

Polymer Subcommittee Minutes

Tom Blanton, Chairman

12 March 2008

Call to Order

Meeting called to order by T. Blanton.

Appointment of Minutes Secretary

T. Kahmer

Roll Call and Attendance

Attendance sheet circulated.

Approval of Minutes

Minutes of the 2007 Polymer Subcommittee Meeting were approved.

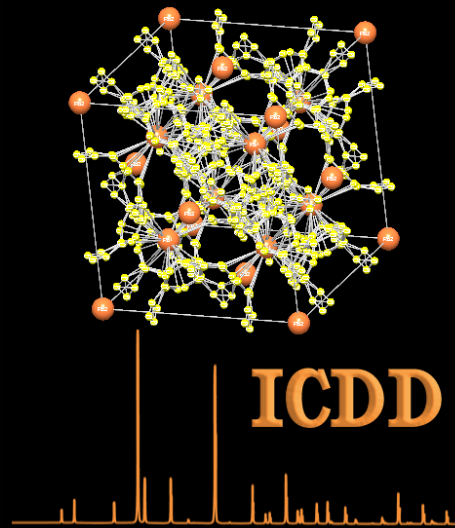
Status of Polymer Activity and Feedback to T. Fawcett

- T. Fawcett – review of ICDD activity on PDF3/Full pattern database
- T. Fawcett gave a presentation (he also gave it at the 2007 DXC Meeting, [“A Reference Diffraction Database for Non-Crystalline, Partially Crystalline and Amorphous Materials”](#)).
 - List of critical issues:
 - No international conventions/acceptance on term definitions
 - Requires more information and more storage capacity
 - Data includes blends (crystalline + amorphous for polymers and nanomaterials)
 - New methods required for automated identification (integral index, similarity index)
 - New methods for editing, analyzing and reviewing data
 - Visualization is important and techniques need to be developed to translate visual to automated identification
- We now have a scanning system in-house and have the diffraction patterns from the Dow Polymer Book entered into our data system.
 - We have additional diffraction scans to work with from our bibliographers, N. Ernst and A. Rohrman
 - Guides/sources to use: Polymer Handbook (has unit cell data, references); ALCOA Report (T. Blanton will submit), J. Faber will also submit ~20 digitized patterns.
 - Need to notify the OEMs that we will be including polymers
 - Need additional, new comments to explain the data
 - We will likely need to pay someone to generate/measure the data, perhaps as a Grant-in-Aid
 - We will need a polymer editor (maybe E. Ryba?)
 - Eventually glasses would be another class of materials to address
- The plan at HQ is to get the first set of PDF3 polymer patterns in the PDF4 product by 2009

Adjournment

T. Blanton adjourned the meeting at 3:00 p.m.

A Reference Diffraction Database for Non-Crystalline, Partially Crystalline and Amorphous Materials

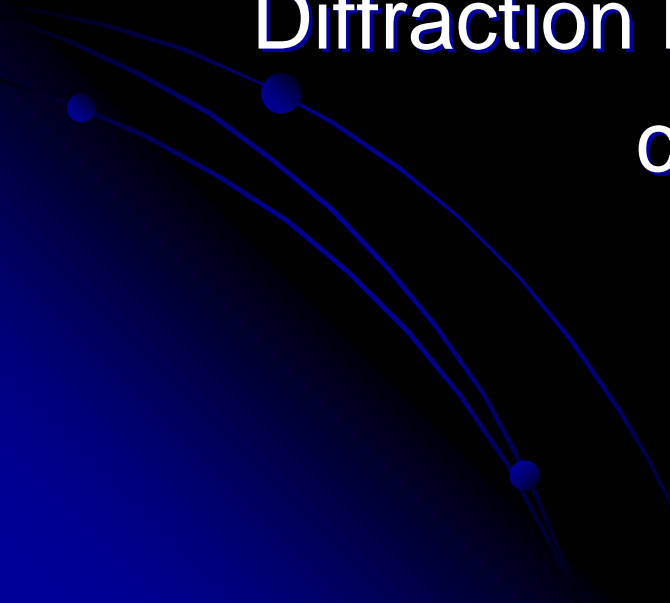


T. G. Fawcett, J. Faber, D. M. Crane
S. N. Kabekkodu, D. E. Sagnella, J. R.
Blanton

International Centre for Diffraction Data

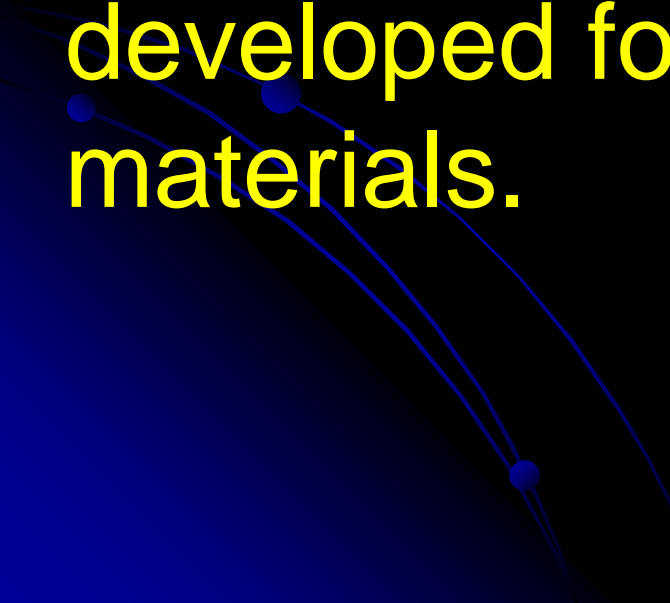
The ICDD Vision circa 1986

To encourage the use of the Powder
Diffraction File for phase identification of
crystalline materials



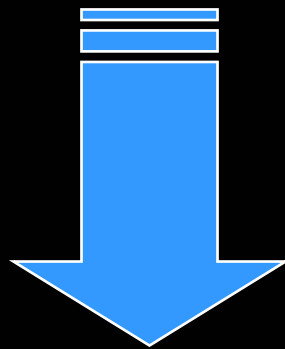
Q. Why only crystalline materials ?

A. There were existing methods developed for identification of materials.



Data Reduction

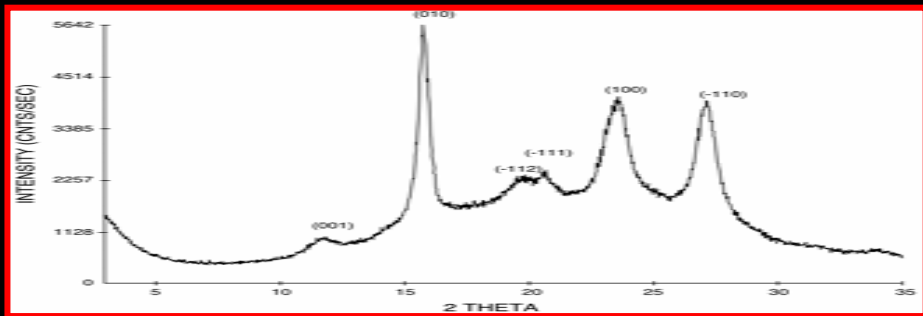
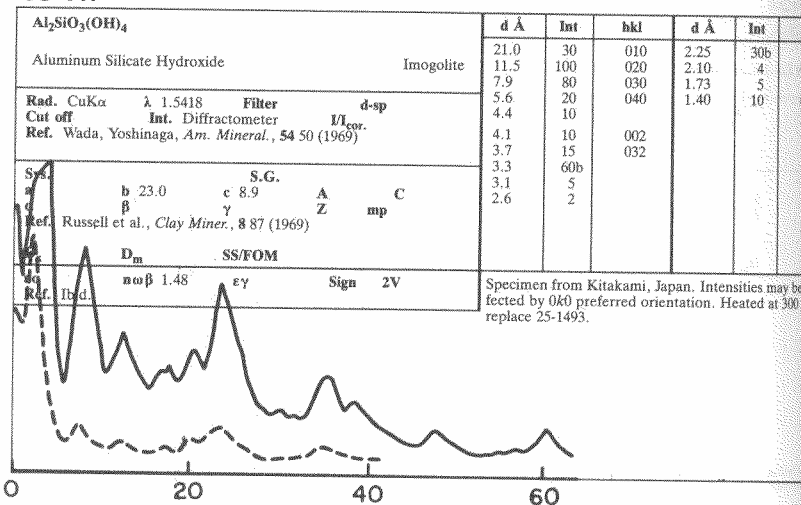
Raw Data - Scan 5-70 degree two theta with a 0.01 step size
requires **6500** pairs of positions and intensities



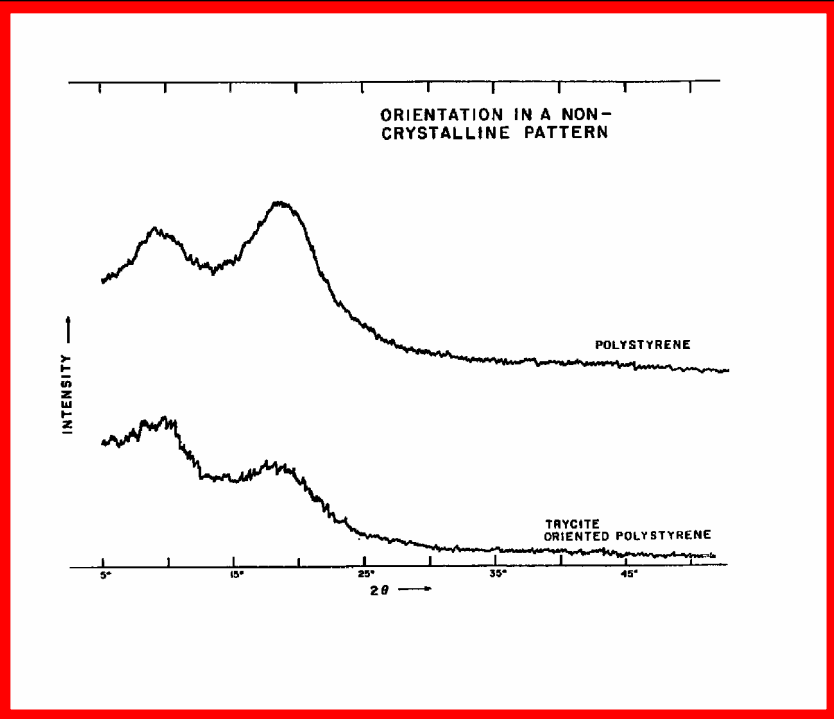
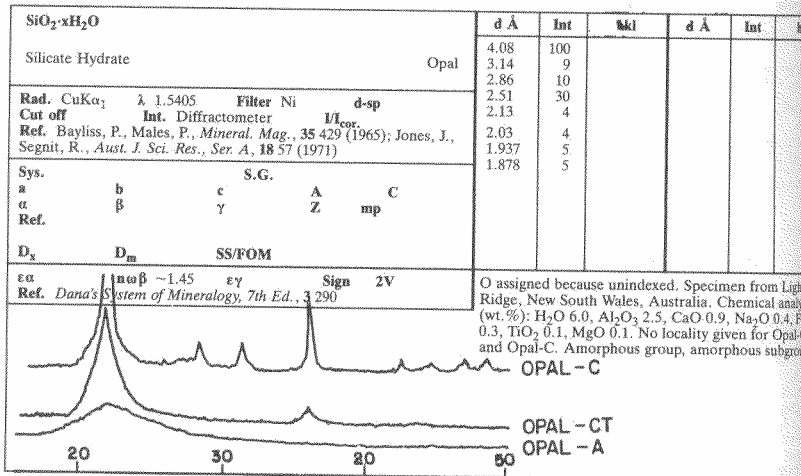
Hanawalt Index – Permuted 3 Lines – **3** d,I pairs

Full Listing – **10-200** d,I pairs
(average = 84)

38-447



38-448



Opal, Imogolite

1988, PDF Book Set 38
Published by ICDD

Polypropylene, Polystyrene
"X-ray Diffraction Patterns of Polymers",
June Turley, Dow Chemical, 1965

Published by ICDD

Critical Issues

for an amorphous, non-crystalline, partially crystalline and nanomaterial database

- No international conventions/acceptance on term definitions (i.e amorphous, nanomaterial)
- Requires more information thus more data fields and storage capability
- Data includes blends (crystalline + amorphous for polymers and nanomaterials)
- New methods required for automated identification
- New methods for editing, analyzing, and reviewing data
- Visualization is important and techniques need to be developed to translate visual to automated analyses

The Powder Diffraction File for Advanced Materials Analysis

- **Material Identification**
- **Quantitation**
- **Structure Solution**
- **Crystallinity and Crystallite Size Measurements**
- **Orientation**
- **Order –**
 - amorphous**
 - nanocrystalline**
 - crystalline**

Identification

Comprehensive Database
- *All Data on all Materials*

Quantitation

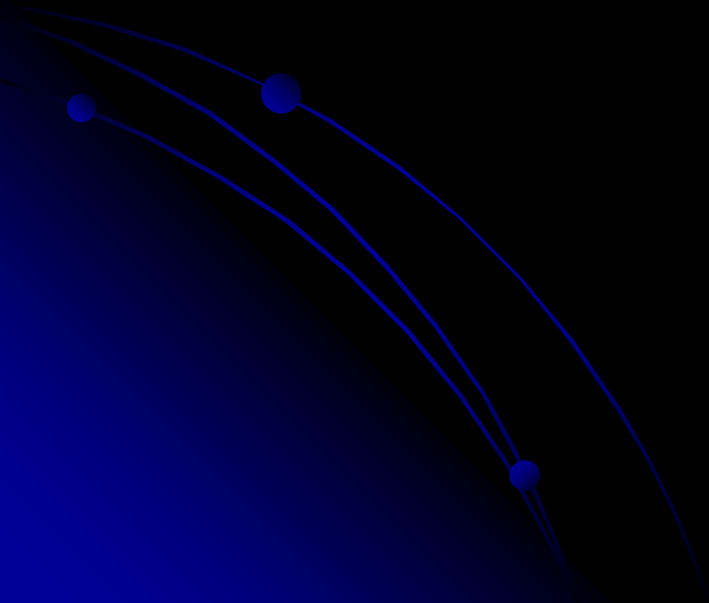
All data - Digital Patterns
I/Ic – Referenced to corundum
Atomic Coordinates

Analysis

Simulate crystallite size
Integral Index (pattern fit)
Quality of the reference

Non-Crystalline and Nanocrystalline Materials

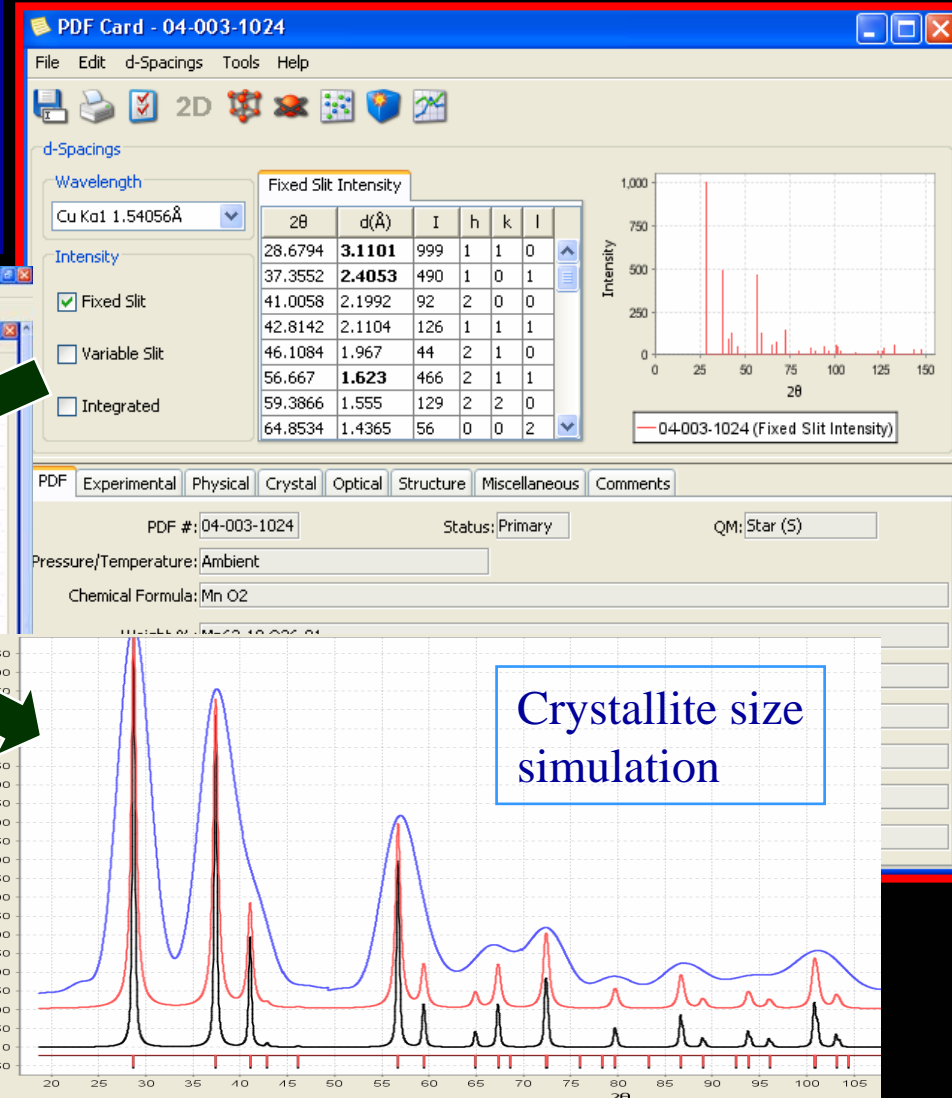
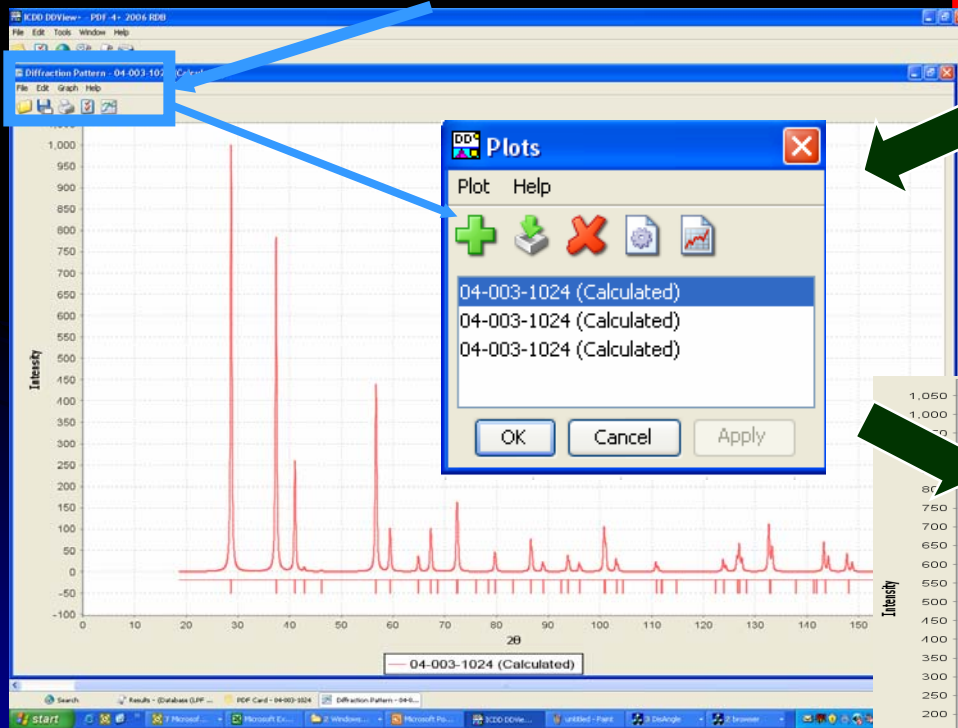
- use of simulations and pattern fitting



Pattern Simulations – PDF-4+

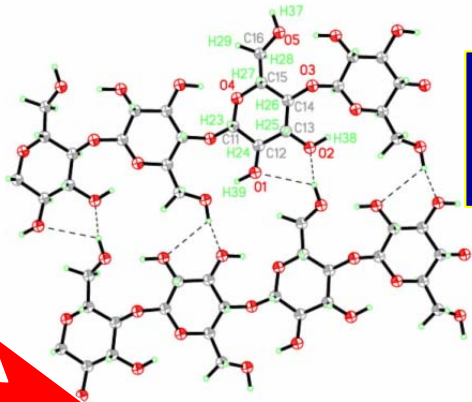
Options for the addition of multiple phases,
instrument and specimen factors,
wavelengths

Options for import/export and graphic
display calculations

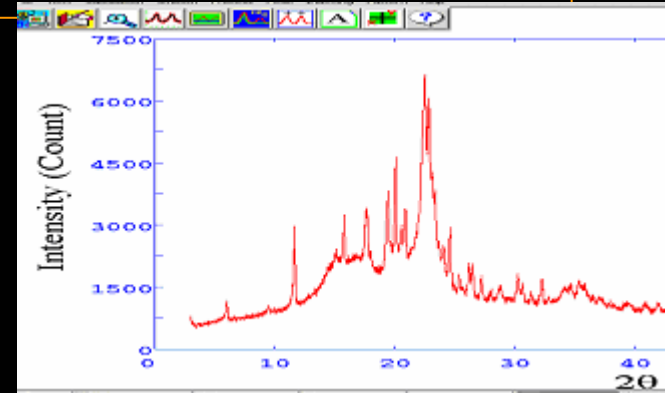


Pattern Fitting - Polymorphs of Cellulose

Use the known microfibril size of cellulose

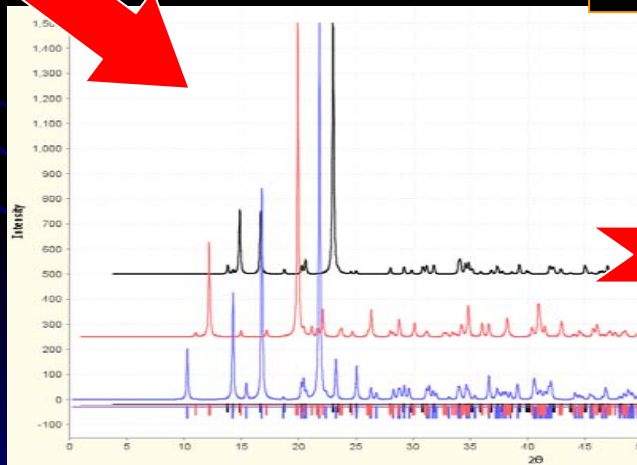


PDF 00-056-1717 Cell II
PDF 00-056-1718 Cell I beta
PDF 00-056-1719 Cell I alpha

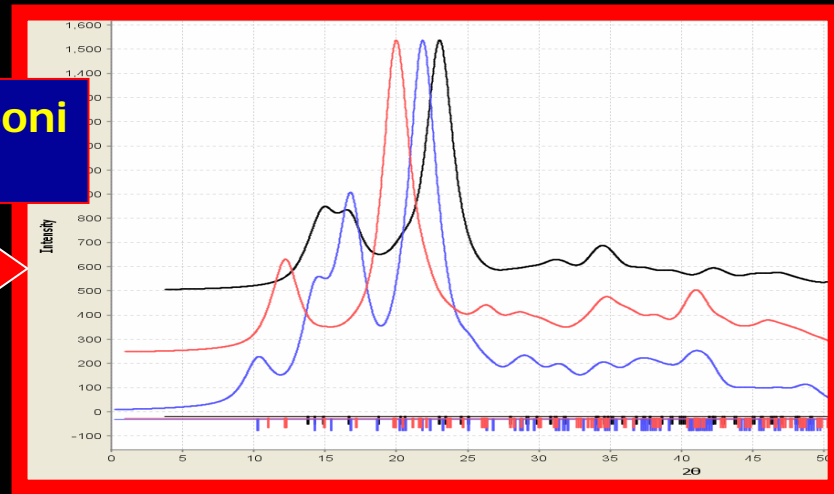


Peppid AC

Via PDF-4+



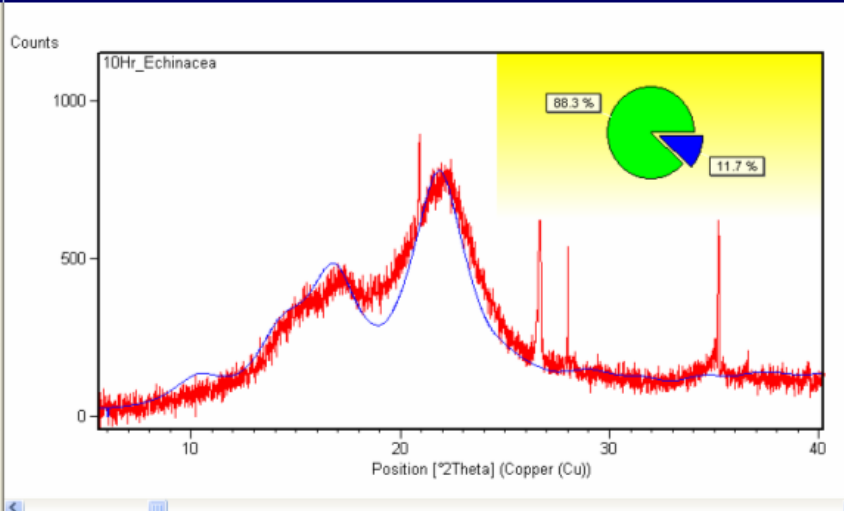
Scardi, Leoni
Faber



References for Form I alpha,
Form I beta and Form II

Simulation of microcrystalline
states of cellulose

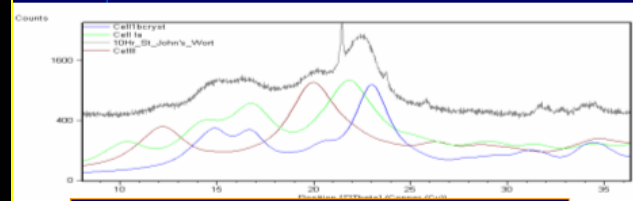
Echinacea



88 % Cellulose Ia (50 A), 12 % Amorphous + Quartz

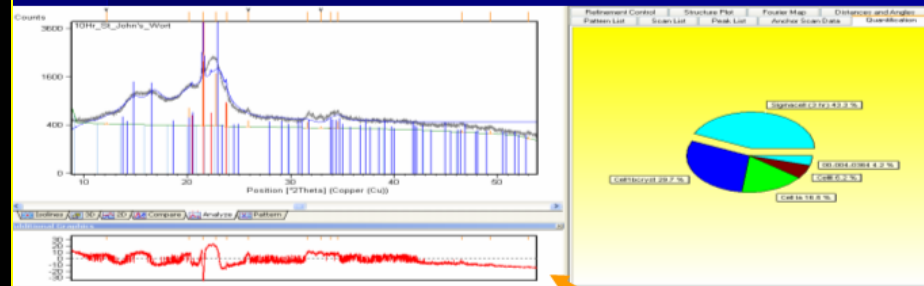
St John's Wort

"Serial Parts Plant Extract"



Polymorph simulations vs Experimental Data

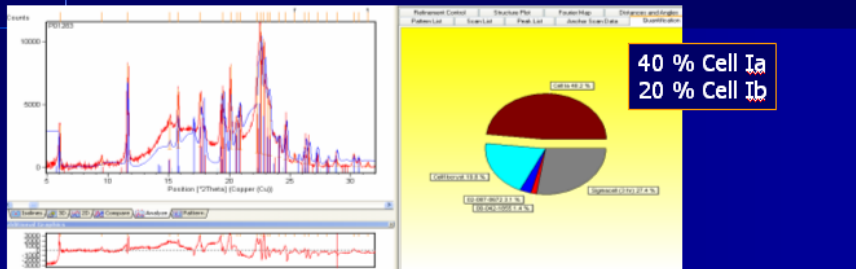
30 % Cellulose Ib
16 % Cellulose Ia
6 % Cellulose II
43 % Amorphous
+ 4 % Stearic Acid



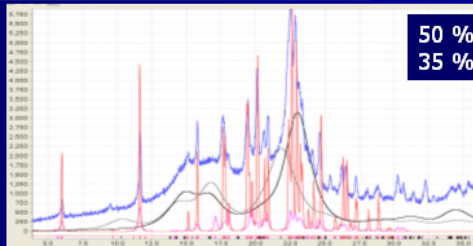
Pattern Analysis – 5 Phase Solution

Pepcid AC

2 Polymorphs Cellulose Ia, Ib
2 Polymorphs Famotidine I and II
Amorphous Cellulose

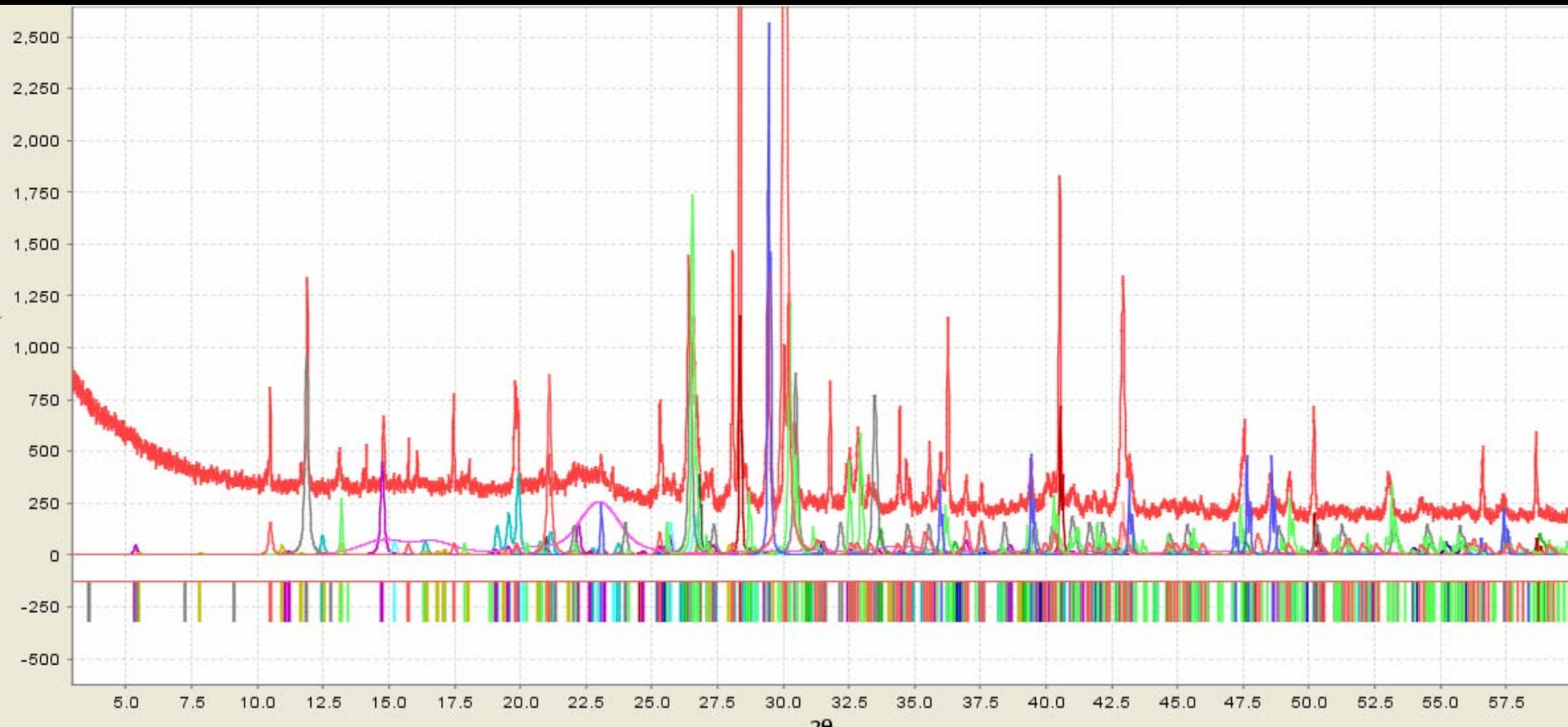


50 % Cell Ib
35 % Cell Ia



Enchinacea – Majority Cellulose Ia
Pepcid AC – Majority Cellulose Ib
(pharmaceutical microcrystalline)
St. Johns Wort – 1a, Ib, II polymorph mix

Hanawalt, Fink and Long 8 - *EXTREME*



16 Phase Solution for Centrum Performance

Mg Stearate, Niacin, Nicotinamide, Vitamin C (oriented), Cellulose Ibeta (microcrystalline), MgO, KCl, CaCO₃, ZnO, CaHPO₄, Iron Fumarate, TiO₂, SiO₂, Lactose Hydrate, MnSO₄, Riboflavin


149 out of 181 Peaks matched !

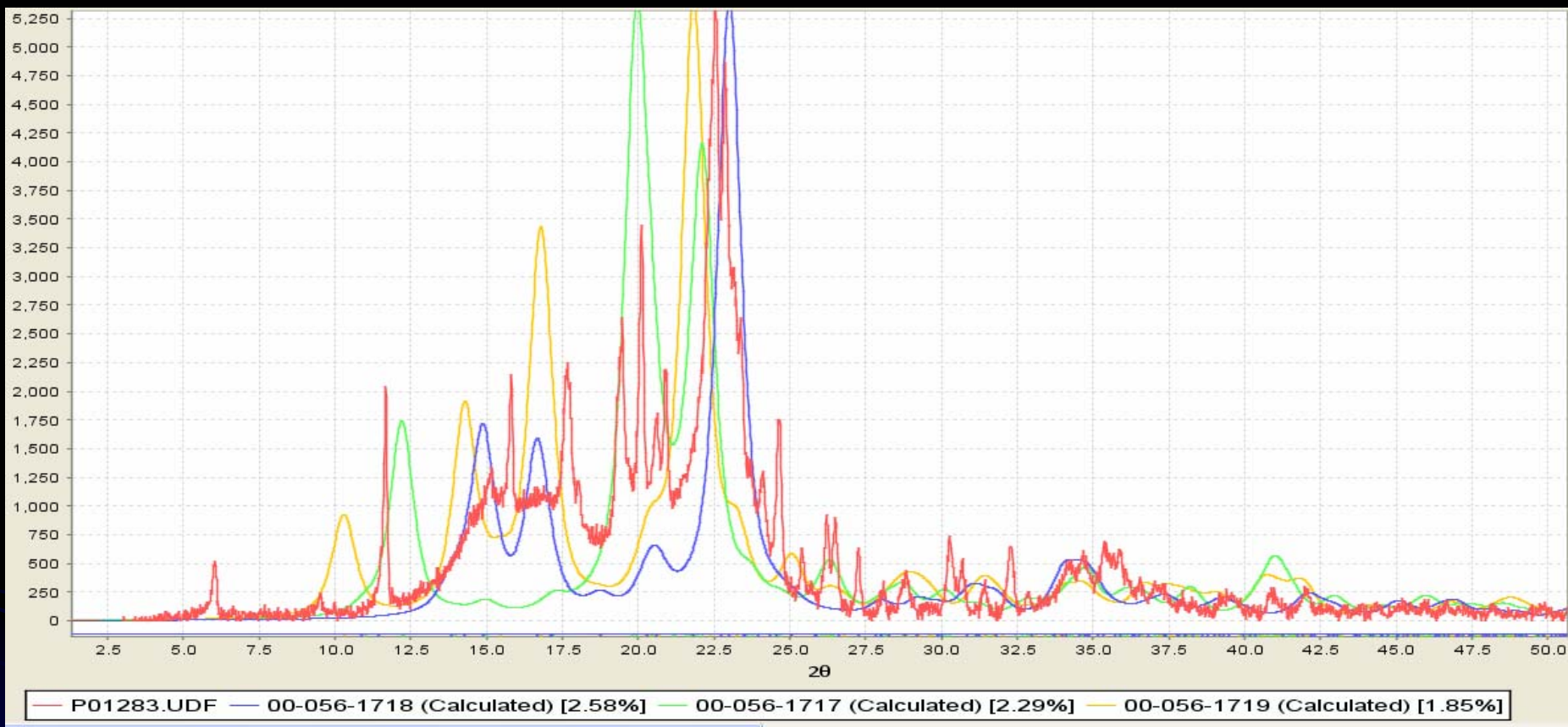
Plan

- 1) Calculations for Digital Patterns for all data – Done, PDF-4+ Release 2003
- 2) Simulations for nanocrystalline domain sizes – Done, PDF-4+ Release 2006
- 3) Definition and characteristics of amorphous and microcrystalline states as well as incommensurate structures - Started
- 4) Collect, edit and input experimental digital data in a standardized format
 - Started, first publication in PDF-4+ Release 2008
 - > 9,000 patterns collected primarily from ICDD grants, ongoing since 1995
- 4) Automated programs to process data - Started
- 5) Classification and editing of digital data groups - Started

Methods for **automated identification** of amorphous and nanomaterials

Similarity Indices

- PolySNAP, SNAP – Bruker-AXS
 - Cluster Analysis – PANalytical
 - Integral Index – PDF-4+ Release 2007
- 



Pepcid AC experimental data
compared to “best fits” of all reference
cellulose patterns
based on a point by point analysis

Calculated Index

PDF #	QM	Author	Chemical Formula	Compound Name	D1	D2	D3	SY	Integral Index ▼
00-039-1737	I	Okamura, K., Kyoto University, Kyoto, Japan.	(C15 H22 O8)x	Cellulose tripropionate	11.270000	7.640000	4.660000	M	15.24
00-003-0021	O	Trogus, C., Hess, K.	C24 H32 O17	Triacetylcellulose	10.500000	8.640000	6.680000	X	10.87
00-003-0192	O	Hess, Trogus.	C6 H10 O5	Cellulose	4.450000	8.900000	4.170000	X	9.27
00-036-1609	I	Sviridov, A., Myasnikova, R., Titova, E., Tsvankin, D., Pertsin, A.	C6 H6.28 N3.72 O16.2 · C4 H8 O3	Cellulose nitrate glycerinformal	9.300000	4.650000	5.230000	M	8.29
00-003-0289	O	Andress.	(C6 H12 O6)x	Native cellulose	3.890000	5.940000	2.570000	M	8.16
00-050-2243	O	Abou-Sekkina, M., Sakran, M., Saafan, A.	(C6 H19 N3 O5)n	Ammonia cellulose	4.230240	7.375030		X	7.55
00-036-1608	B	Sviridov, A., Myasnikova, R., Titova, E., Tsvankin, D., Pertsin, A.	C6 H6.28 N3.72 O16.2	Cellulose nitrate	7.160000	4.420000	3.680000	M	6.19
00-003-0022	O	Clark, Parker.	(C6 H10 O5)n - N H3	Ammonia cellulose	10.300000	5.150000	4.570000	X	5.71
00-050-2242	O	Abou-Sekkina, M., Sakran, M., Saafan, A.	(C6 H14 N2 O5)n	Ammonia cellulose	3.833840	5.790960	5.404930	X	5.61
00-050-2241	O	Abou-Sekkina, M., Sakran, M., Saafan, A.	(C6 H10 O5)n	Cellulose	3.900180	5.906090	5.372400	X	5.53
00-003-0203	B	Andress, Reinhardt.	(C12 H24 O12 · H Cl O4)x	Cellulose perchloric acid	4.420000	4.650000	3.560000	M	5.3
00-053-1861	O	Liang, X.-H., Guo, Y.-Q., Gu, L.-Z., Ding, E.-Y.	(C6 H10 O5)n · 19 H (O C2 H4)n O H	Poly(ethylene glycol) cellulose	3.790340	4.605930	3.386020	X	5.28
00-003-0114	O	Andress.	C12 H25 N O15	Nitrocellulose	5.340000	3.900000	2.570000	M	5.27
00-003-0226	B	Barry et al.	(C6 H10 O5)x	Cellulose	4.300000	5.140000	7.550000	M	4.29
00-047-2462	B	Zugenmaier, P., Kuppel, A.	(C10 H16 O5)n	Poly(trimethylcellulose)	10.720000	4.630000	4.250000	O	3.73
00-003-0223	O	Clark, Parker.	C6 H10 O5	Cellulose	4.310000	7.480000	5.150000	X	3.43
00-003-0188	O	Barry, Peterson, King.	(C6 H10 O5)n - N H3	Ammonia cellulose	4.470000	8.860000	4.050000	X	2.92
00-056-1718	C	Kaduk, J., BP Chemical, Naperville, IL, USA.	(C6 H10 O5)n	Cellulose β	3.866600	5.958580	5.314400	M	2.58
00-056-1717	C	Kaduk, J., BP Chemical, Naperville, IL, USA.	(C6 H10 O5)n	Cellulose II	4.453200	7.256690	2.576900	M	2.29
00-056-1719	C	Kaduk, J., BP Chemical, Naperville, IL, USA.	(C6 H10 O5)n	Cellulose Iα	4.072980	5.281940	6.205270	A	1.85

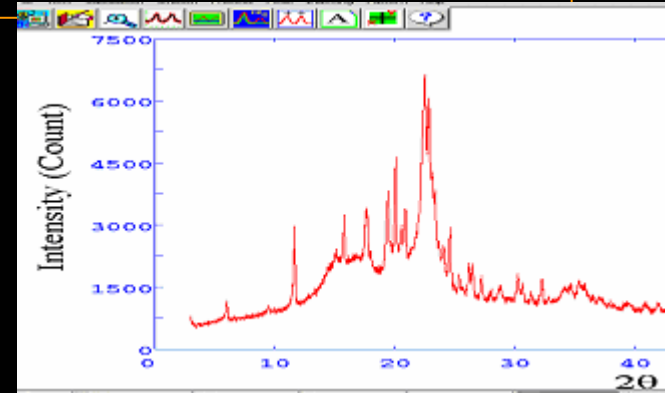
Three lowest values (best fits) are the most recent cellulose patterns

Pattern Fitting - Polymorphs of Cellulose

Use the known microfibril size of cellulose



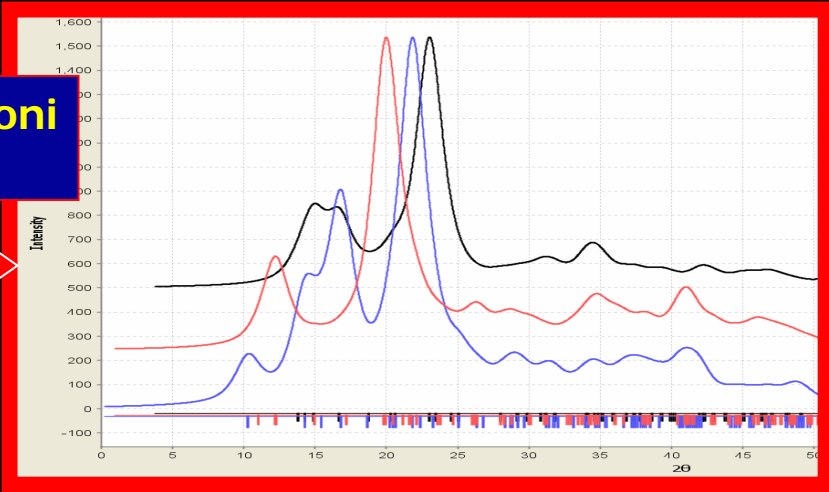
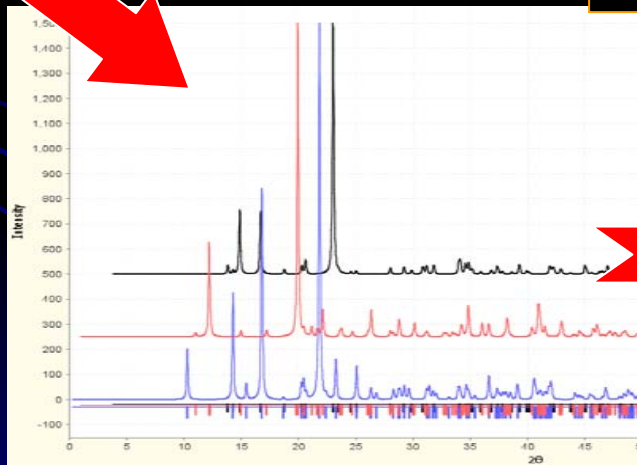
PDF 00-056-1717 Cell II
PDF 00-056-1718 Cell I beta
PDF 00-056-1719 Cell I alpha



Peppid AC

Via PDF-4+

Scardi, Leoni
Faber



References for Form I alpha,
Form I beta and Form II

Simulation of microcrystalline
states of cellulose

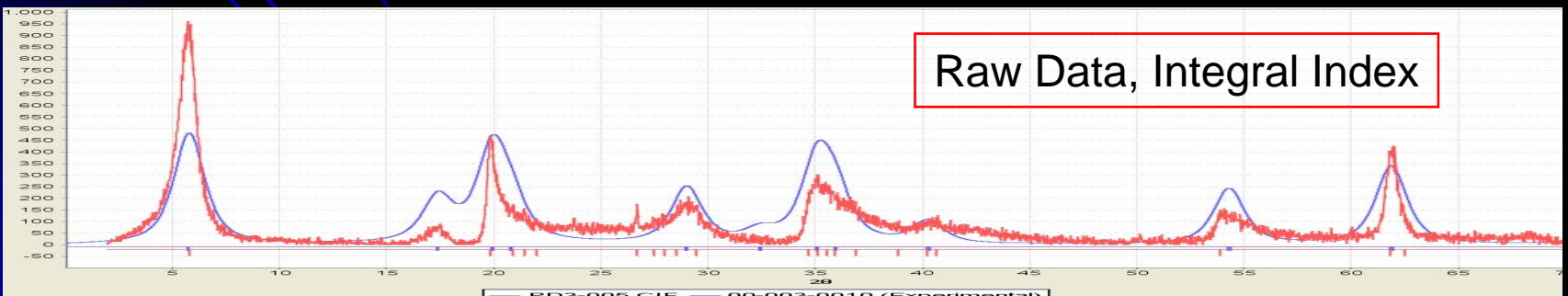
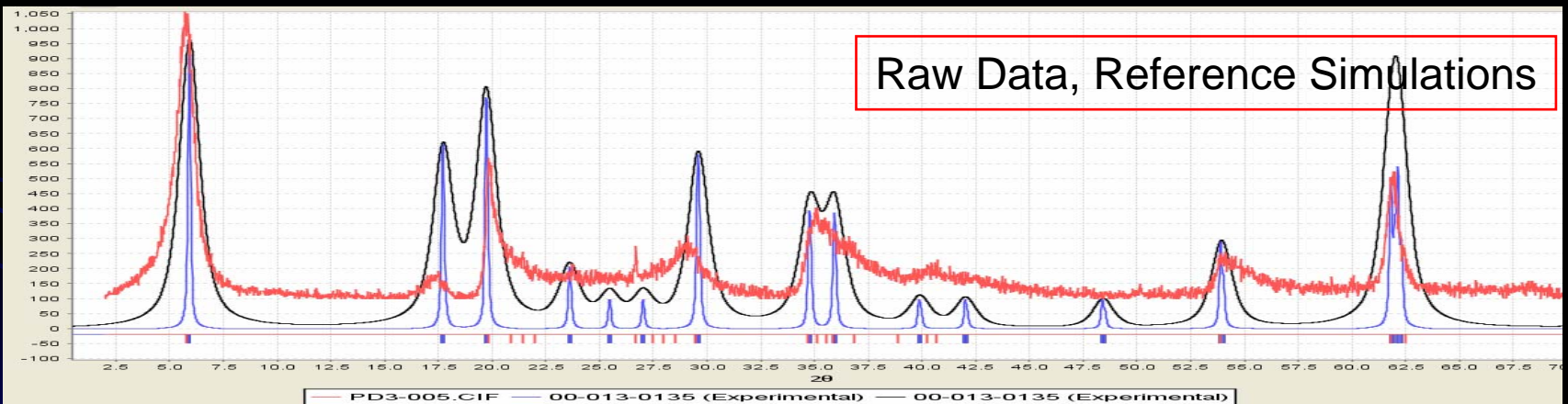
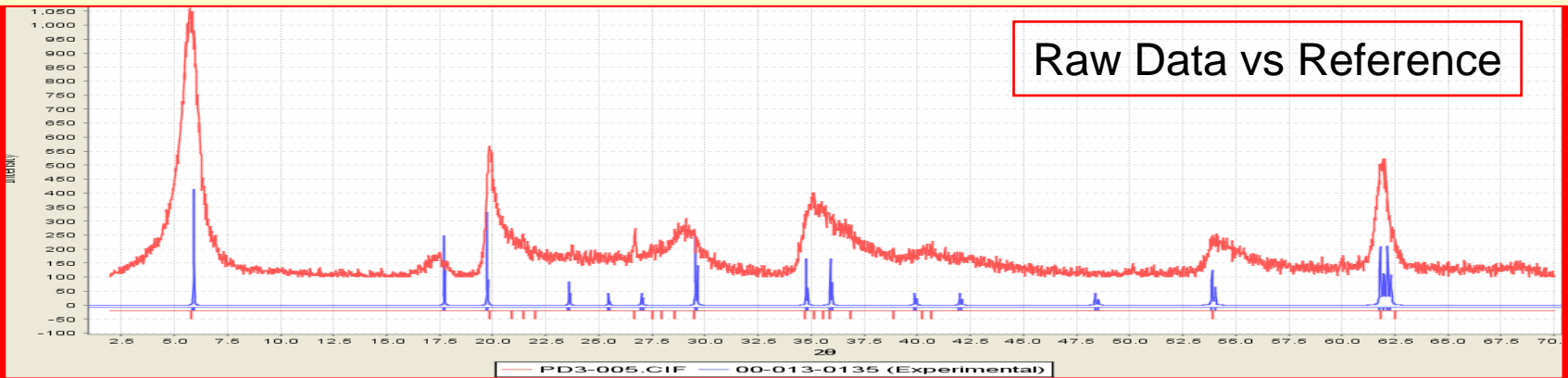
Using similarity indices

- current status

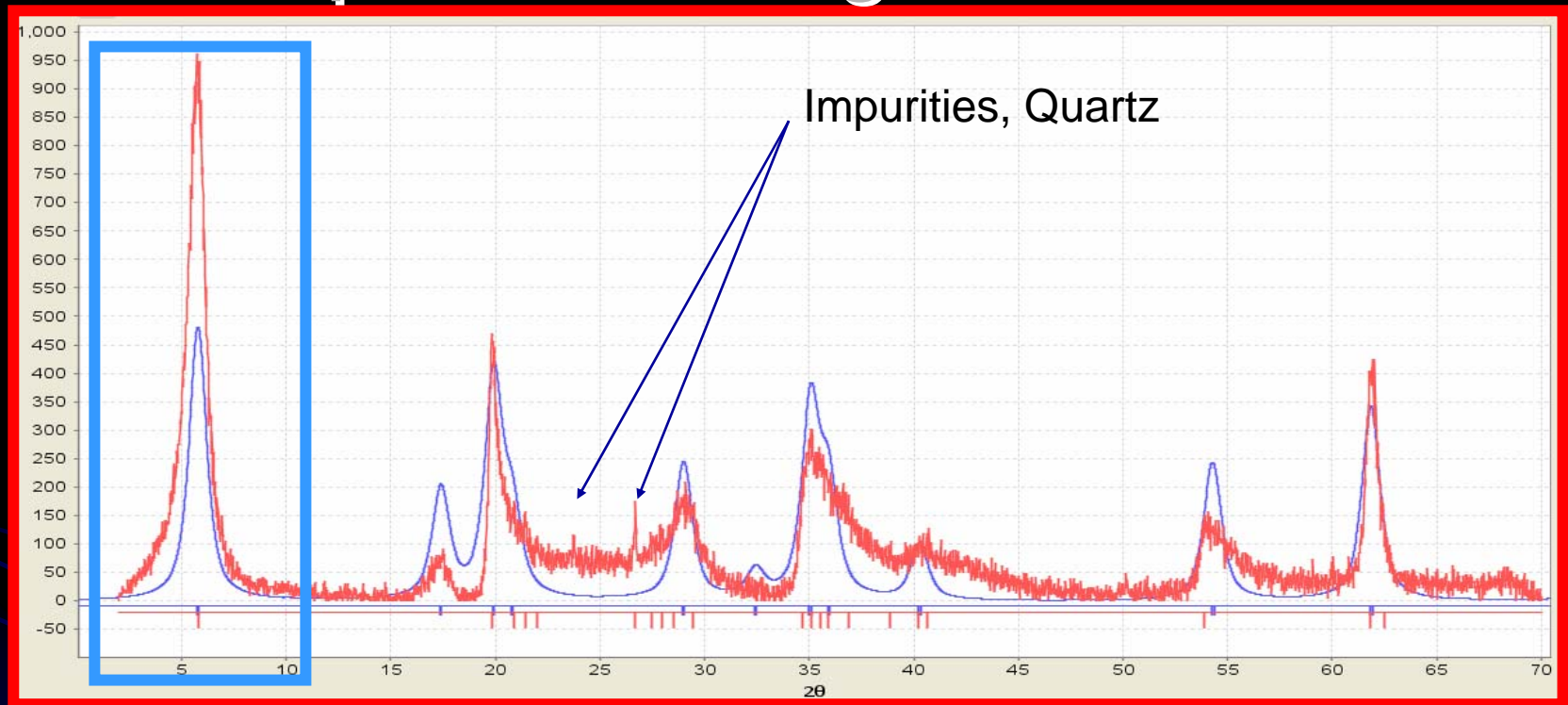
- All data must be adjusted for background (separate air scatter from amorphous content from microcrystalline content)
- All data must be adjusted for crystallite size effects (could be automated)
- Best results obtained when experimental conditions are similar

Montmorillonite

Raw Data – PSU, D.K. Smith collection

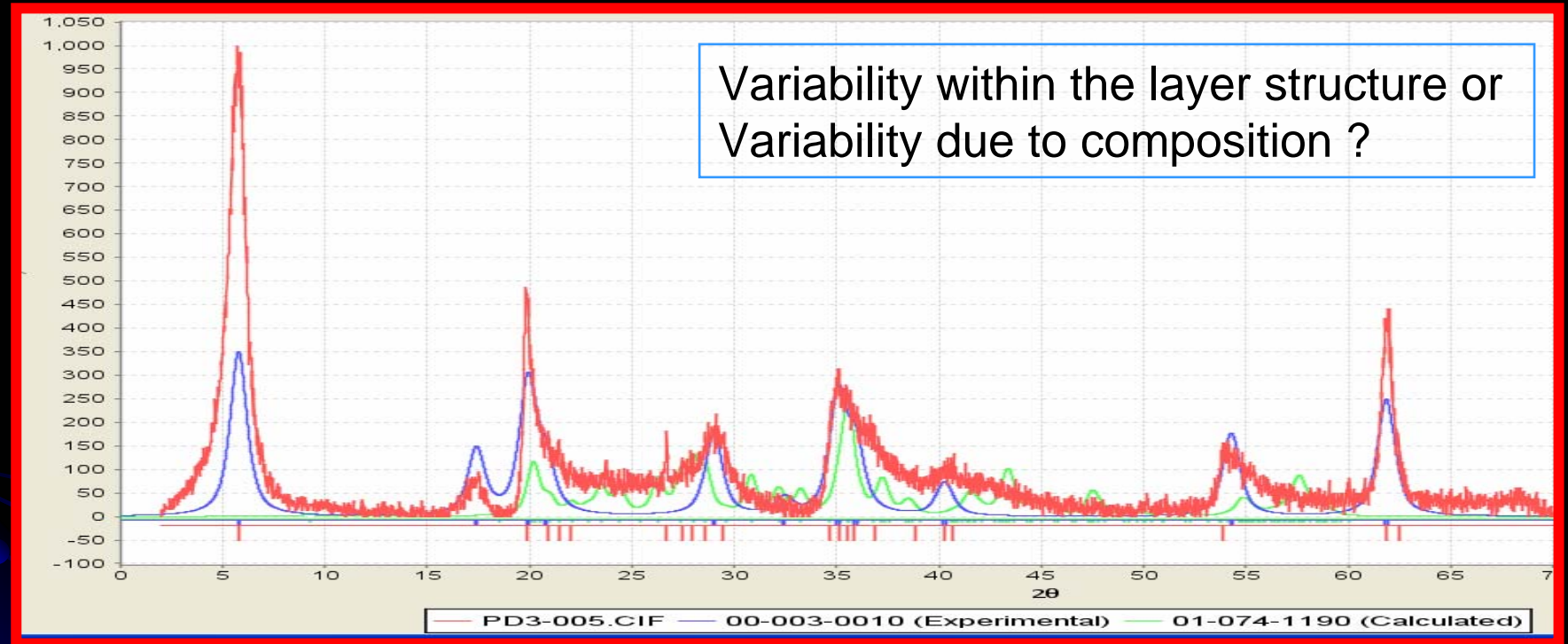


Real Data requires editing and review



- 1) Different optics – fixed vs variable slits, raw data is fixed, simulation is variable – effects Intensities and scaling
- 2) Impurities
- 3) Dimensional variability in layer structure ? – peak assymetry

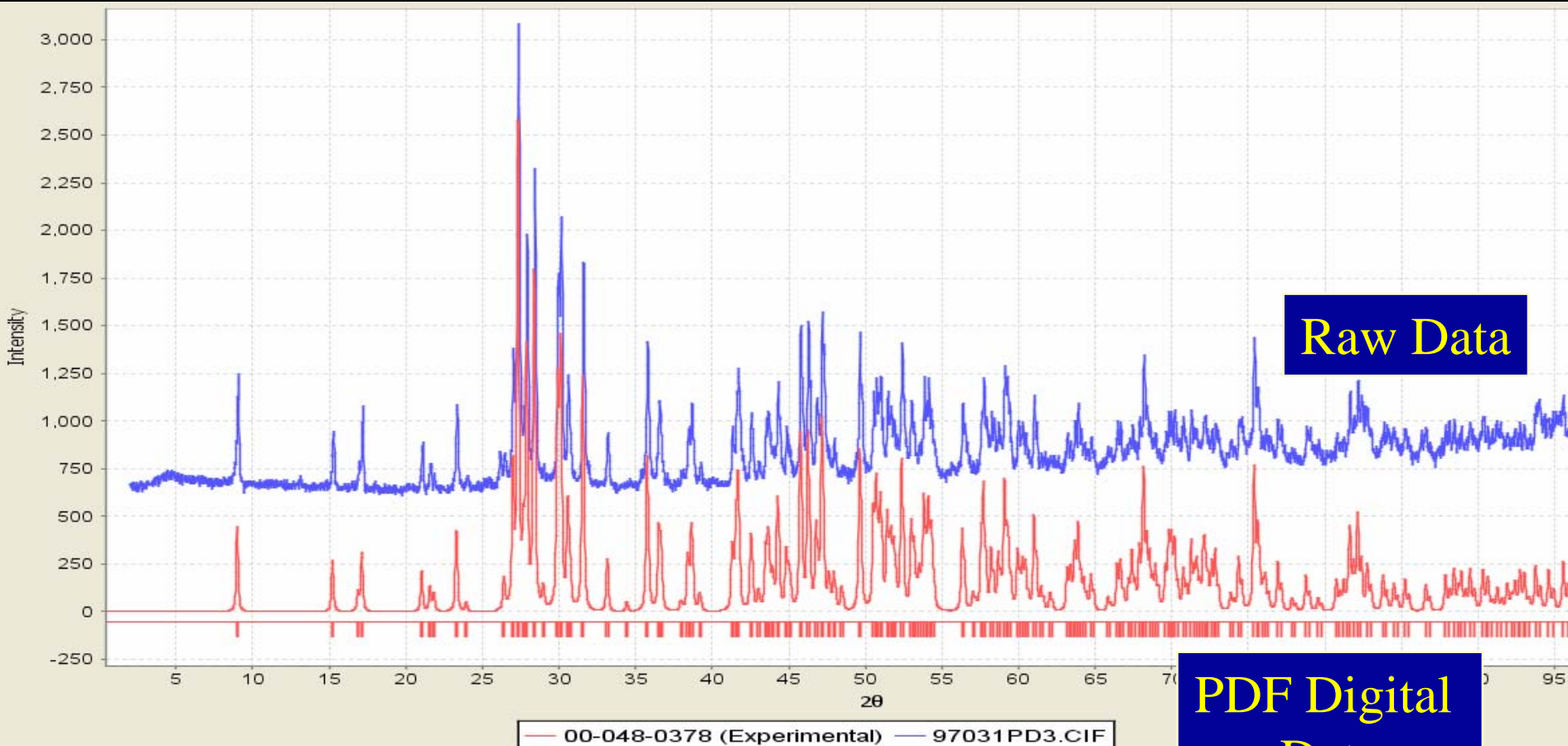
Dealing with Real Data



2- Phase ? Montmorillonite with Margarite
or 2 montmorillonites

Can this pattern be used as a reference ?

Raw experimental data vs PDF-4+ simulation

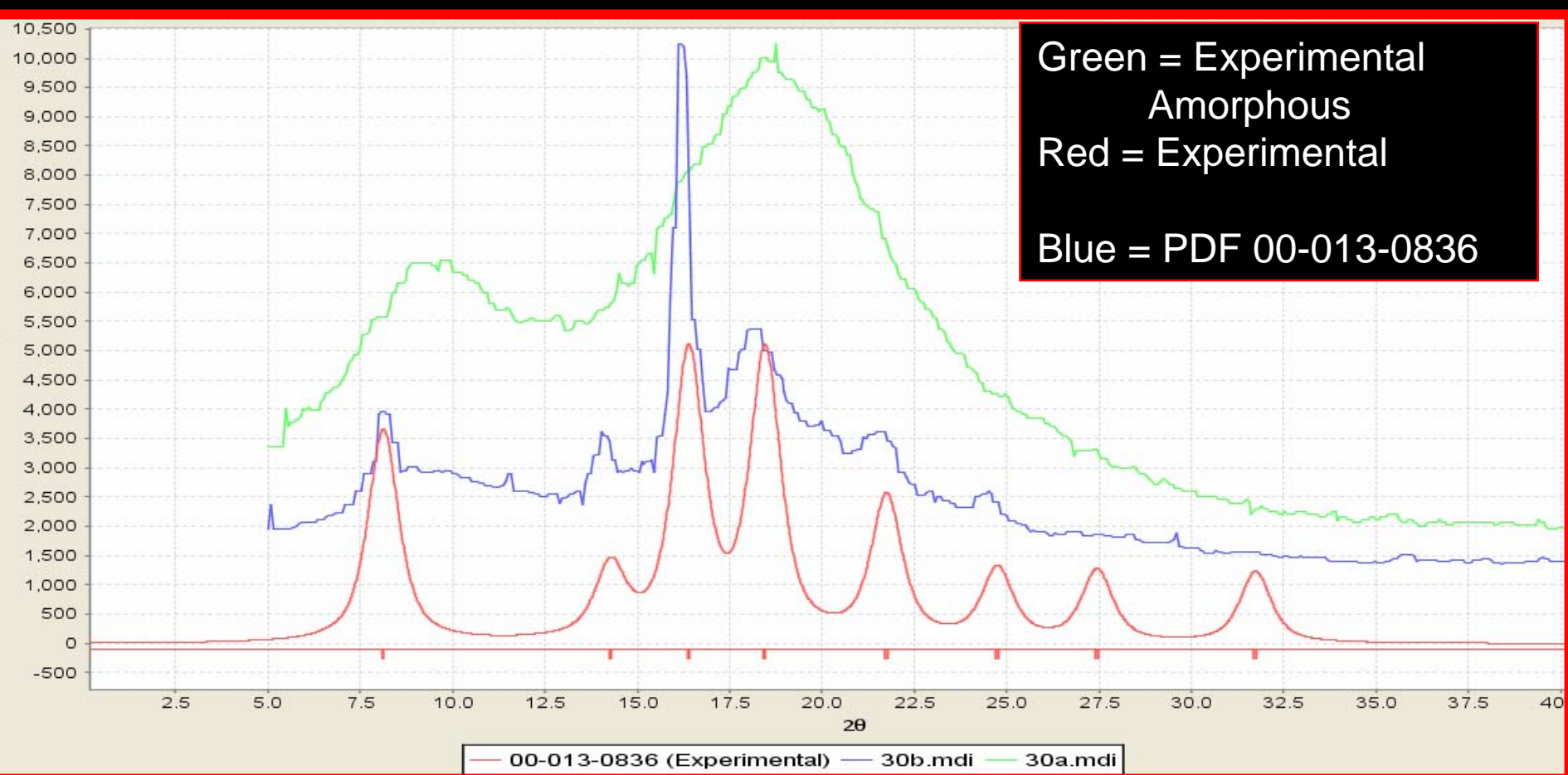


Raw Data

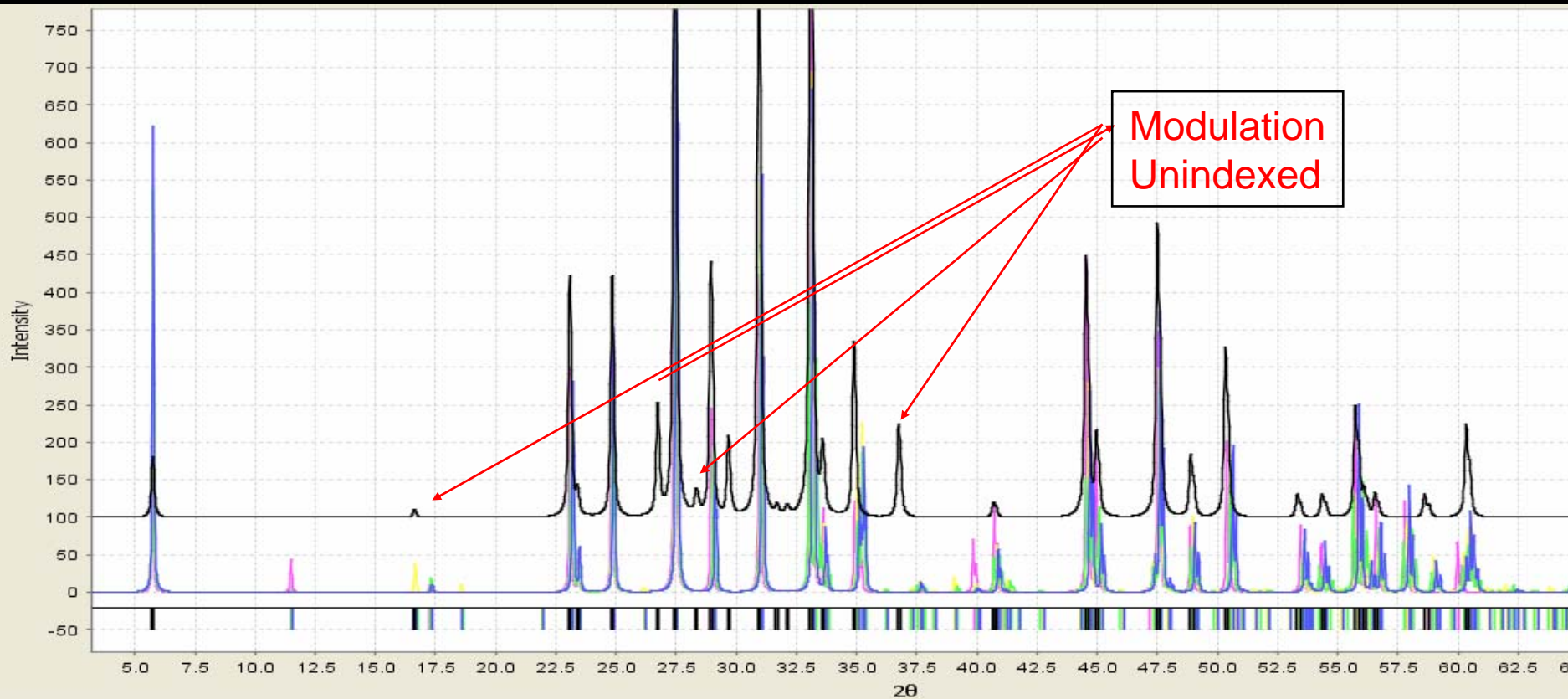
PDF Digital
Data

Isotactic Polystyrene

- 1, 2 or 3 reference entries ?



Incommensurate Structures



— 00-057-0957 (Experimental) — 01-070-2512 (Calculated) — 01-079-0897 (Calculated) — 01-079-2183 (Calculated)
— 01-080-0396 (Calculated)

Database for amorphous, microcrystalline, nanocrystalline materials

- Plan has been outlined, work has started
- Definitions and standard procedures are being developed *but not finalized*
- New analysis tools are being developed
- New capabilities planned for PDF-4+
Releases 2008-2010

This is a great time for input from the scientific community

