Powder X-ray Diffraction

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NSLS-II & CFN Users’ Meeting Workshop 3: Synchrotrons 101: Accelerator, Science and Applications

Brookhaven National Laboratory – May 20, 2019
Examples of Powders

Multi-grained
i.e. each grain can
diffract x-rays,
neutrons or electrons
Polycrystalline
materials
Examples of Powders

Multi-grained i.e. each grain can diffract x-rays, neutrons or electrons

Polycrystalline materials
Examples of Powders

- Metal parts
- Multi-grained i.e. each grain can diffract x-rays, neutrons or electrons
- Polycrystalline materials

- Powdered milk
- Cosmetic powder
- Gunpowder
- Powdered sugar
- Sand
- Pharmaceuticals
- Fine snow
- Potassium bromate
- Zymin
- Brightening agent
- Ground coffee
- Polymers
- Flour
- Ceramics
Multi-grained
i.e. each grain can
diffract x-rays,
neutrons or electrons
Polycrystalline
materials

Highly disordered
Nanocrystalline
Amorphous

Use of Powder Diffraction
Use of Powder Diffraction

- Multi-grained (i.e., each grain can diffract x-rays, neutrons or electrons)
  - Polycrystalline materials

- Highly disordered
  - Nanocrystalline
  - Amorphous

- Time-dependent
- Space-resolved
Single Crystal Diffraction is preferred in most cases BUT:

• the product naturally occurs as a powder
• the functionalized (working) form of the product is a powder
• a single crystal of sufficient size or quality cannot be synthesized
• Lattice parameters and micro-structure
• Crystal may shatter during a process or a phase transformation
From Laboratory...
... to NSLS-II X-ray Diffraction Beamlines
Perform diffraction using the lab machine first and assess data quality:

- Flux (weak scatterer, diluted, film or surface, time-dependent)
- Energy tunability (less absorption, anomalous, white beam)
- Optics (resolution → minimize peak overlap, small beam size → location or mapping)
A series of intensity values (detector photon counts) vs. diffraction angle. Crystal information is compressed into 1D (2θ scale): good and bad!!
Use of Powder Diffraction

1. Qualitative Analysis

Phase ID
Any powder pattern can be used like a fingerprint to see if it matches the powder pattern of an already known compound.

The International Centre for Diffraction Data (ICDD) (PA) maintains a database of known powder diffraction patterns (www.icdd.com)

- 365,900 standardized entries
- 42,800 Minerals
- 502,000 Organics

Automatic data mining, search & match
Phase identification

e.g., **Mineralogy**: natural Granodiorite is a mix of Quartz, Feldspar, Albite, Biotite; lesser Clinochlore, Hornblende; traces of Zircon (from webmineral.com)

e.g., **Pharmaceutical**: Mannitol, Sucrose, DL-Valine, Starch, Nizatidine.
1. Qualitative Analysis  Phase ID

2. Quantitative Analysis

  Lattice parameters (thermal expansivity, compressibility)
  Phase mass fraction (mixture)
Quantitative Analysis

- Effect of substitution
- Occupancy Factor
Science motivation: Doping of nanocrystals is a key, yet underexplored, approach for tuning of the opto-electronic properties of semiconductors. An important route for doping of NCs is by vacancy formation.

Results: Transformation from Cu$_2$S to Cu-depleted phases. Reaction efficiency is observed to depend on the size of the NCs. Competing processes are formation of Cu vacancies and occurrence of a Cul phase on the surface.

Qualitative Analysis

• phase content: weight % of each phase inside a mixture

• \(A + B \rightarrow A + C + D \rightarrow A + D\)
  follow the reaction pathway from start to finish
  identify the end products (D) but also metastable phases (C)
  measure the kinetics: mass fractions \(f(t)\)

• follow structural changes and phase transformations as a function of a process variable

• **Goal**: structural behavior under complex environments
(A) Operando XPD patterns from the sulfur-CuS hybrid electrode aligned with its electrochemical capacity-voltage profile during lithiation; diffraction peaks from the cell are labelled with “*”
(A) Operando XPD patterns from the sulfur-CuS hybrid electrode aligned with its electrochemical capacity-voltage profile during lithiation; diffraction peaks from the cell are labelled with “*”

(B) Diffracted intensity of S (222), CuS (103), and Li$_2$S (111) are plotted as a function of depth of discharge in comparison with the cell discharge voltage profile (solid black lines)

H. Gan et al. Scientific Reports (2017)
In Situ and Operando Conditions

In-situ, high temperature oxidation studies of HfB₂ composites using a quadrupole lamp furnace.

P. Sarin, Univ. of Oklahoma

Develop oxidation-resistant HfB₂ and HfB₂-SiC composites as emerging Ultra High Temperature Ceramics for applications beyond 2,000°C (thermal protection for atmospheric re-entry of space shuttles)
Microwave Synthesis

**Science motivation:** to study the crystallization process from the stage of nucleation inside a MW reactor (out of equilibrium).

**Applications:** Hydro-Solvothermal synthesis, solid state synthesis, thin film growing in solution

**Features:**
- Remote control for safe operation
- Large scattering angle (~45°) for PDF
- Temperature monitoring

First in situ PDF measurement during MW assisted Titania (TiO$_2$) thin film growing @ 28-ID-2 (April 2017)

R. Jayan et al. Carnegie Mellon University
MW-assisted Hydrothermal Synthesis of Layered Oxide Cathodes for Li-ion Battery

- Ultrafast kinetics: the synthesis completed in 4 minutes almost in single step.
- Reaction temperature less than 160°C
- Understanding the roles of the MW irradiation in the synthesis process by monitoring the structural and morphological evolution.

F. Wang, J. Bai et al. BNL.
Solid State Synthesis of MgAl₂O₄ using Electrical Flash Sintering

- **Scientific Achievement**
  Fast reactive flash sintering method used for solid state synthesis of dense single phase ceramic materials i.e. MgAl₂O₄ from multiple powders.

- **Significance and Impact**
  Compared to thermal treatments at high temperatures, Electrical Flash shortens the time for sintering and the ceramic powders transform into a single phase dense ceramic at significant lower temperature.

- **Research Details**
  Flash experiments with three phase powders of yttria stabilized zirconia (8YSZ), MgO, and α-Al₂O₃ produce polycrystals of high density single phase spinel MgAl₂O₄. Flash Sintering proceeds through an incubation step, before the onset of a rapid, nonlinear increase of the current flowing through the specimen under constant applied voltage. The whole process takes less than 50s.

Significance

Synthesis of a HT superconductor
Explore new synthesis routes and elucidate the sequence of chemical reactions.

Parallel DFT computations of the stabilities of possible compounds that could form.

Summary

• Whether or not La$_2$CuO$_3$S and La$_2$CuO$_2$S$_2$ could be synthesized from a mixture of La$_2$O$_3$, CuO, La$_2$S$_3$, CuS, Cu$_2$O and S

• Redox reaction between the Cu$^{2+}$ and S$^{2-}$ containing starting materials impedes the desired oxidation states.

Hua He, M. Aronson et al.
Proc Natl Acad Sci (2018)
In Situ & Operando Conditions

• Lamp furnace (RT- 2000°C)
• Linkam flat plate furnace (RT- 1500°C)
• Hot air blower (RT - 1000°C)/ Coil heater ( RT-1300)
• Gas flow reactors and flexible coil heater for capillaries
• High pressure reaction cell (up to 400°C & 1500psi) (gas, hydrothermal)
• Cryostream (80K - 500K)
• He cryostat (10K – 500K)
• Multi-purpose cell (oxidative or corrosive gases, 3D stress, vertical and axial loads up to 20 lbs)
• Microwave furnace
• Electric Flash Sintering
• Colloidal Nano Synthesis
Current Trends in Powder Diffraction

• **Real materials** ≠ lab prepared (synthetic)
• **Real conditions** (*in situ*, operando) ≠ room T, P
• **Real time** ≠ static observation
XPD Robotic Sample Changer
1. Qualitative Analysis
   Phase ID

2. Quantitative Analysis
   Lattice parameters (thermal expansivity, compressibility)
   Phase mass fraction (mixture)

3. Structure Determination
Crystal Structure: lattice

the unit cell

Crystal data
- Formula: O₂ Ti
- Crystal system: tetragonal
- Space group: P 42/m n m (no. 136)
- Unit cell:
  - \( a = 4.5937 \, \text{Å} \)
  - \( c = 2.9587 \, \text{Å} \)
- Cell volume: 62.40 \( \text{Å}^3 \)
- \( Z = 2 \)

Rutile TiO₂
### Crystal Structure: + symmetry

- **the unit cell**
- **the space group**

<table>
<thead>
<tr>
<th>Crystal data</th>
<th>O₂ Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
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<tr>
<td>Crystal system</td>
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<tr>
<td>Unit cell</td>
<td></td>
</tr>
<tr>
<td>Cell volume</td>
<td>( 62.40 \ \text{Å}^3 )</td>
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<tr>
<td>( Z )</td>
<td>2</td>
</tr>
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</table>

- \( a = 4.5937 \ \text{Å} \quad c = 2.9587 \ \text{Å} \)

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**Rutile TiO₂**

[Diagram of Rutile TiO₂ crystal structure]
**Crystal Structure: + atomic motif**

- **the unit cell**
- **the space group**
- **the asymmetric unit**

### Crystal data
- **Formula**: O$_2$ Ti
- **Crystal system**: tetragonal
- **Space group**: $P 42/m n m$ (no. 136)
- **Unit cell**: $a = 4.5937$ Å, $c = 2.9587$ Å
- **Cell volume**: $62.40$ Å$^3$

### Atomic coordinates

<table>
<thead>
<tr>
<th>Atom</th>
<th>Ox.</th>
<th>Wyck.</th>
<th>x</th>
<th>y</th>
<th>z</th>
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<tr>
<td>Ti</td>
<td>+4</td>
<td>2$a$</td>
<td>0</td>
<td>0</td>
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<tr>
<td>O</td>
<td>-2</td>
<td>4$f$</td>
<td>0.30469</td>
<td>0.30469</td>
<td>0</td>
</tr>
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</table>

### Bond lengths, bond angles (Å, °)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle (°)</th>
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<tr>
<td>Ti–O</td>
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<tr>
<td>O–O</td>
<td>2.959</td>
<td>Ti–Ti</td>
</tr>
<tr>
<td>Ti–Ti</td>
<td>3.569</td>
<td></td>
</tr>
</tbody>
</table>
Structure Determination of $\text{Mo}_2\text{P}_4\text{O}_{15}$

One of the largest structures solved with TOPAS (simulated annealing)

Single crystal data (Bruker AXS SMART 6000)

- SG: Pn (7)
- $a = 24.1134(6)$ Å
- $b = 19.5324(5)$ Å
- $c = 25.0854(6)$ Å
- $\beta = 100.015(1)$°
- $V = 4450.9$ Å$^3$
- 441 atoms in asymmetric unit

Lister et al., Chem. Commun., 2004, 2540
XPD (hi-throughput) vs. 11-BM data (hi-res)
S. Gill (Brookhaven), Greg. Morrison (University of South Carolina)

Gadolinium and Uranium based Salts for nuclear waste form applications
Use of Powder Diffraction

1. Qualitative Analysis  Phase ID
2. Quantitative Analysis
   - Lattice parameters (thermal expansivity, compressibility)
   - Phase mass fraction (mixture)
3. Structure Determination
4. Microstructure and Texture  Peak Shape Analysis
   - Crystallite orientation distribution
   - Crystallite size distribution (preferred orientation)
   - Anti-phase domains, dislocations, stacking faults,...
Where is the Information in PD?

1. **Peak Positions**
   - Lattice parameters determination
   - Thermal expansivity or compressibility
   - Macro-stress

2. **Peak Widths and Shapes**
   - Microstructure (crystallite size, stacking faults, etc)

3. **Peak Intensities**
   - Structure solution
   - Site occupancies, substitution
   - Accurate displacement parameters

4. **Between the Bragg Peaks**
   - Short Range Order

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15x419
FT of the signal $\rightarrow$ far in reciprocal space  
$\rightarrow$ High photon energy (>60keV)  
$\rightarrow$ 2D detector close to the sample
Pair distribution function (PDF) gives the probability of finding a neighbor atom at a distance “r” from a given atom.

\[ Q = 4\pi \frac{\sin(\theta)}{\lambda} \]
**Scientific Achievement**

Mechanism of formation of NaGdF4:Yb:Er nanocrystals (~10 nm) in organic media and their crystal structures.

**Significance**

Capacity to convert near-IR photons into near-UV or visible light. Depends on size, morphology and chemical composition.

D. Hudry, D. Nykypanchuk, J. H. Dickerson et al.
Total Scattering

• “Conventional” Powder Diffraction is applied to crystalline materials (long range order) with limited disorder. PD only looks at the Bragg peaks, background is treated as a baseline that is subtracted.

• Pair Distribution Function extends the PD technique over to non-crystalline materials, materials that contain a high degree of disorder and defects, and nanomaterials (short range order). PDF treats the signal that is contained both in the Bragg peaks and in the background.

Current Trends in Powder Diffraction

• **Real materials** ≠ lab prepared (synthetic)
• **Real conditions** (*in situ*, operando) ≠ room T, P
• **Real time** ≠ static observation

• **Complexity**: Defects, nano and multi-scale structures, heterogeneities, nanoscale disorder etc.
• **Properties** that often depend on SRO deviation w/ respect to LRO (average)