



Quantitative X-Ray Diffraction Analysis

Rietveld Refinement

Materials Characterization Facility (MCF)

Dr. Ian Lightcap



UNIVERSITY OF
NOTRE DAME

RESEARCH



Materials Characterization Facility (MCF)

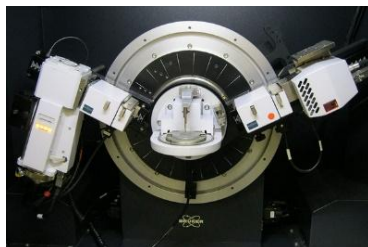
Mission Statement

The MCF provides researchers with high quality data, driving every aspect of its major goals, including to provide excellent training, customer service, education, and instrument acquisition.

Internal Services

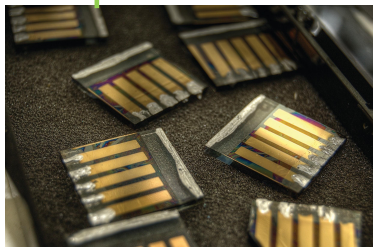
- Free Consultation (with complimentary sample analysis)
- Individual Training and Group Workshops
- Instrument Utilization Grants

Instruments and Capabilities



Crystallography

- Powder X-ray Diffractometer (XRD)
- Single Crystal XRD
- High Resolution XRD with X-ray Reflectometry (XRR), Reciprocal Space Mapping (RSM) and Grazing Incidence Diffraction (GID)



Electrochemistry

- Potentiostat with rotating disc electrodes and electrochemical impedance capabilities



Gas Analysis

- Gas Chromatograph with Mass Spectrometry (GC-MS)
- GC-FID and GC-TCD
- GC-MS Triple Quad
- Thermal Desorption and SPME Capabilities



Polymer/Particle Analysis

- Size Exclusion Chromatography (SEC)
- Dynamic Light Scattering (DLS) with Zetasizer
- Particle Size and Shape Analyzer

Materials Characterization Facility (MCF)

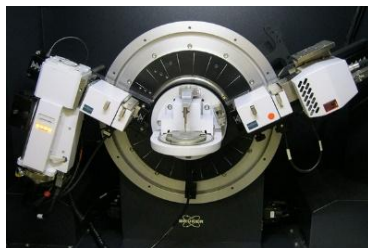
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Instruments and



Crystallography

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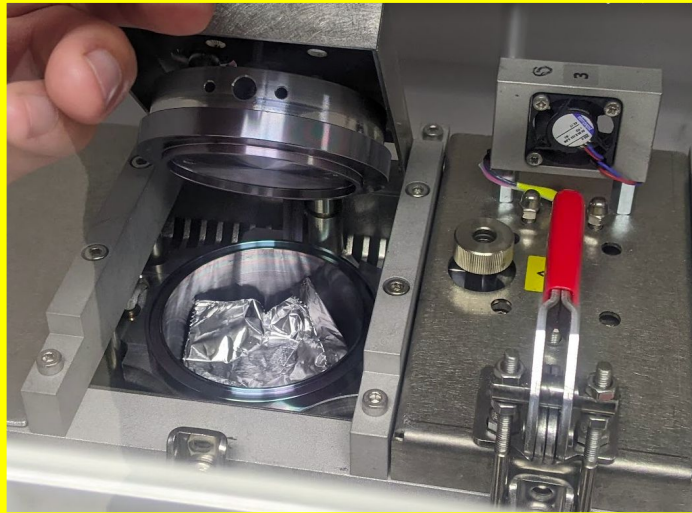
Materials

Mission Statement

The MCF provides exceptional analytical services to our customers.

Internal Services

- Free Consultation (with complimentary sample analysis)
- Individual Training and Group Workshops
- Instrument Utilization Grants



Facility (MCF)



Capabilities

- GC-FID and GC-TCD
- GC-MS Triple Quad
- Thermal Desorption and SPME Capabilities
- Dynamic Light Scattering (DLS) with Zetasizer
- Particle Size and Shape Analyzer

Materials Characterization Facility (MCF)



- High Resolution XRD with X-ray Reflectometry (XRR), Reciprocal Space Mapping (RSM) and Grazing Incidence Diffraction (GID)

Impedance capabilities

- GC-FID and GC-ICD
- GC-MS Triple Quad
- Thermal Desorption and SPME Capabilities

- Size Exclusion Chromatography (SEC)
- Dynamic Light Scattering (DLS) with Zetasizer
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Materials Characterization Facility (MCF)



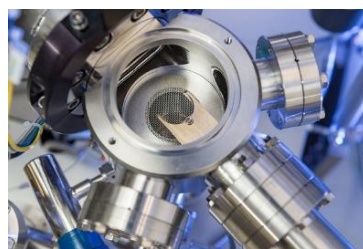
Rheometry/DMTA/ Tribology

- Hybrid Rheometer



Spectroscopy

- FTIR
- Confocal Raman Microscope
- Solar Simulators
- UV-Vis with near-IR, integrating sphere, and in-situ environmental capabilities



Surface Analysis

- BET ASAP 2020 Surface Area and Porosity Analyzer
- Profilometer for film step heights and surface topography
- Atomic Force Microscopy (AFM)
- XPS with imaging and depth profiling capabilities
- Electron Microprobe
- X-ray Fluorescence (XRF) analyzer



Synthesis

- Microwave Reactor
- Thermal Evaporator



Thermal Analysis

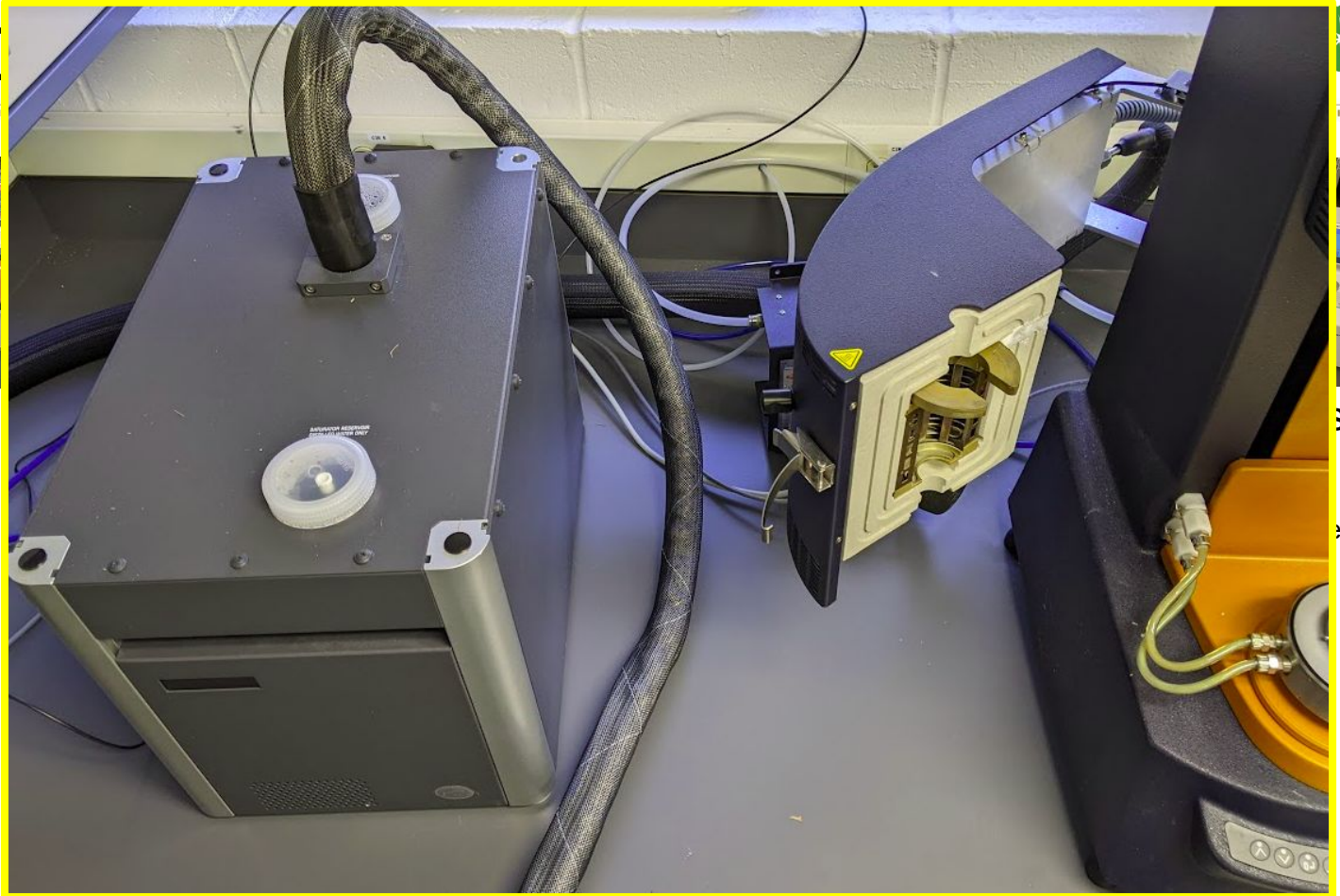
- Calorimeter – Drop Solution
- Isothermal Calorimeter for reactions and mixing
- DSC and TGA/DSC with Mass Spectrometry

Materials C



Rheometry/DMTA/
Tribology

- Hybrid Rheometer



(XRF) analyzer

Materials Characterization Facility (MCF)



Rheometry/DMTA/ Tribology

- Hybrid Rheometer

Spectroscopy

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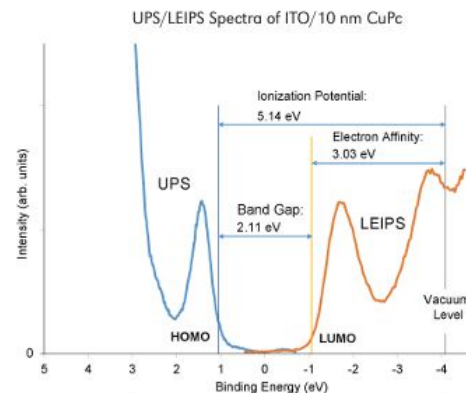
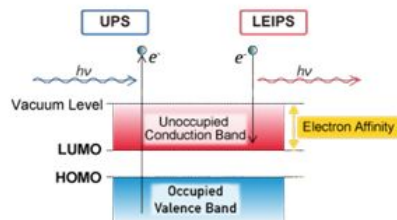


Thermal Analysis

- Calorimeter – Drop Solution
- Isothermal Calorimeter for reactions and mixing
- DSC and TGA/DSC with Mass Spectrometry

Measurement of Both the Occupied and Unoccupied Electronic Energy Levels of a Sample

Combining the energy measurement of the occupied (valence) level obtained by UPS and the energy of the unoccupied (conduction) level obtained by LEIPS provides the whole picture of the band structure for a semiconductor film:



- The ionization potential can be obtained from the highest occupied molecular orbital (HOMO) of the UPS measurement.
- The electron affinity can be obtained from the lowest unoccupied molecular orbital (LUMO) of the LEIPS measurement.
- *From the difference in these two values, the semiconductor band gap energy can be calculated.*



Thermal Analysis

DSC – Drop
on
Thermal Calorimeter
Reactions and
g
and TGA/DSC
Mass
Spectrometry

(XRF) analyzer

Material



Rheometry/ Tribology

- Hybrid Rheome



Thermal Analysis

Calorimeter – Drop
Solution

Isothermal Calorimeter
for reactions and
mixing

DSC and TGA/DSC
with Mass
Spectrometry

Materials Characterization Facility (MCF)



Location: 146 Stepan Chemistry Hall

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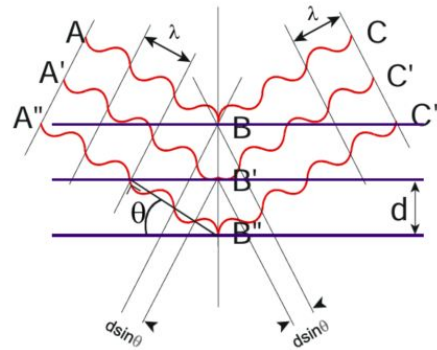
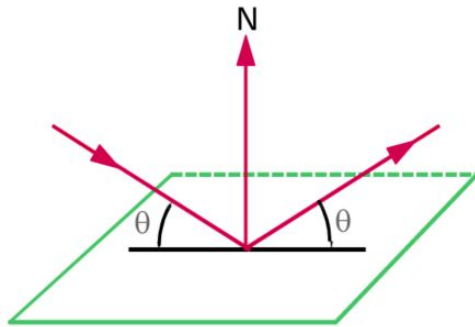
Next Workshop: Bandgap analysis using UPS and LEIPS on XPS, XPS best practices and fitting peaks, GC-MS and thermal desorption for volatile and semivolatile analysis, Particle size and shape analysis, Overview of surface analysis techniques: AFM, optical profilometer and stylus profilometer, Raman mapping and best practices

Outline

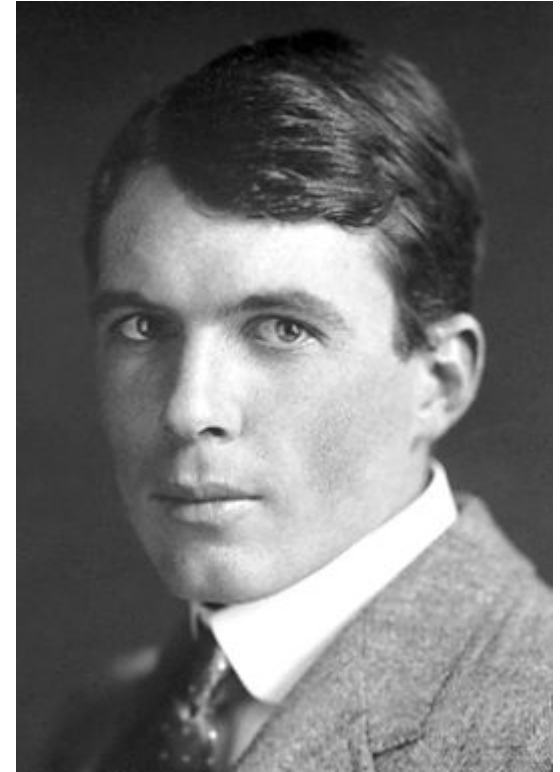
- MCF overview
- XRD basics
- Acquiring Data
 - What's important?
- Quantitative Phase Analysis Methods
- HighScore Software
 - How to access
 - How to import data
- Rietveld Refinement

Sir William Lawrence Bragg: $n\lambda = 2d \sin\Theta$

Diffraction angle is a function of d-spacing (distance between neighboring parallel planes) and x-ray wavelength.

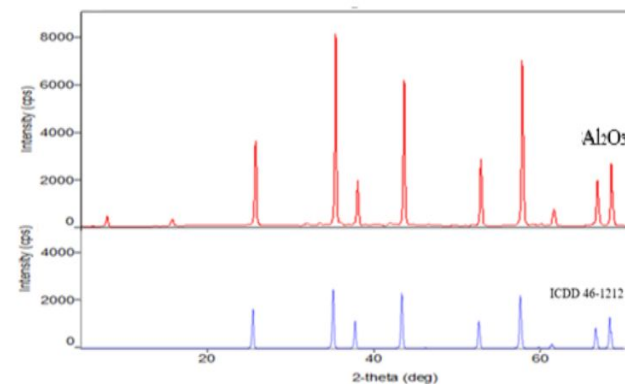
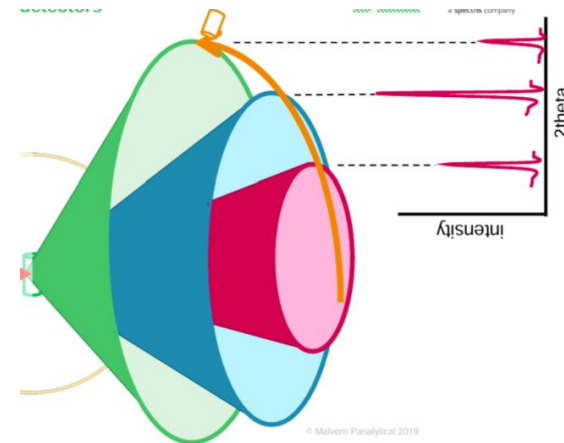
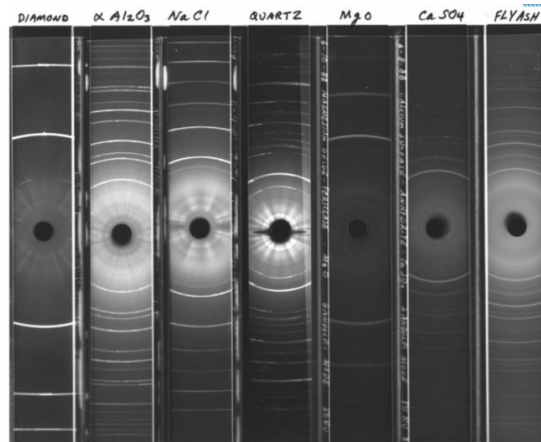
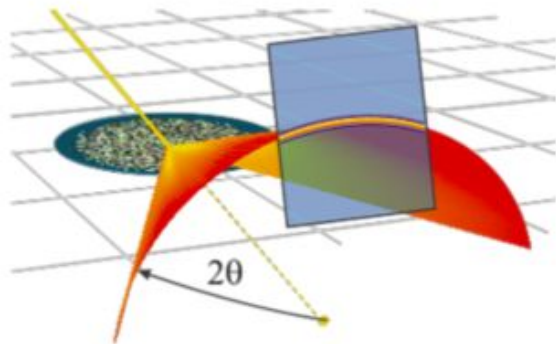


Reflected waves interfere constructively when Bragg conditions are met (each angular peak position corresponds to a d-spacing in the sample).



XRD Basics

X-rays scatter spherically (Debye diffraction cone)



Data Acquisition: What's Important?

Only a few things...

1. Representative sampling
2. Sample amount
3. Grinding, milling (particle size: 40um diameter have ~12 crystalites that diffract, 1um diameter have ~38k, so smaller sizes give you a random distribution) Over-milling can induce amorphous state or even phase changes
4. Pressing, surface alignment (preferred orientation). Overcome by backloading, using grinding aids (coffee powder), capillary spinner
5. Surface height and flatness (peak position accuracy, peak broadening)
6. Crystalline nature: amorphous to crystalline

Data Acquisition: What's Important?

Just remember

1. Surface should be flat
2. Surface should be at the correct height (match border of holder/mount)
3. Set your measurement parameters (step size, time per step, slit size, etc...) to match what you want to see in your data

Quantitative Phase Analysis

RIR (Reference Intensity Ratio): Estimates mass fractions of identified phases. Based on relative net peak height ratio of the strongest line of the phase and of the strongest line of corundum in a mixture of equal weight percentages (e.g. 50/50). Often reported in databases as I/Ic or RIR value.

DDM (Direct Derivation Method): Calculates mass fractions from observed integrated intensities and chemical compositions of phases.

Rietveld Refinement (Hugo Rietveld, 1969): Raw data is used to make a calculated pattern which can give you structural information.

Calibration Curves: Manual approach

Partial Least Squares: Correlates information in one data matrix to the information from another matrix

Cluster Analysis: Data reduction/analysis from 100s of scans

HighScore Software

How to access this software: We have a limited number of licenses available (about 10). A shared computer in the MCF (with remote access) has HighScore installed and can be used whenever.

Import: File, Open or drag a file from Explorer into HighScore window. Open command opens one window per scan. Import command places all selected scans into one window.

Auto Processing is available

Let's do an example!!

Rietveld Refinement

Software that can model measured data well is a huge help. HighScore can do this.

1. Insert measured diffraction pattern
2. Insert first calculated diffraction pattern
3. Begin refinement

Terms: scan (raw user-acquired data), pattern (reference pattern from a database), phase (a crystal structure file that goes into a refinement tab)

Standard Profile Fitting

Open CPD-1E.RD

Treatment: Determine Background (Accept), Search Peaks (Accept)

Search Peaks will scale reference patterns to match data peak intensity

Toggle icon: Show calculated profile, show peaks inside and outside

Check your Peak List tab

Fit isn't perfect: Zoom in to see how the calculated pattern matches the data (33-40)

See how some peaks have the K-alpha2 (dashed line) (55-59), however, peak at 94.5 isn't marked as such (we have different x-ray energies coming out of our x-ray tube).

Adjusting peaks: Delete directly from peak list. To insert, go to Treatment: Insert Peak. This gives you a peak add cursor. You have to turn this off when you're done.

Standard Profile Fitting

Profile Fitting (refining)

Analysis Menu: Fitting: Start Fit: Default Profile Fit (make sure the whole pattern is visible)—Refines each peak separate from the other peaks. It refines its area, width, shape and position. Peak list should now be more accurate.

Check Fit: Set to auto scale (icon on left). Now zoom in and scroll across your pattern to check fit visually. The Profile Fit will only refine the peak list that already exists, it won't add or remove peaks. Look at 65-70. The refinement has only identified the K-alpha1 peaks. Select "Show/Hide Individual Peak Profiles" for fun.

What we have so far? Just a more accurate peak list... How do we get meaningful results? We use the peak properties to calculate phase quantity (peak areas), crystallite size (peak width), lattice parameters (peak position)

Rietveld Refinement

Open data and select a phase from the database: Change View to Rietveld or Structures, and Open Corundum (Data: CPD) In Pattern List Tab, “Load Subset to Pattern List” Load “CorrFluorZinc” Accept candidate. Highlight in the pattern list. Right click, go to Convert Pattern to Phase

Refine: Refinement control Tab: expand Corundum, expand Unit Cell. Note that in Global Variables the K-alpha1 wavelength is set. Start pattern simulation (icon at top or find in the Analysis menu: Fitting). We get a calculated diffraction pattern from the crystal structure, assuming a scale factor of 0.01 (in refinement control). Peak positions have been calculated from lattice parameters (unit cell section) which are used to calculate the d-spacing/2theta position. Peak widths have been calculated using the Caglioti model (Profile variables). Peak shape calculated using pseudo voigt.

Refine More: you can go in and manually adjust intensity (scale factor), position (unit cell values), etc... There is an undo icon!

Refine More: If you think you know which parameters need to be adjusted, you can selected the refine box, change the fitting type to manual, then run Analysis: Fitting: Start Fit. For example, you could select Specimen Displacement (global variables), a and c in Unit Cell, and Scale Factor. Execute Fitting icon. Zoom in and visually check match.

120-135... the peak width is off. Select all the cagliotis and refit.

Model Background: Change Y scale to square root. Select Flat, 1/x, and the first 3 coefficients. Refit. This will also help peak heights and positions to be more accurate.

Check how good your model is: Visual. Check the noise in the background. If it's noisy, you should expect the peak intensities to be off by that much. Right click on the bottom left plot, show graphics and show difference plot. Look at the residual value (Rwp). It's a calculated difference indicator between observed and calculated diffraction patterns. Generally, it is good to get this less than 10%. If you have a higher value, but your peak positions are fantastic and you just want lattice parameters, then you're good.

Check how good your model is: You can get into examining individual peaks when trying to determine minor phases or texture, for example. Could refine any of the parameters you want, just see if it makes the fit better.

Object Inspector: Click on global variables. Look at agreement indices: R profile (comprehensive), Weighted R profile (values high intensity points more). R expected looks at the noise of the data and gives you an idea of your best R (2 or 3% is good data). Sometimes you just have to collect better data. Good data usually has >10,000 counts at its highest peak.

Avoid: Adjusting these parameters: extinction, flat plate absorption, porosity, roughness (for neutron or synchrotron data—a much higher quality dataset)

You can manually enter a crystal structure and calculate an ideal x-ray powder diffraction pattern

Rietveld Refinement

One more example: Open LaB6 toploaded.hpf

Bring up a database pattern: Search & Match, Restriction set, edit.

Quality—skip patterns without structure data (we need this for Rietveld). Chemistry: all of: type La and B. Click button Add Rest to None of. Close. Search. Ok. Select a candidate. Remove all other candidates to speed things up (right click in the candidate list). Make sure you're using the structures desktop.

Initial Structure: We'll start using the Object Inspector (OI) so make sure it's up. Load crystal structure: pattern list, right click on patter, convert pattern to phase. Should show up in Refinement Control tab. Click on label and check OI. Can change color, title, selected candidate, etc... Now go to Analysis, Fitting, Start Pattern Sim (or use icon at top).

Customize: Feel free to turn off some display elements: view, turn off explained features, ref pattern, etc.. Once you have the view you want, Customize, Document Settings, Save to Normal Template (can change line width, can reset all to default). Change to Top left icon

(maximize main graphic)

Rietveld Refinement

Check fit and refine data: Set fitting mode to automatic. Fitting, start fit, Default Rietveld (Phase fit). The display will show what it has fit and any corresponding parameter adjustments. To find it manually, go to Customize, Program Settings, Fitting/Rietveld, Show R value graphics, Keep R value graphics open after refinement. Data grid tab will show you R expected. Look at the difference plot (right click in additional graphics). Also check Agreement Indices (in OI, shown if RC tab is selected).

Continue Checking: Since the R_w is quite a bit different, we should keep refining. Intensities appear over-calculated at high angles, under at low. So we should try refining width or thermal displacement. Could also be an effect of sample prep (not enough sample, roughness). Type “error” in OI so you can find Calculate Errors, and check that. Fit again (Default Rietveld). Now we will have Deviation values in the LaB6 data. This can give you an idea of what you need to fix (displacement in GV), or what data you should have confidence in (unit cells)

Just so you know...

Our XRD can also be used to...

- run non-ambient experiments
- calculate residual stress and texture
- acquire surface sensitive data (grazing incidence)
- examine air-sensitive samples