BCA Course 2005

A Brief Overview of Powder Diffraction

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Outline

- Historical background
- Diffraction: physical phenomenon
- Samples, experiment and data obtained
- Applications
- Conclusions

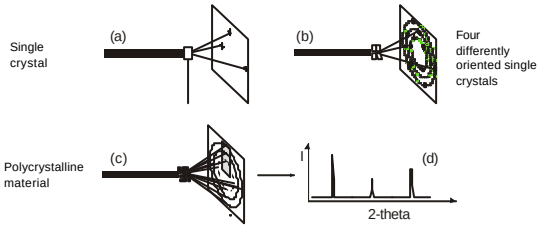
Historical background

- 1895: Röntgen discovers X-rays (Nobel Prize 1901)
- 1912: von Laue discovers X-ray diffraction on crystals (Nobel Prize1914)
- 1913: Bragg & Bragg discover structure analysis by XRD, NaCl (Nobel Prize 1915)
- 1916: Debye & Scherrer discover powder X-ray diffraction, LiF
- 1963: Zachariasen solves the structure of β-Pu from PXRD by direct methods
- 1969: Rietveld method
- 1990: direct space approaches to structure solution
- 2000: work on 100+ atom structures, proteins

Diffraction: physical phenomenon

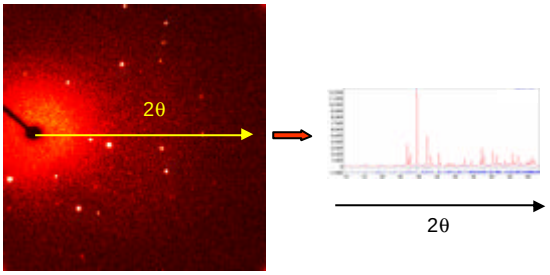
- Crystalline state of matter
  - long-range 3D order
- Diffraction
  - scattering on periodic arrays
- Crystallography
  - $2d_{hkl}\sin\theta = \lambda$
  - $F_{hkl} = \Sigma f_j e^{2\pi i(hx_j+ky_j+lz_j)}$

Samples



Experiment

'…data compressed into one dimension…'



A modern take

"Probably the best known and widely used application of powder diffraction is as an analytical tool for both qualitative and quantitative analysis of crystalline materials".

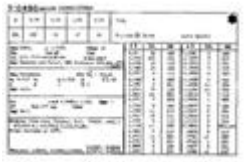
(Fundamentals of Crystallography, ed. by C. Giacovazzo, pg. 297)

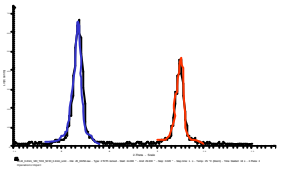
Not quite as simple as this…

Qualitative analysis

- JCPDS cards

Quantitative analysis





Many multibillion £££££ drug patents based on this!!!!

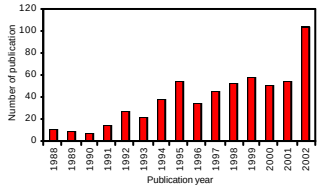
…but it does much more

- Thermal expansion
- Structure determination
- Kinetics studies
- Particle size
- Phase transitions
- **Powder Diffraction**
- Particle strain
- Ionic migration
- In-situ chemistry
- Crystallization/ amorphization
- Polymorphism

Crystal structure publications

~ 100

Structure solution from powder diffraction data



~ 20,000

⇒ try hard to grow crystals!

Structure determination

Indexing

Space group determination

Extraction of integrated intensities (?)

Structure solution

Structure refinement

What is the difficulty?

This slide illustrates personal experience – the only serious statement is the final line!

Crystal → (95%) Indexing → (95%) Space group → (98%) Solution → (98%) Refinement → Total 81%

Powder → (20%) Indexing → (20%) Space group → (25%) Solution → (30%) Refinement → Total 0.3%

81% : 0.3% ~ 270 ⇒ comparable to the ratio of publications!!!!

⇒ every step is difficult!!!!

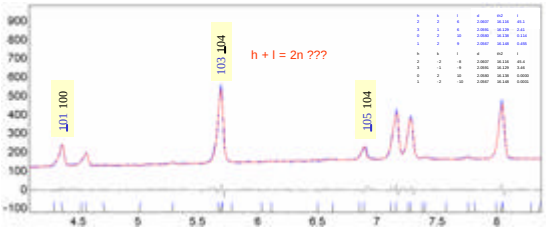
An illustration

a = 7.723 Å
b = 5.841 Å
c = 29.544 Å
β = 100.86°
V = 1308.8 Å^3

NO sensible set of systematic absences
NO space group
NO structure solution

a = 7.723 Å
b = 5.842 Å
c = 29.084 Å
β = 94.32°
V = 1308.5 Å^3

sensible set of systematic absences
space group
structure solution



Structure solution

Examples of approaches to structure solution include:

- Reciprocal space methods
  - direct methods
  - Patterson methods
- Direct space methods
  - simulated annealing
  - genetic algorithm

Refinement: pre Rietveld

- Integrated intensity refinement
  - State of the art until late 60's early 70's
  - Poor observation-to- parameter ratio
  - Problems due to overlap
  - Limited applicability
  - Suitable for high symmetry systems
  - Used extensively for high T nonstoichiometric phases

$Fe_{0.925}O$ 800°C

hkl	I(obs)	I(calc)	hkl
111	6092	6315	111
200	89766	89604	200
220	79186	79285	220
311	3378	3484	311
222	26340	26139	222
400	12697	13064	400
331	1540	1377	331
420	31104	31301	420
422	23695	23438	422
333/511	1061	898	333/511
440	5831	6042	440
600/442	10394	10308	

$R(I) = 0.78\%$

- 12 observations
- 4 variables
  - Scale factor
  - Uiso(Fe)
  - Uiso(O)
  - Occ(O)

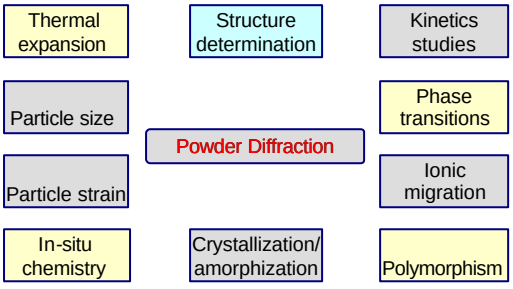
Cheetham et al., 1971.

Refinement: the Rietveld method

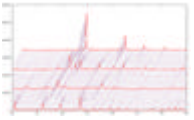
- Rietveld, 1969: diffraction pattern analysis by a curve fitting procedure
- First proposed for constant wavelength neutron data
- The difference between the observed and calculated profiles is minimized
  - typical Rietveld plot:

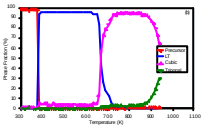
- Parameters refined:
  - structural parameters (atomic positions, displacement parameters, occupancies, unit cell parameters)
  - instrumental parameters (zero point, background parameters)
  - peak shape function parameters

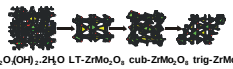
Powder diffraction can give you



Applications







$(ZrMo_2O_7(OH)_2.2H_2O$ 303 K | LT-$ZrMo_2O_8$ 543 K | cub-$ZrMo_2O_8$ 763 K | trig-$ZrMo_2O_8$ 953 K

$ZrMo_2O_8$

- NTE material
- Rich phase system
- Interesting behaviour vs T

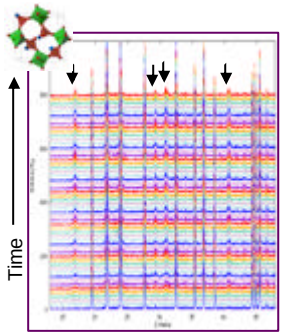
Lab powder XRD data:

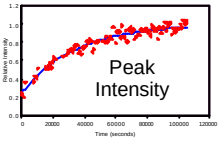
- In-situ chemistry
- Quantitative phase analysis
- Thermal expansion
- Phase transitions
- Polymorphism
- Structure solution

Powder diffraction can give you

Thermal expansion	Structure determination	Kinetics studies
Particle size	Powder Diffraction	Phase transitions
Particle strain		Ionic migration
In-situ chemistry	Crystallization/ amorphization	Polymorphism

Applications





$ZrWMoO_8$

- Order-disorder PT
- Oxygen mobility at low T (down to 200K)
- Diffraction vs. time gives kinetic information

Powder diffraction can give you

Thermal expansion	Structure determination	Kinetics studies
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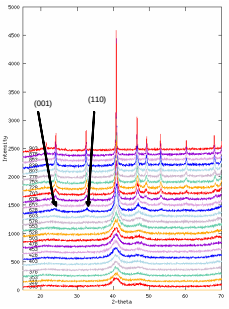
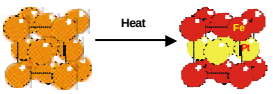
Applications



FePt nanoparticles vs T

- PT from a disordered FCC structure to an ordered atomic FCT arrangement (Fe and Pt alternate in a and b layers) gives extra peaks
- Peaks get sharper with heating, as particles grow from about 4 nm to about 150 nm



Powder diffraction can give you

Thermal expansion	Structure determination	Kinetics studies
Particle size	Powder Diffraction	Phase transitions
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Conclusions

- Single crystal diffraction superior for structure determination
- Powder diffraction more versatile
- For full and thorough characterization of functional materials - use both!!!