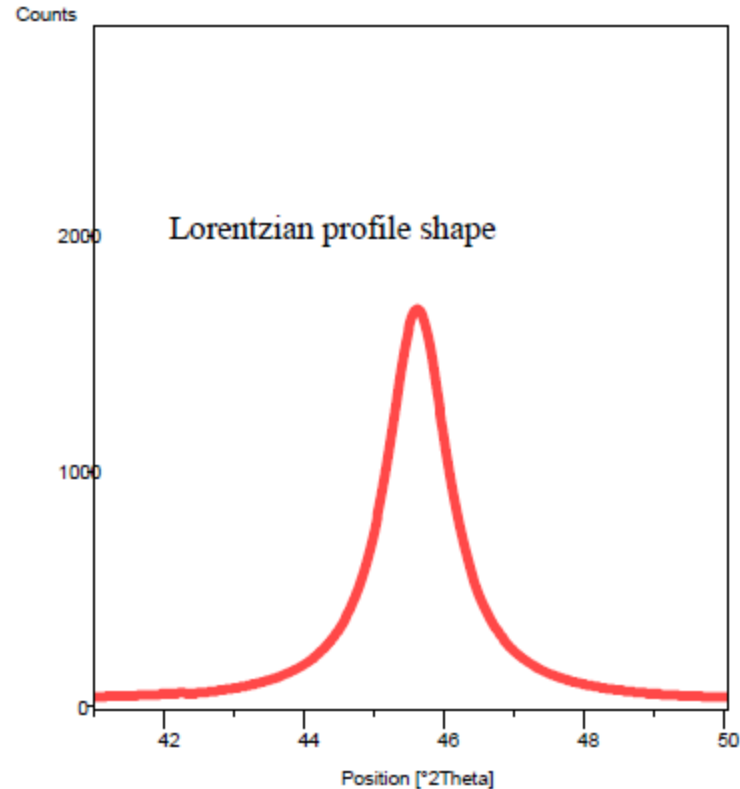
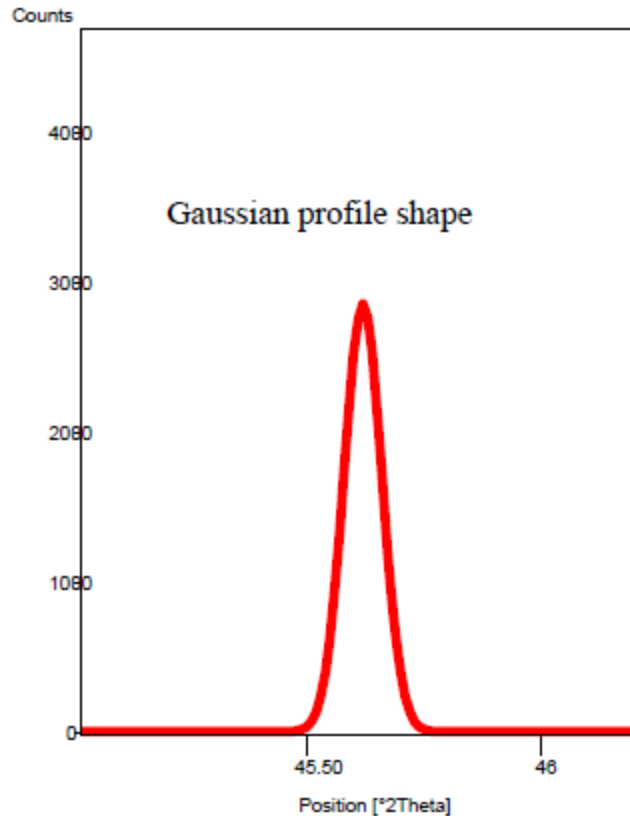


# Anomalous Scattering Factors $f'$ & $f''$ depends on radiation choice



# Different instruments yield different peak shape

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





# Quality of the Fit

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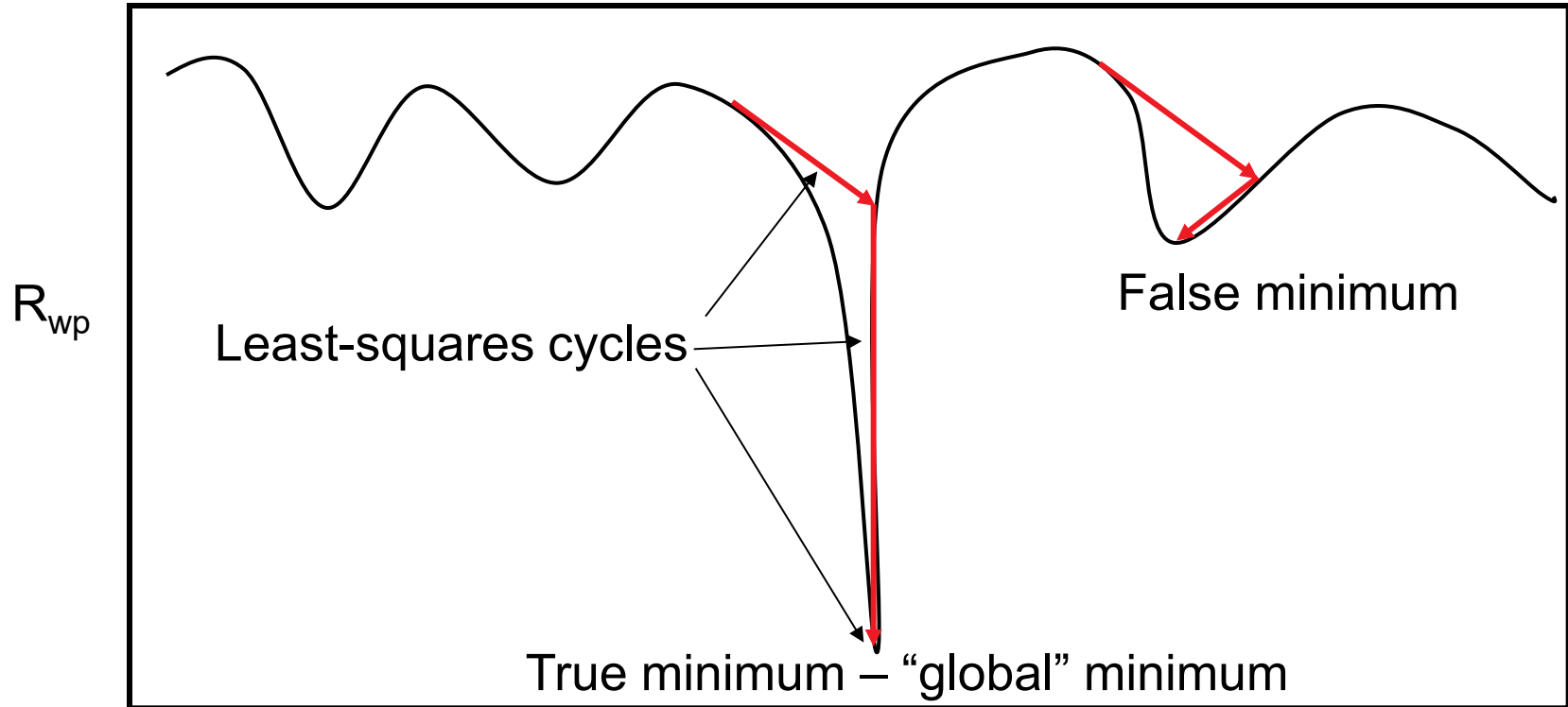
- ▶  $R_p$  is the difference between the observed and the calculated value
- ▶  $R_{wp}$  weights the residual so the higher intensity peaks are more important than low intensity ones

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

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

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

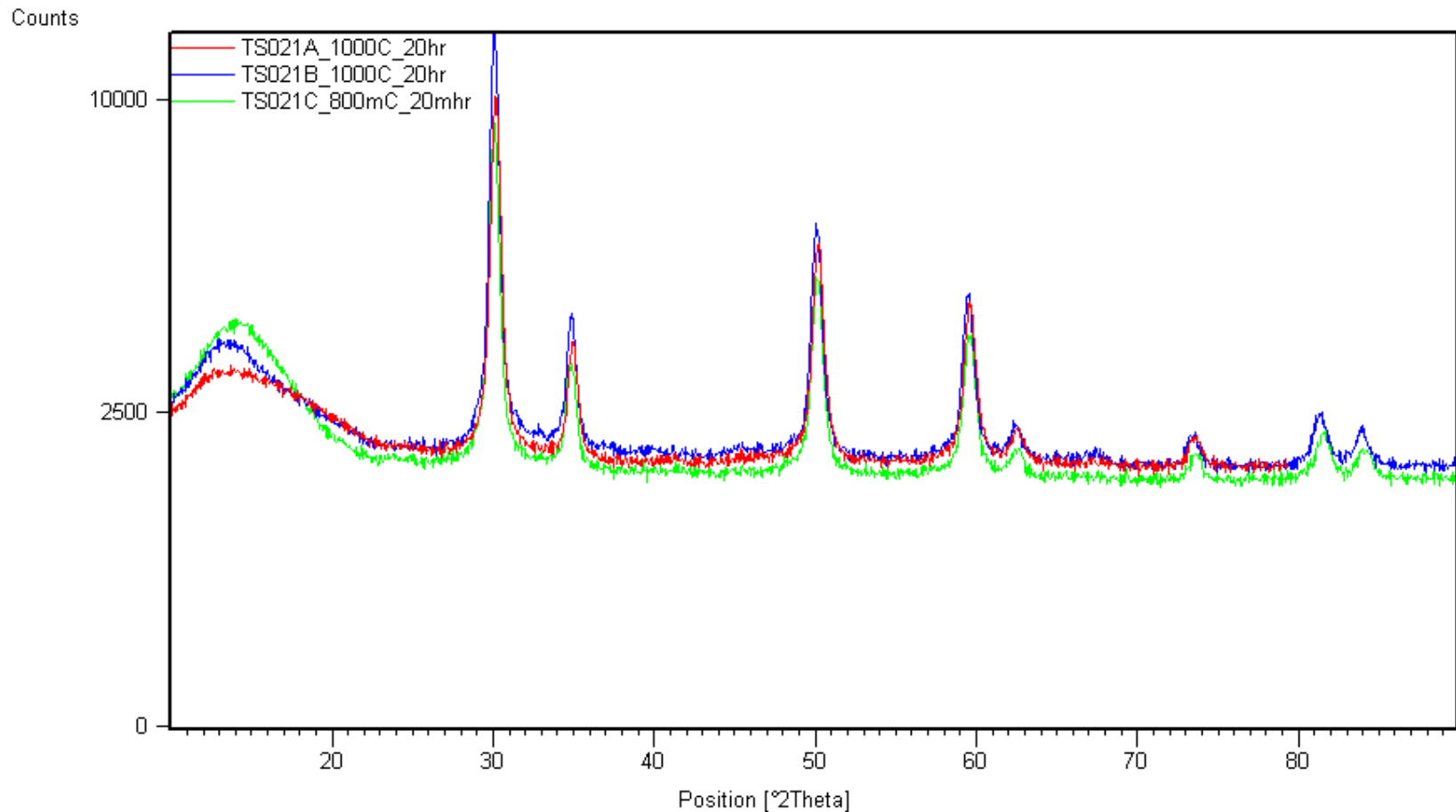
# Multiple cycles required to find the true global minimum in error



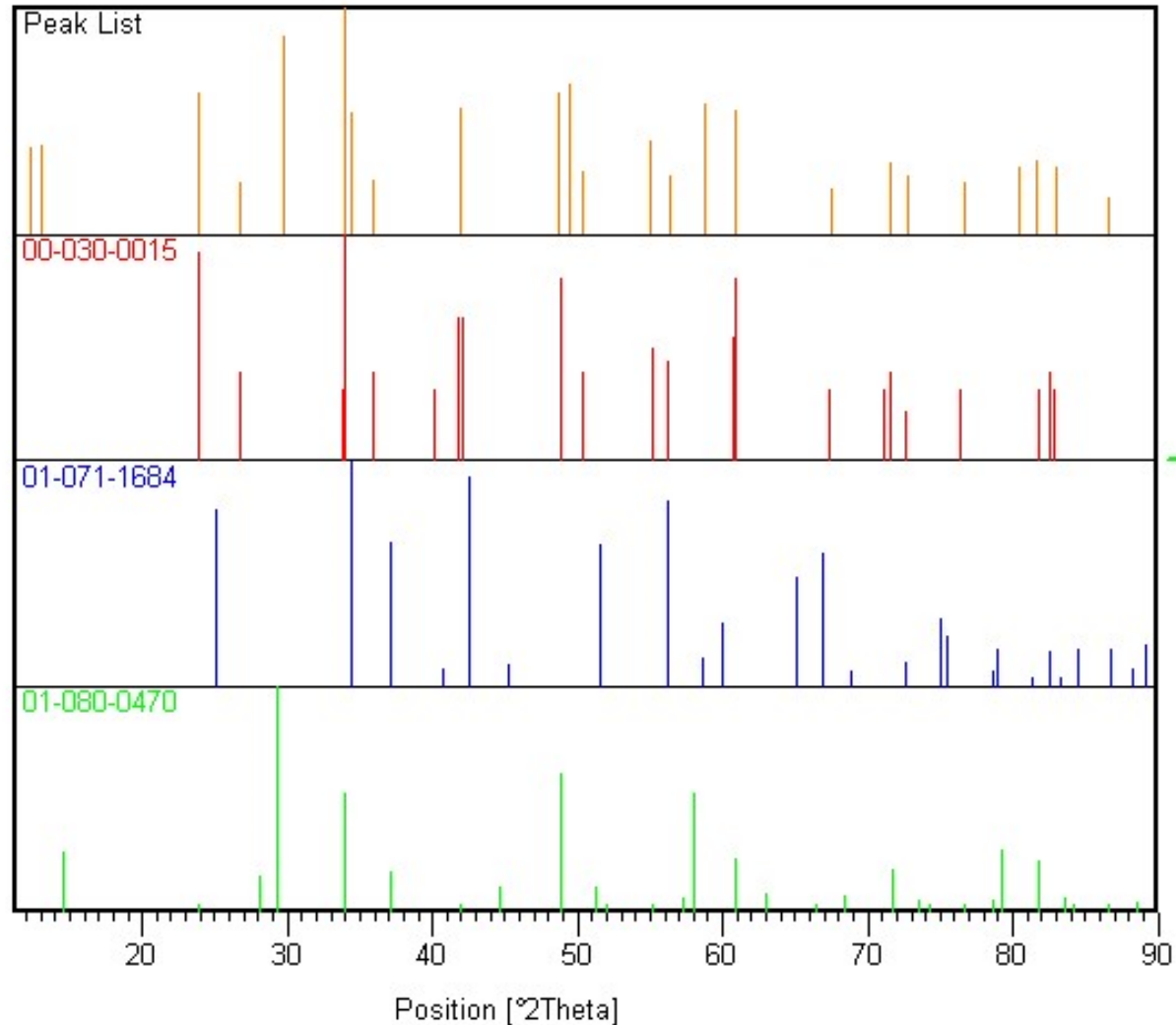
“A Rietveld refinement is never finished, only abandoned”  
- P.W. Stephens

# Quantitative Analysis of Multiple Phases Mixture

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# Quantitative Analysis of Multiple Phases Mixture



# Weight Fraction: “SMZ” Method

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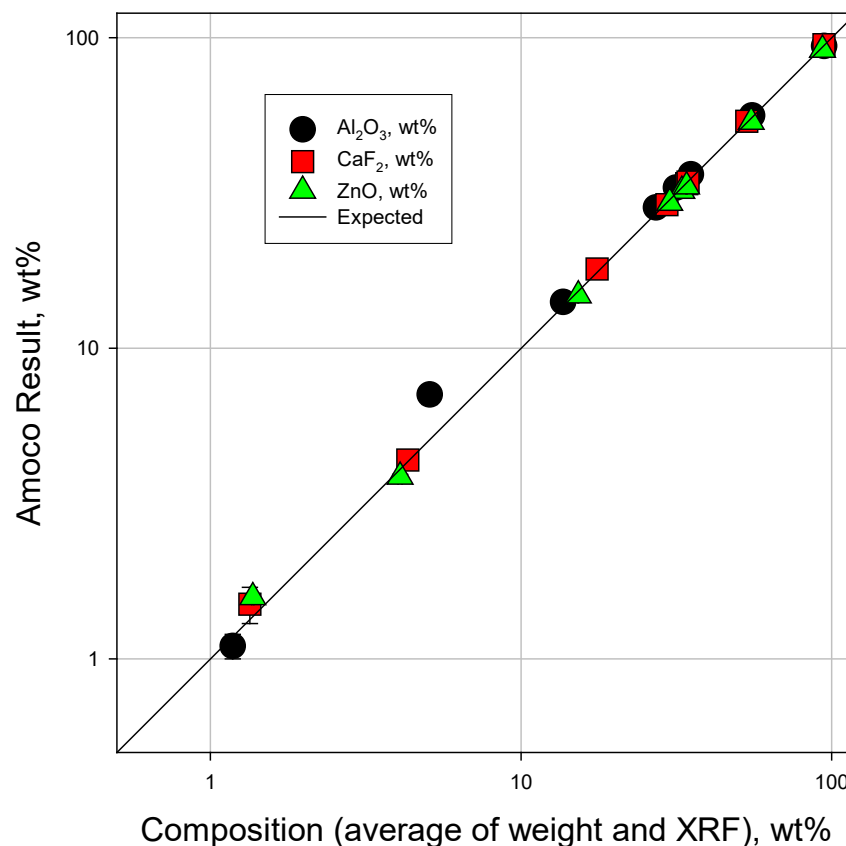
- ▶ S is phase fraction, proportional to number of unit cells measured
- ▶ M is the molecular weight
- ▶ Z is the number of formula units per unit cell
- ▶ SMZ is proportional to the concentration

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

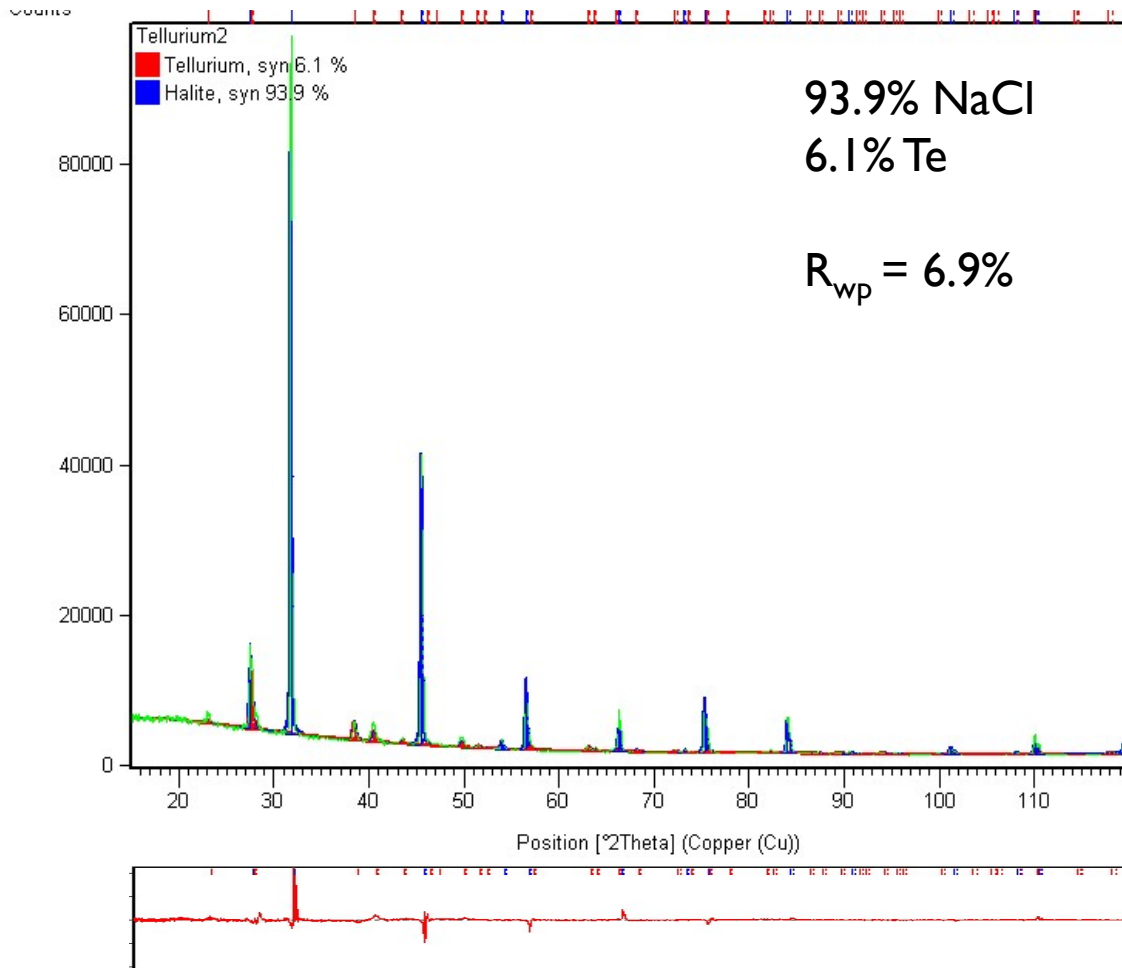


# How Good is the Quantitative Analysis?

CPD Rietveld QPA Round Robin  
Sample 1 Series  
Amoco Results



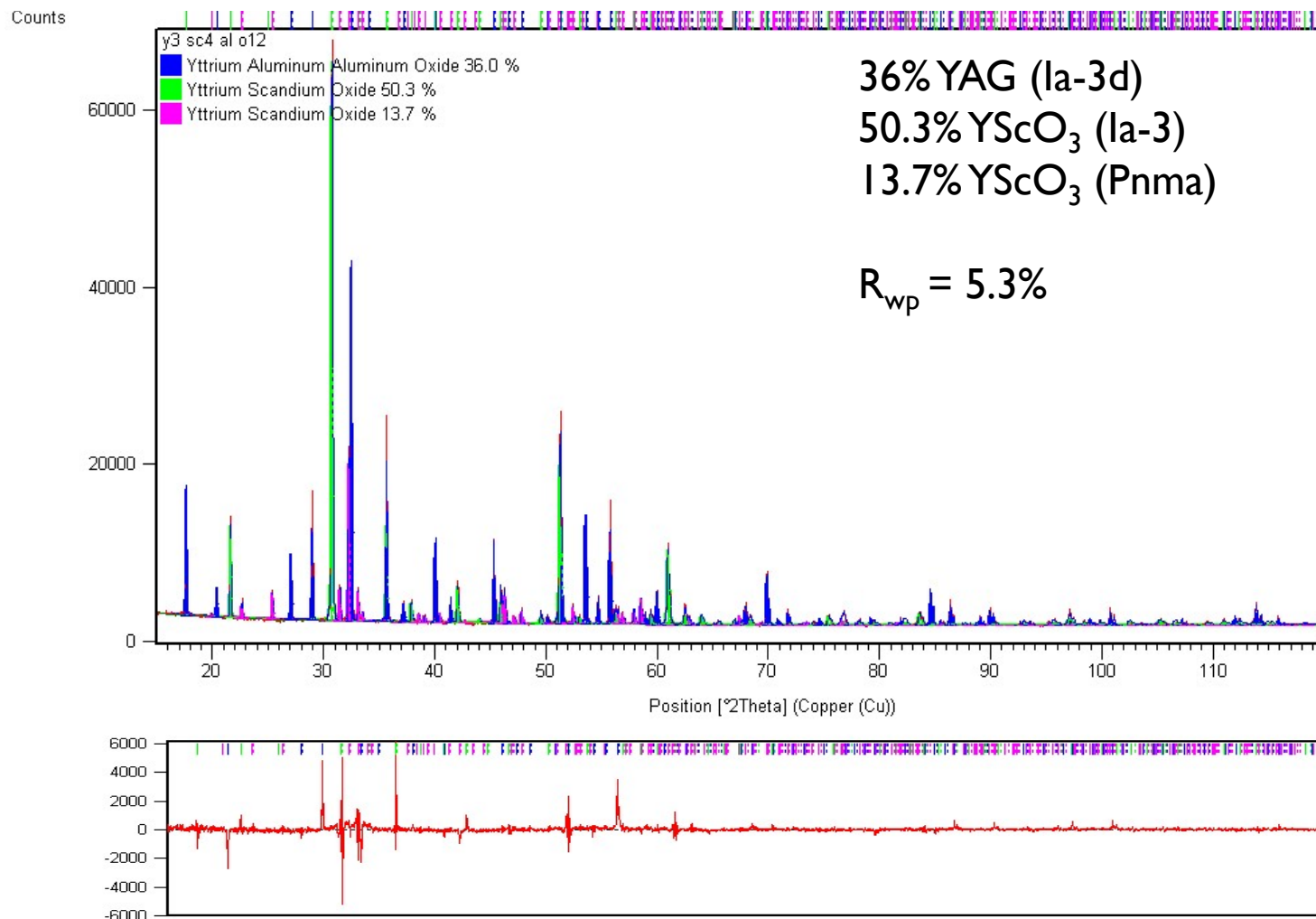
# Te Fraction in Seawater Medium



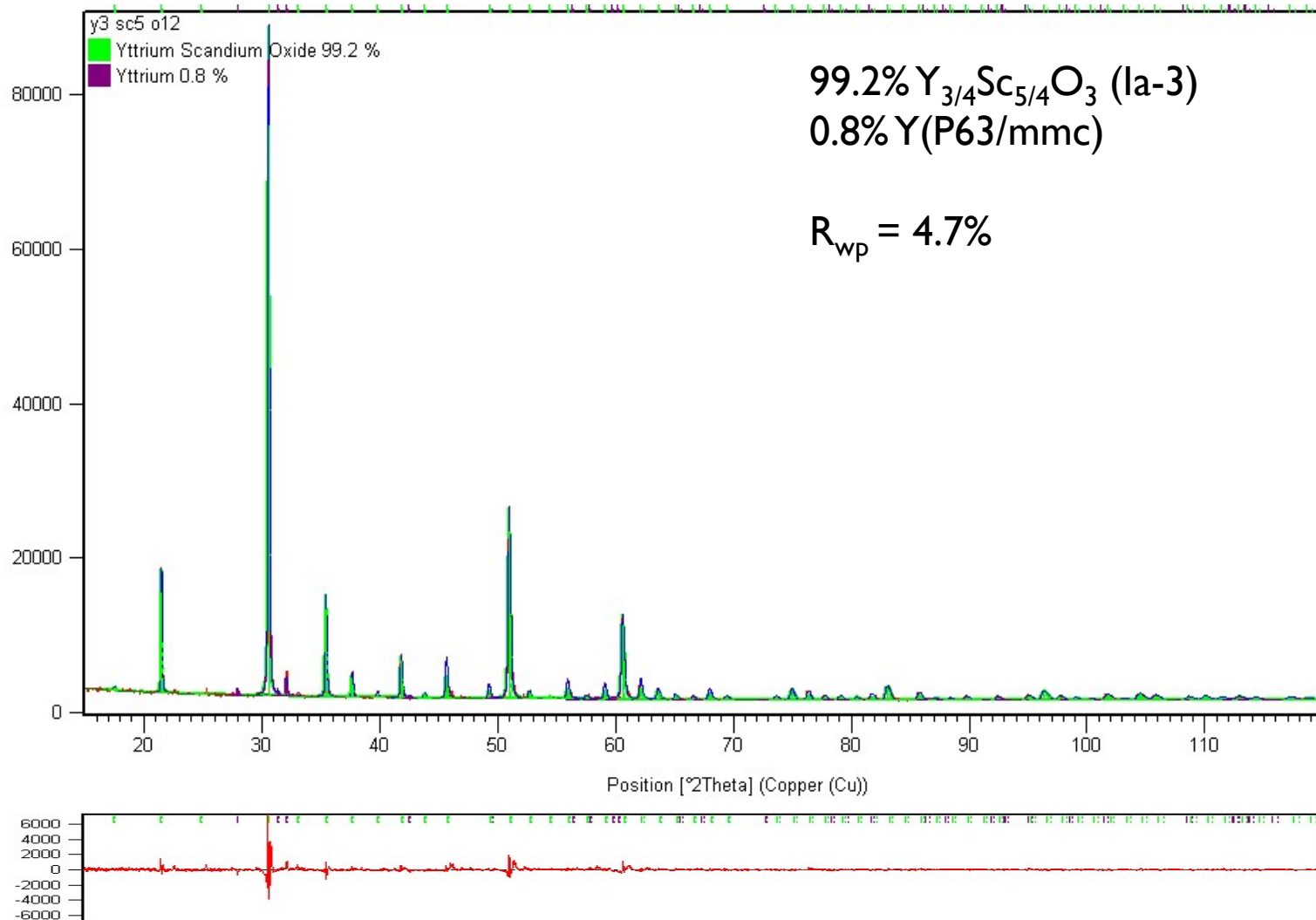
Errors: absorption (transparency), sample volume (more powder)



# $\text{Y}_3\text{Sc}_4\text{AlO}_{12}$ Intended Composition



# $\text{Y}_3\text{Sc}_5\text{O}_{12}$ Intended Composition



# Debye Equation for Amorphous Materials

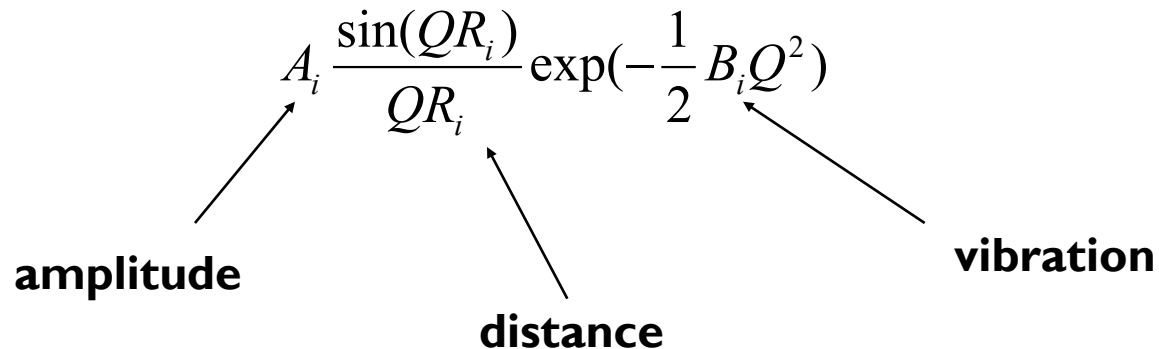
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Possible to determine percent amorphous material if standard is added in known amount.

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

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

**amplitude**                      **distance**                      **vibration**

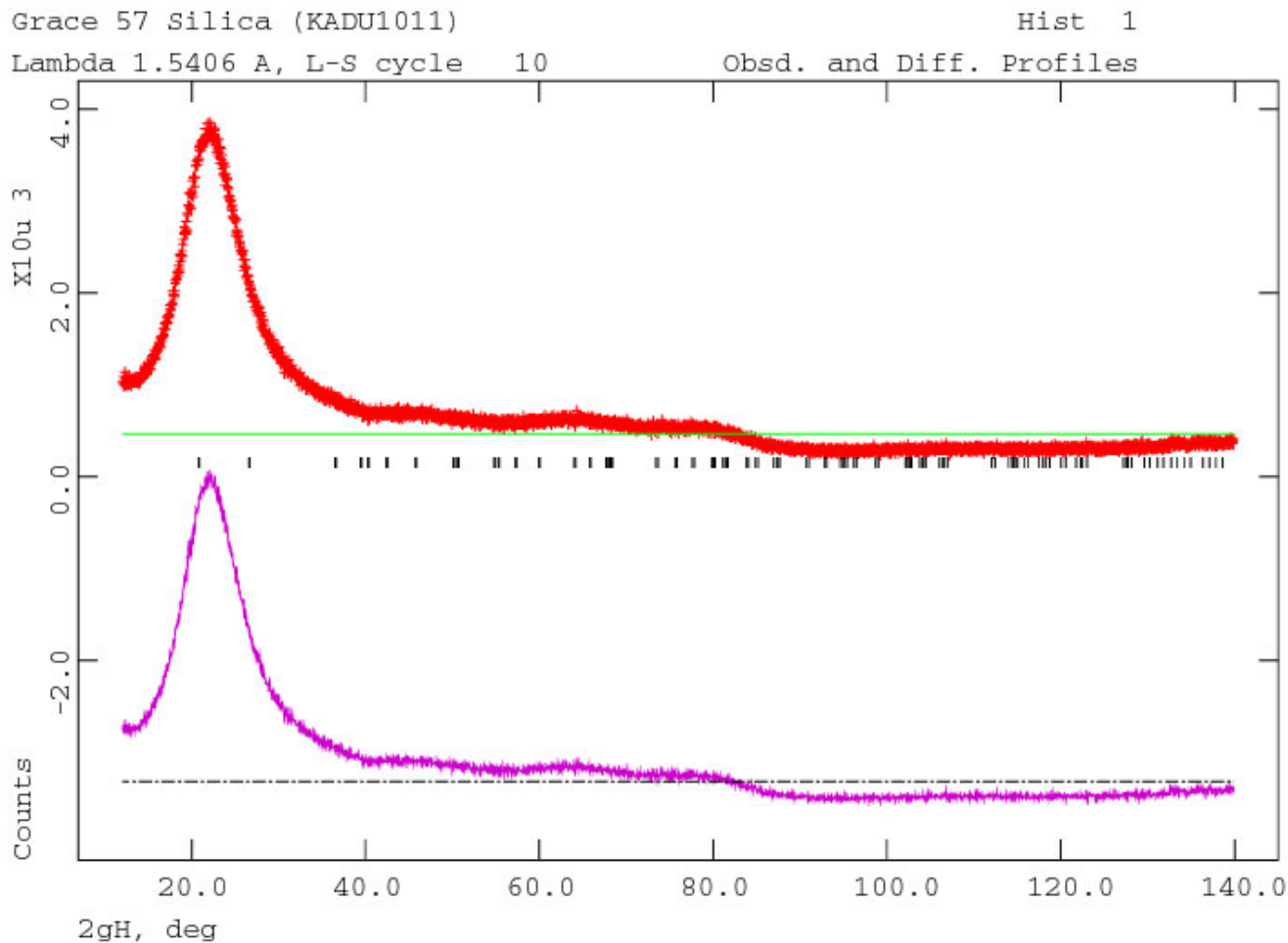


Need radial distribution function to determine bond distances for analysis

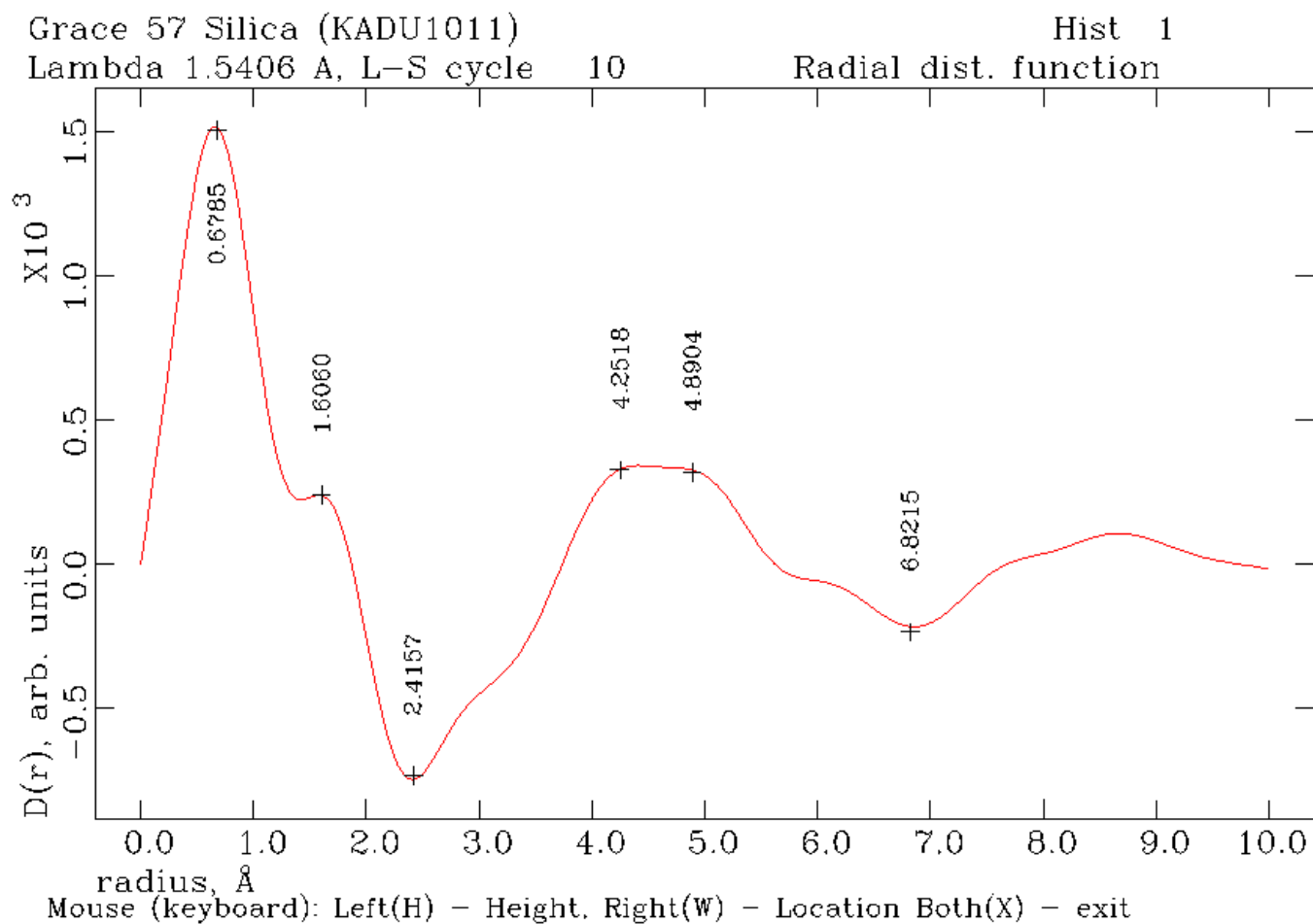
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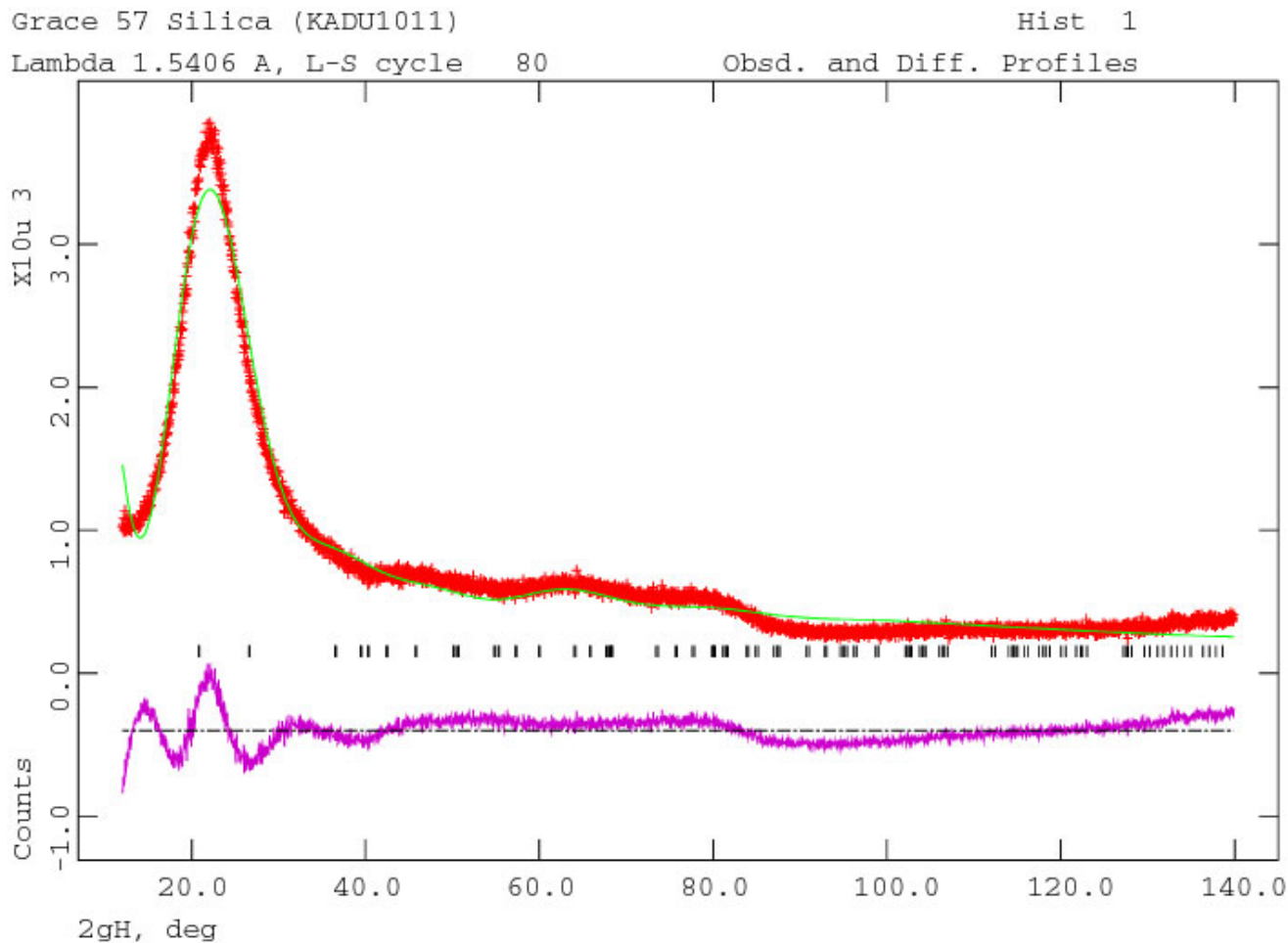
# Diffuse Scattering



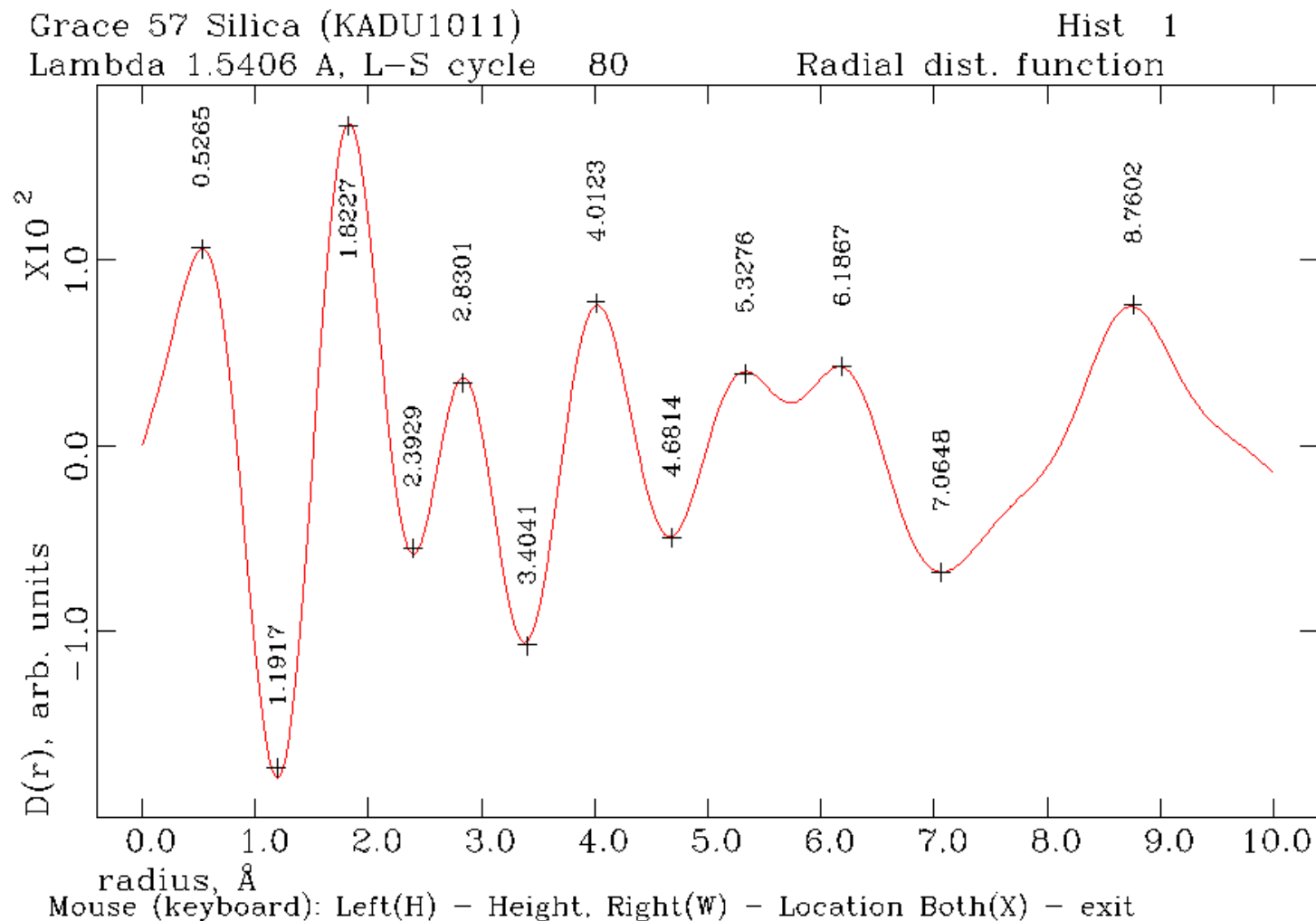
# Diffuse Scattering



# Diffuse Scattering

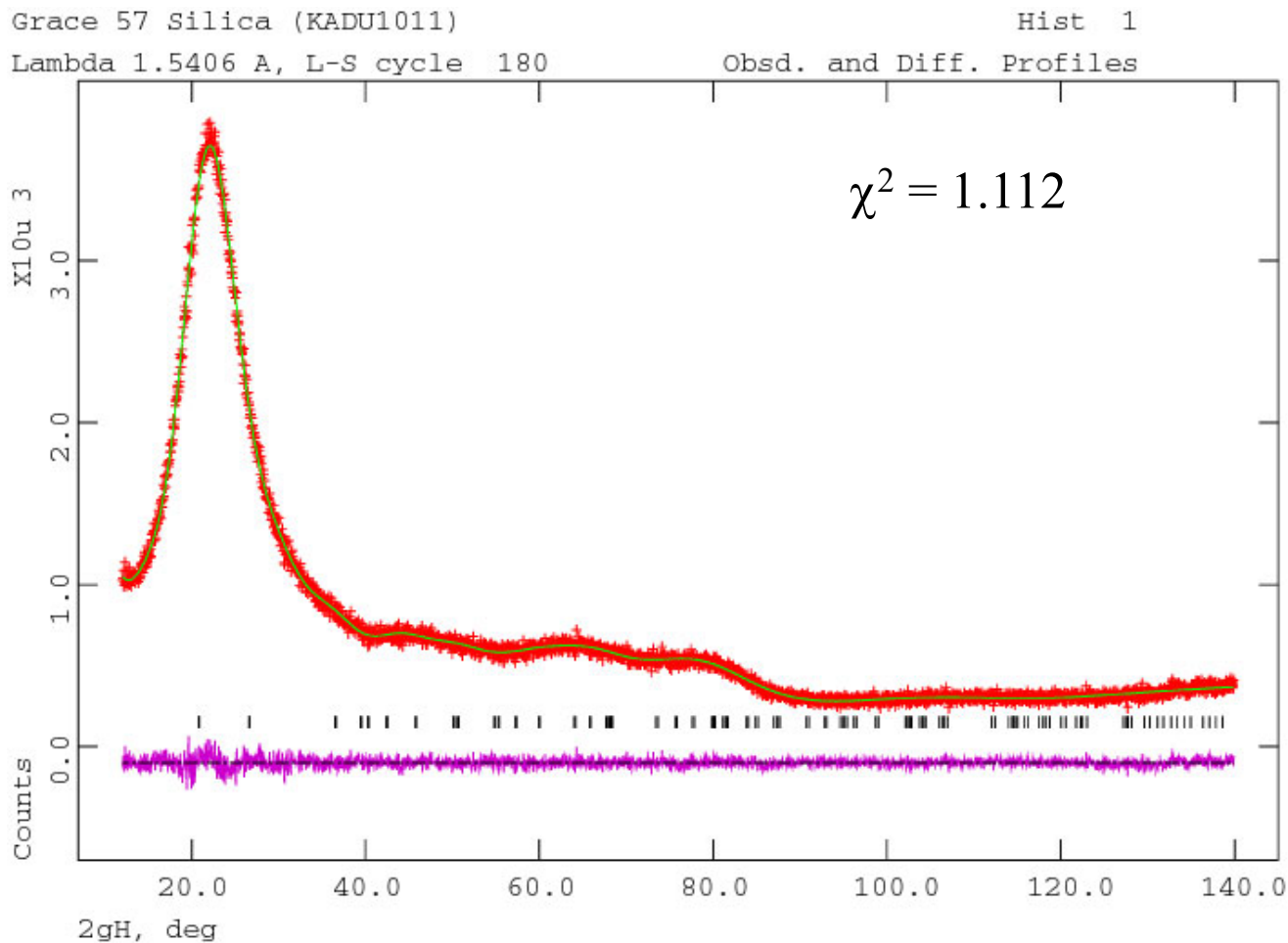


# Diffuse Scattering





# Diffuse Scattering



# Atomic Position & Site Occupancy

## ▶ $\text{Gd}_{8+x}\text{Ca}_{2+y}(\text{SiO}_4)_6\text{O}_{2+3x/2+y}$ system

### ▶ Anion/cation vacancies

## ▶ Lab XRD insufficient

- ▶ Impurity wt%?
- ▶ Volume change?
- ▶ Cation site preference?
- ▶ Meta-prism twist?

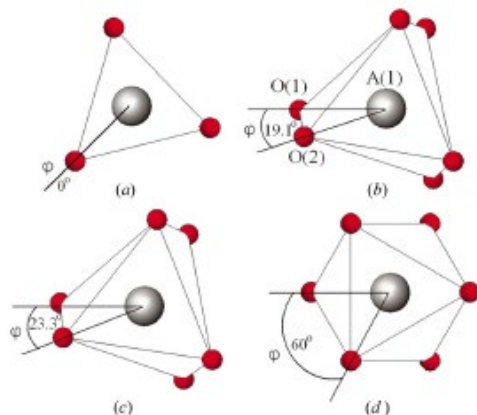
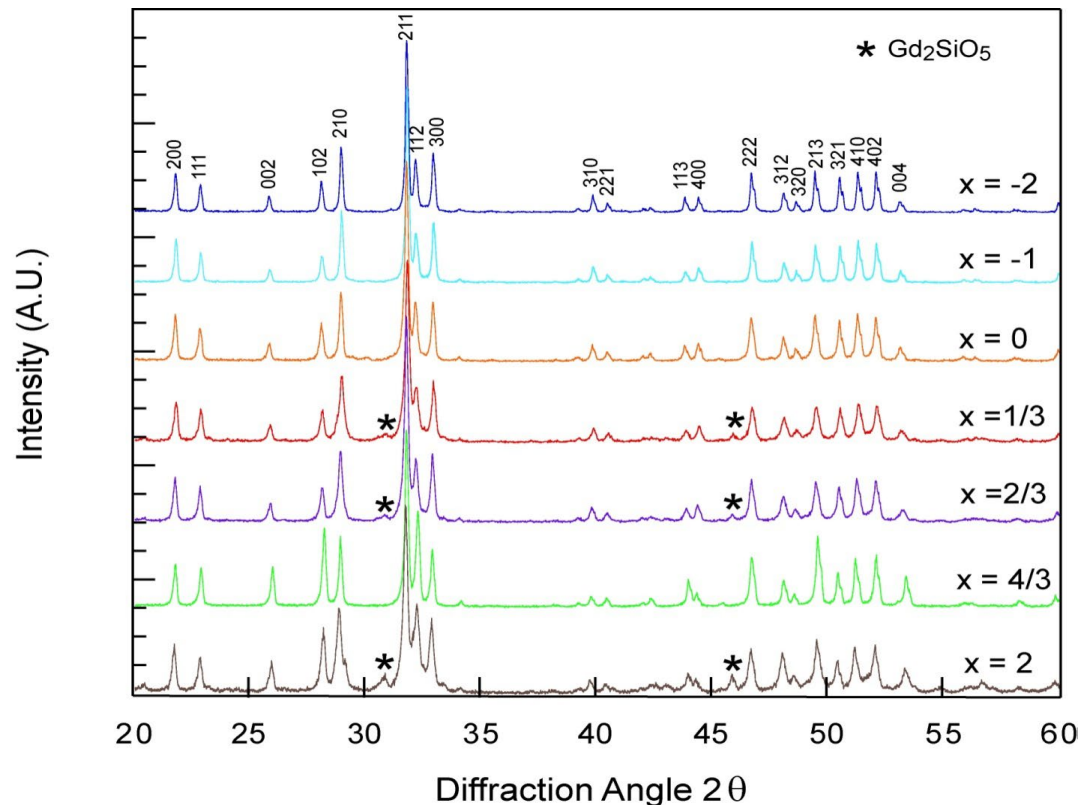
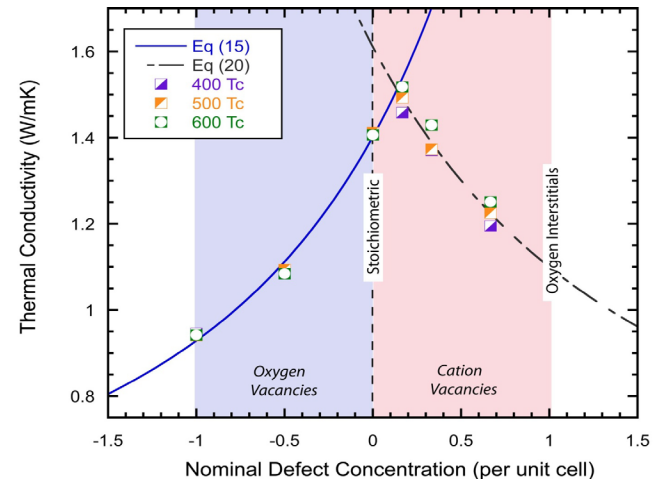


Figure 6  
Twist angles of  $A(1)O_6$  polyhedra in (a) models I and II, (b) chlorapatite, (c) fluorapatite, and (d) model III (as found in glaserite).

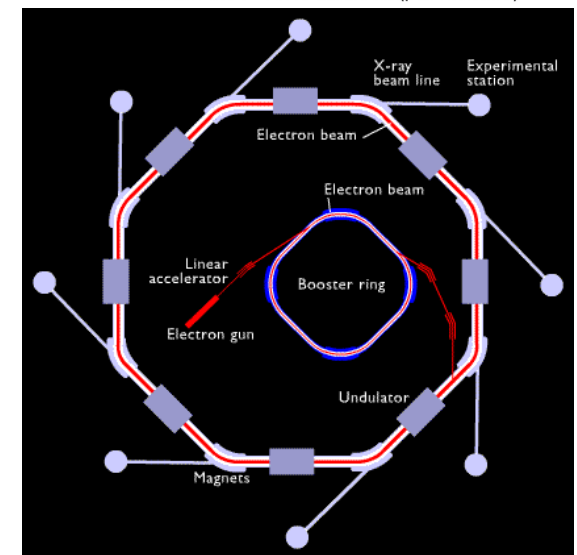


# Atomic Position & Site Occupancy

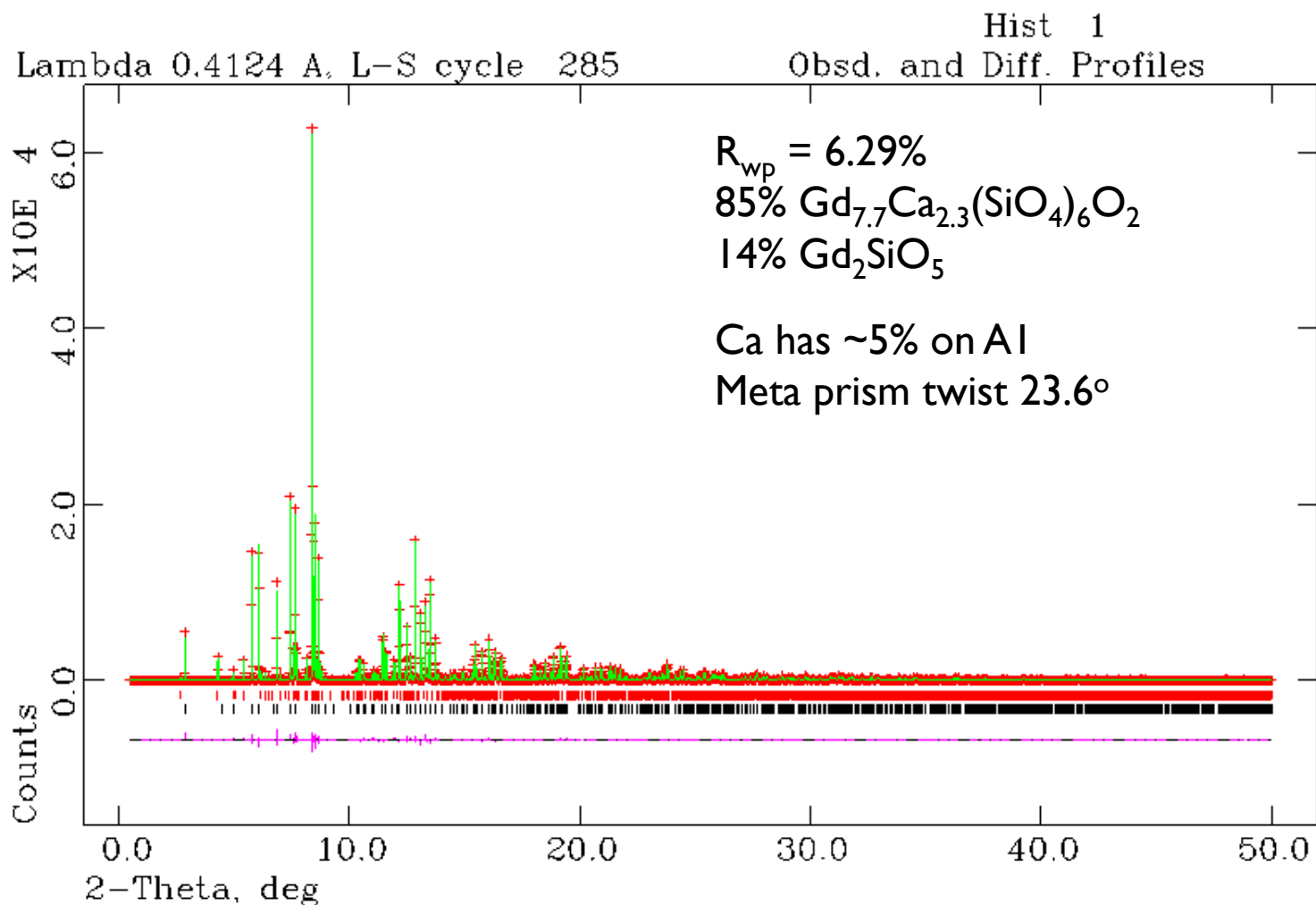
- ▶ Stoichiometric composition should have highest thermal conductivity
  - ▶ Phase separation?



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



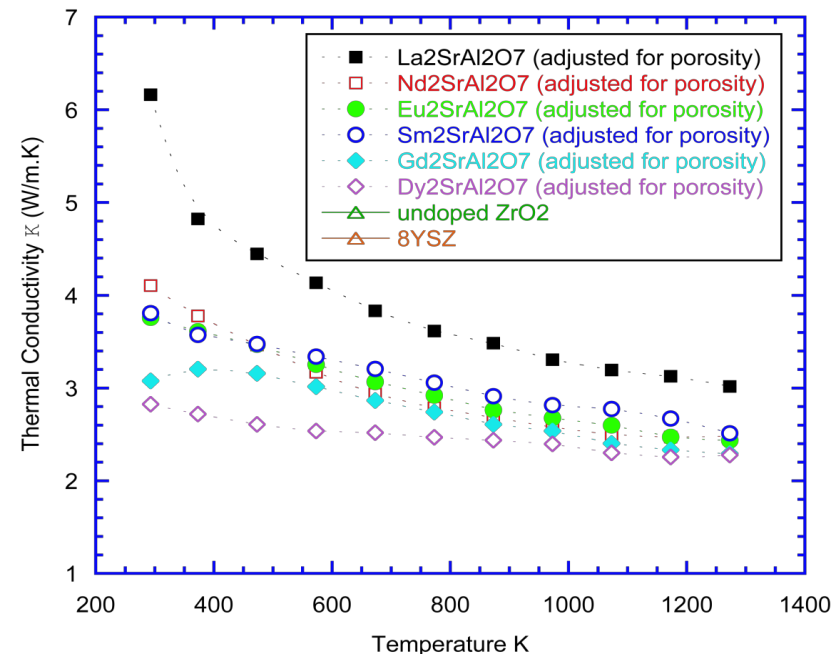
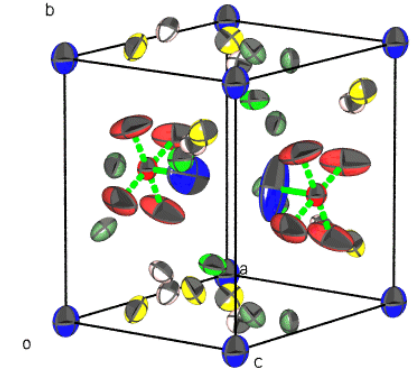
# Atomic Position & Site Occupancy



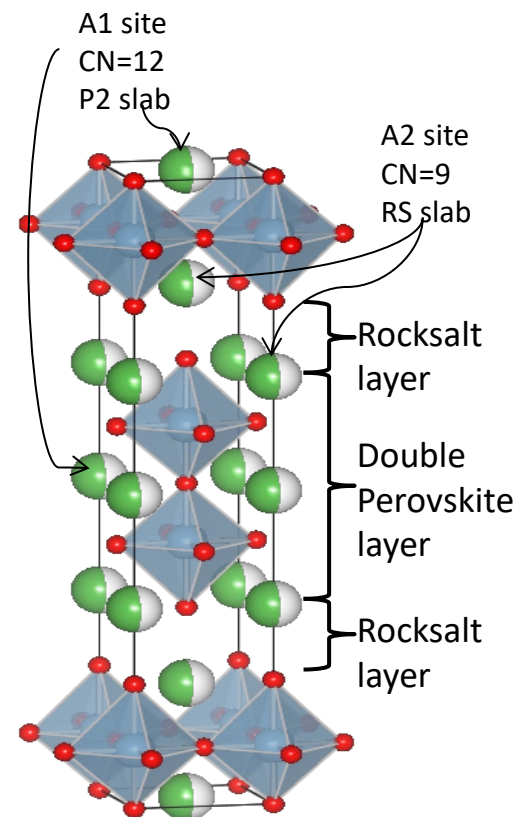
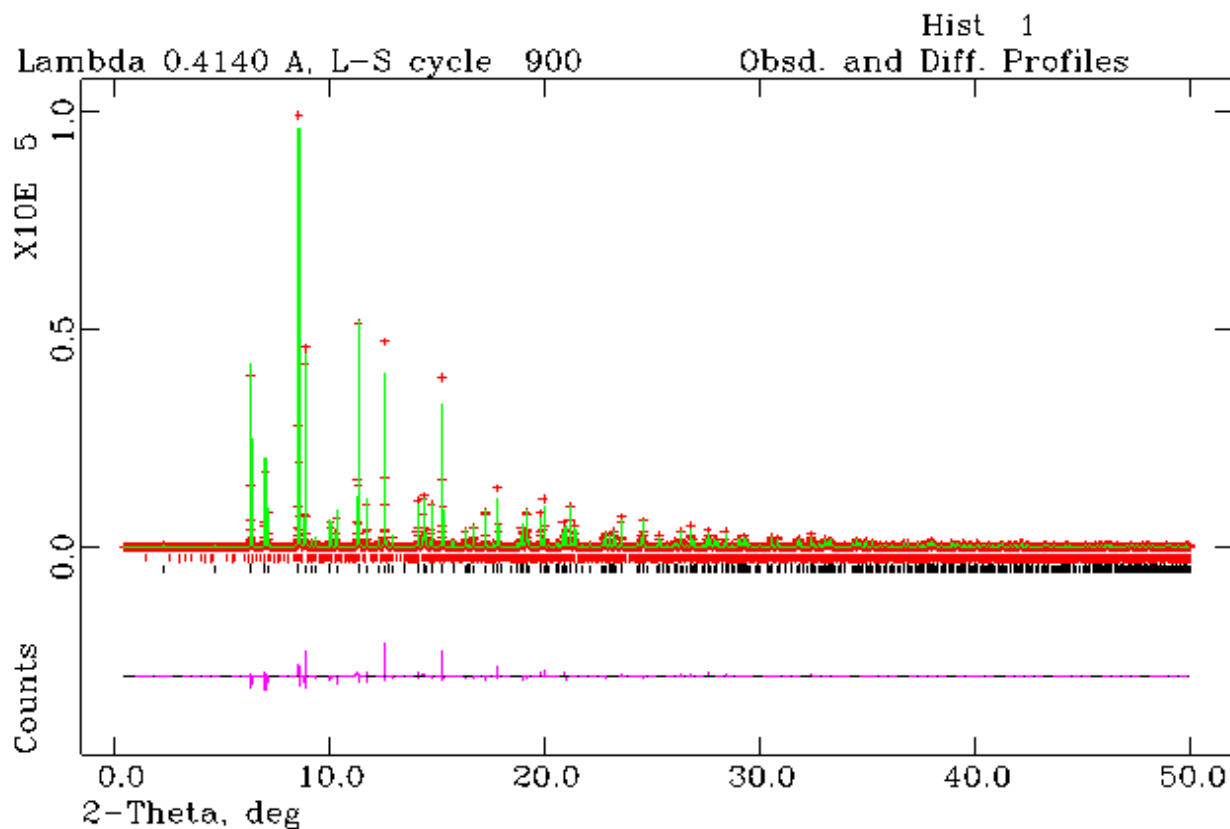
► Initial composition  $Gd_{8.333}Ca_{1.5}(SiO_4)_6O_2$

# Thermal Displacement Parameters

- ▶ Thermal vibrations quantitatively studied in Rietveld refinement
  - ▶  $U_{\text{iso}}$  or  $U_{ij}$  for anisotropic vibration
- ▶ Large  $U$  values could be due to rattling
  - ▶ Explanation of  $\text{RE}_2\text{SrAl}_2\text{O}_7$  thermal conductivity?

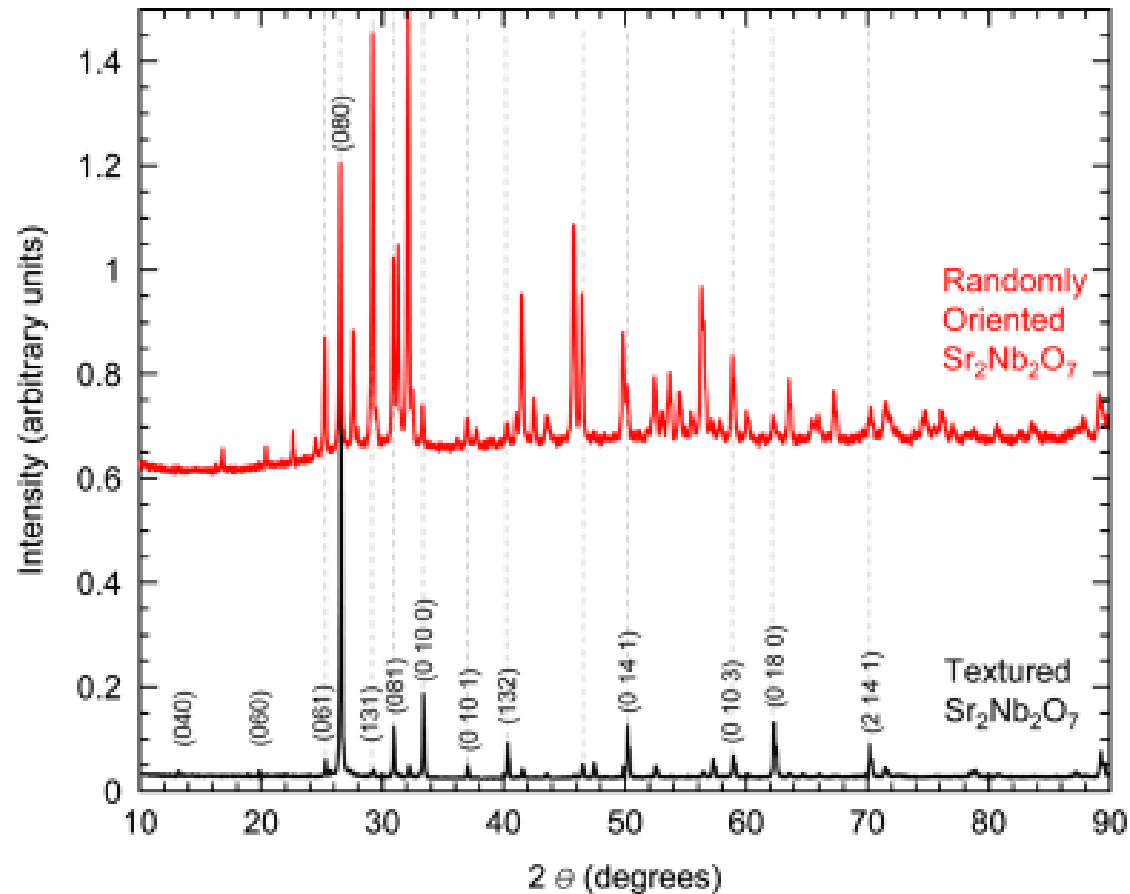


# Thermal Displacement Parameters



Composition	$\text{La}_2\text{SrAl}_2\text{O}_7$	$\text{Nd}_2\text{SrAl}_2\text{O}_7$	$\text{Sm}_2\text{SrAl}_2\text{O}_7$	$\text{Eu}_2\text{SrAl}_2\text{O}_7$	$\text{Gd}_2\text{SrAl}_2\text{O}_7$	$\text{Dy}_2\text{SrAl}_2\text{O}_7$
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

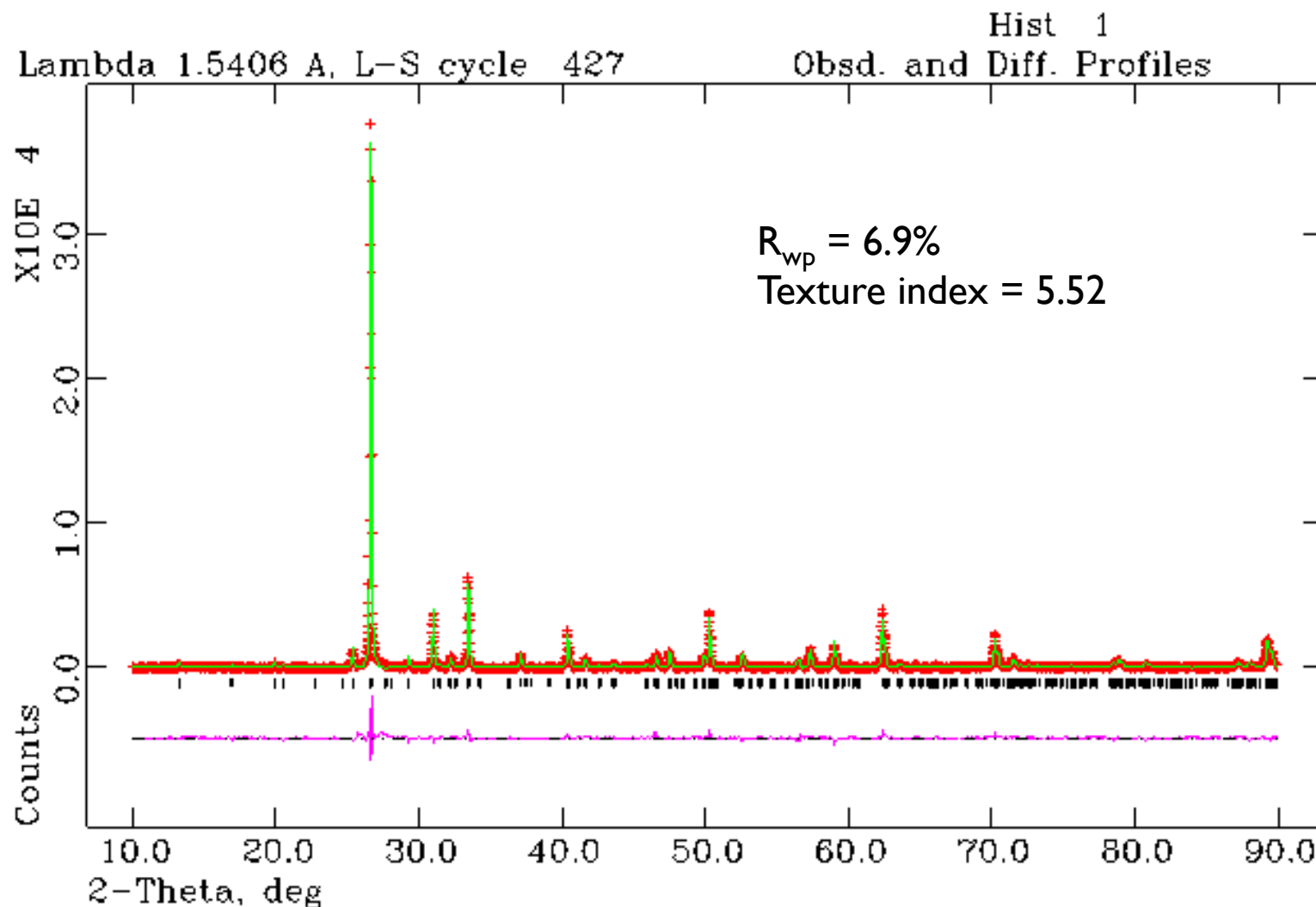
# Preferential Orientation: $\text{Sr}_2\text{Nb}_2\text{O}_7$



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



# Preferential Orientation $\text{Sr}_2\text{Nb}_2\text{O}_7$



► Note: Actual compound had small amount of  $\text{La}^{3+}$  doped on  $\text{Sr}^{2+}$  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.

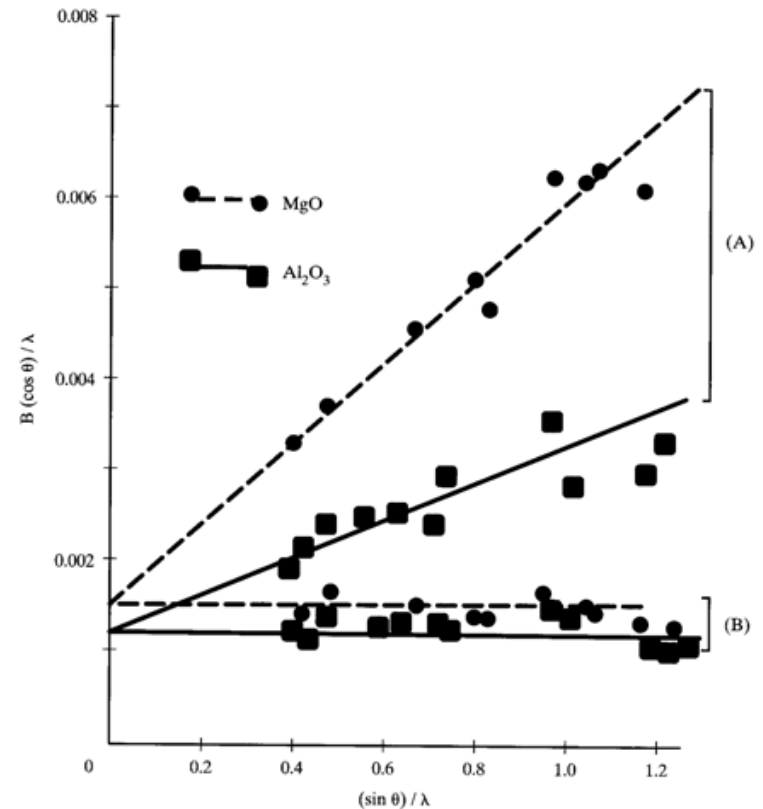
$$D_v = K\lambda / \{\beta \cos \theta\} \quad \varepsilon = \beta / \{4 \tan \theta\}$$

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

Williamson-Hall plot

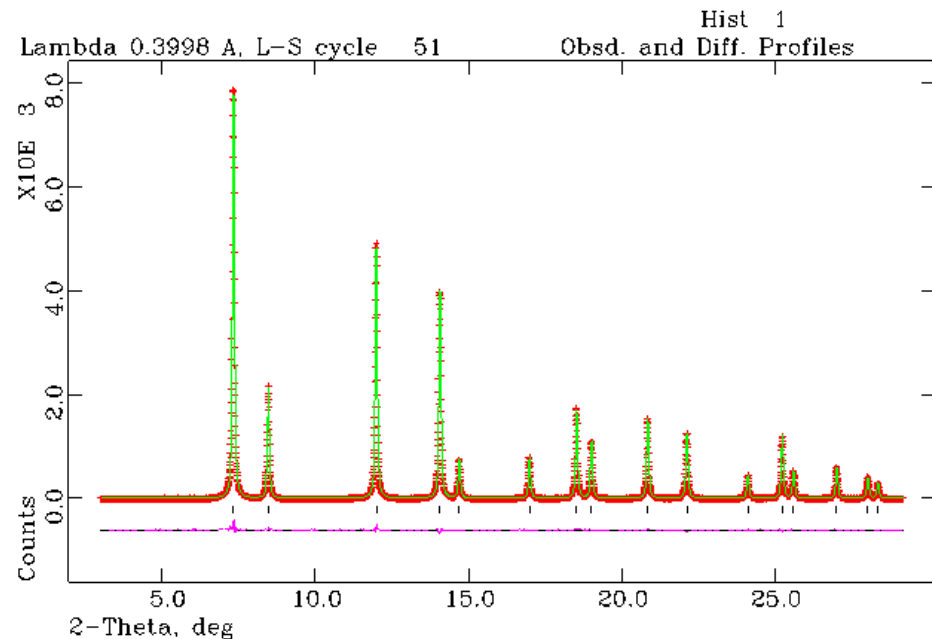
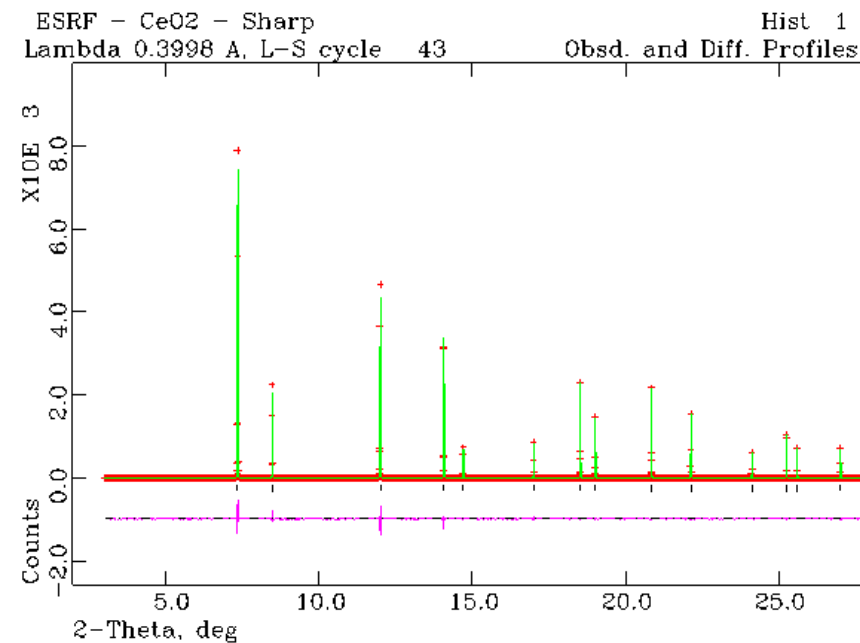
-Plot  $\beta \cos(\theta) / \lambda$  against  $4 \sin(\theta)$

-Slope & intercept give size and strain



# Size & Strain

CeO<sub>2</sub> before and after micronizing



Volume weighted domain size,  $D_v$ , of broadened CeO<sub>2</sub> is 226 Å and maximum strain,  $e$  is 0.011%

# Summary

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- ▶ 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)

