75 Years of the Powder Diffraction File™: An Overview of Database Development for Materials Characterization

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ISO 9001:2008 QUALITY ASSURED COMPANY CERT.NR. 11409.1

Celebrating 75 years 1941–2016 ICDD® International Centre for Diffraction Data

International Centre for Diffraction Data

A non-profit scientific organization dedicated to collecting, editing, publishing, and distributing powder diffraction data for the identification of materials. The membership of the ICDD consists of worldwide representation from academe, government, and industry

Mission - The International Centre for Diffraction Data will continue to be the world center for quality diffraction and related data to meet the needs of the technical community. ICDD promotes the application of materials characterization methods in science and technology by providing forums for the exchange of ideas and information

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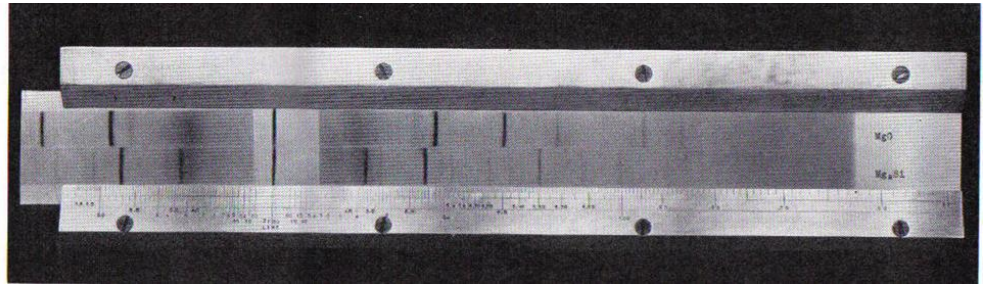
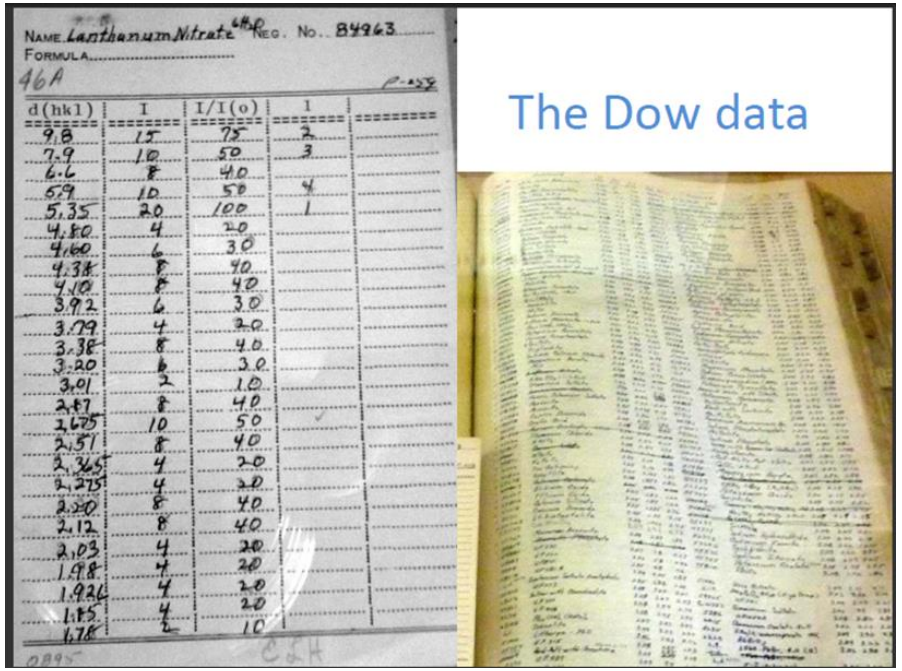
Phase Identification





The Dow data

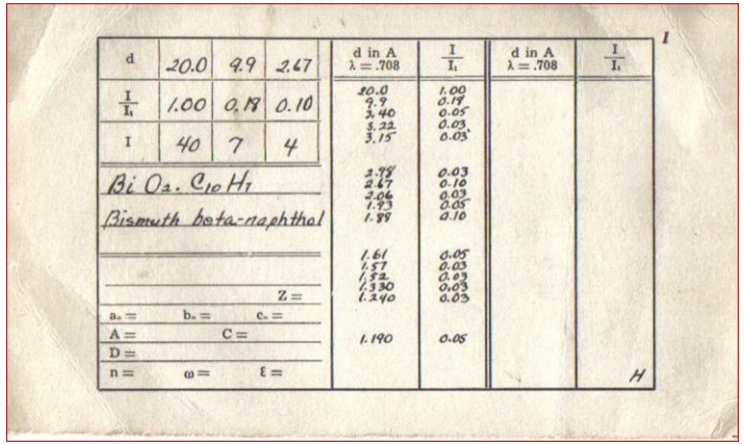
Hanawalt Method

Collect powder patterns

Reduced data to d-spacings (peaks) and Intensities (series of xy data)

Use the strongest 3 lines and permute their order in an index

Match unknowns with the index then match the full pattern



1938
Ludo Frevel, Don Hanawalt and Sid Rinn

Chemical Analysis by X-ray Diffraction

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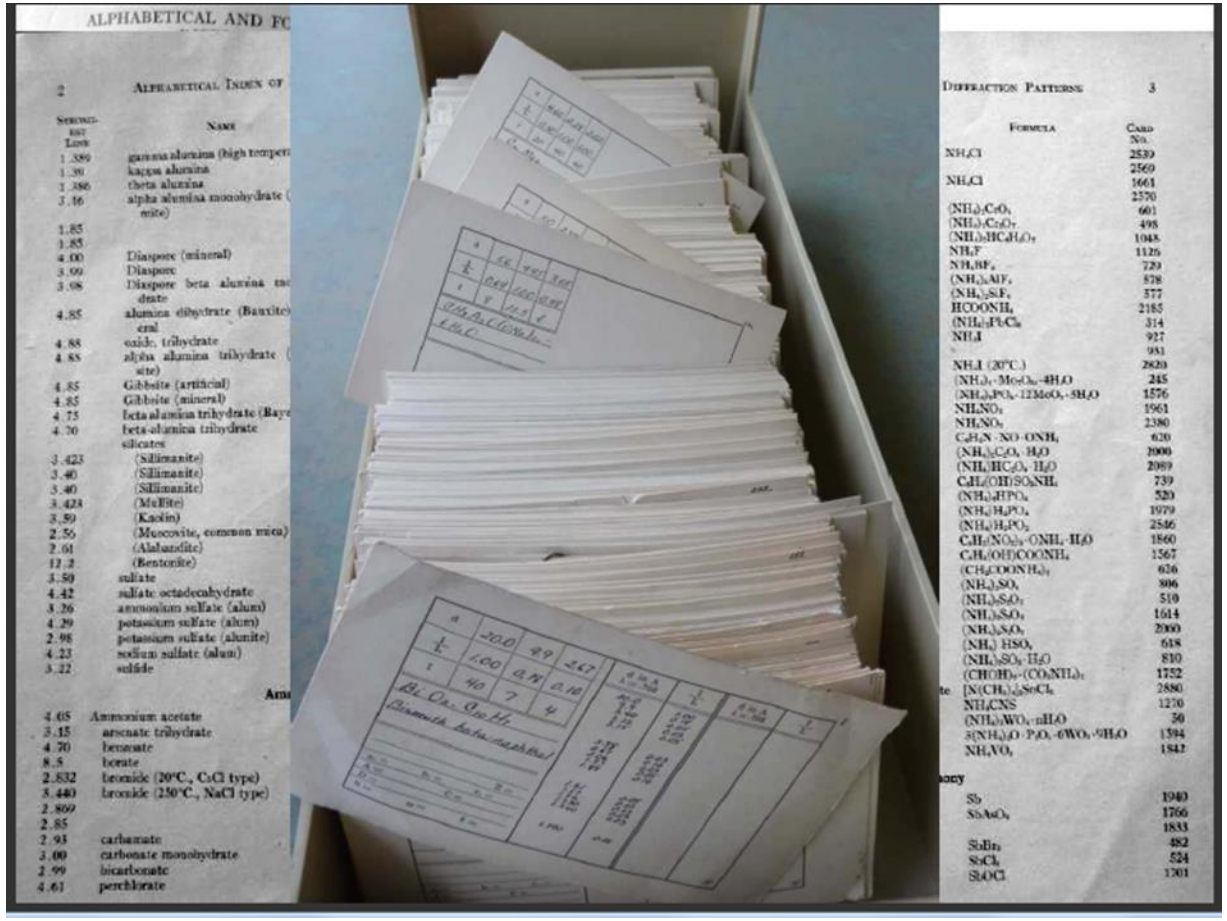
1941



Card Files and Indexes transported from Midland, Michigan to ASTM headquarters in Philadelphia in Don Hanawalt's car, copied by hand – Set # 1 of the Powder Diffraction File

Joint Committee on Powder Diffraction Standard (JCPDS) –

1941, 1945

(ASTM Committee on X-ray and Electron Diffraction, British Institute of Physics, National Research Council)

Davey (Hull)	General Electric (then Penn State)
Pickett, Wyman	General Electric
Hanawalt	The Dow Chemical Co. (Mg)
Wilson, Lawrence Bragg	British Institute of Physics
Barton	Institute of Physics (USA)
Fink	Aluminum Company of America
Fuller	New Jersey Zinc
Bannister	British Museum, Cambridge University
Huggins	Eastman Kodak Co.
Boldyrev	Institute of Mines, Leningrad, Russia
Harcourt	American Mineralogist
Kerr	Columbia University
Nelson	Batelle
Magos	Crane Co.
Richmond	US War Department

The Powder Diffraction File

Celebrating 75 years 1941–2016 ICDD® International Centre for Diffraction Data

1986
Cards

46,000 entries

1987
CD-ROM
<1GB
46,000 Entries

2016
DVD
27 GB
9 GB
Inorganic
19 GB
Organic
848,757 Entries

Celebrating 75 years
1941–2016
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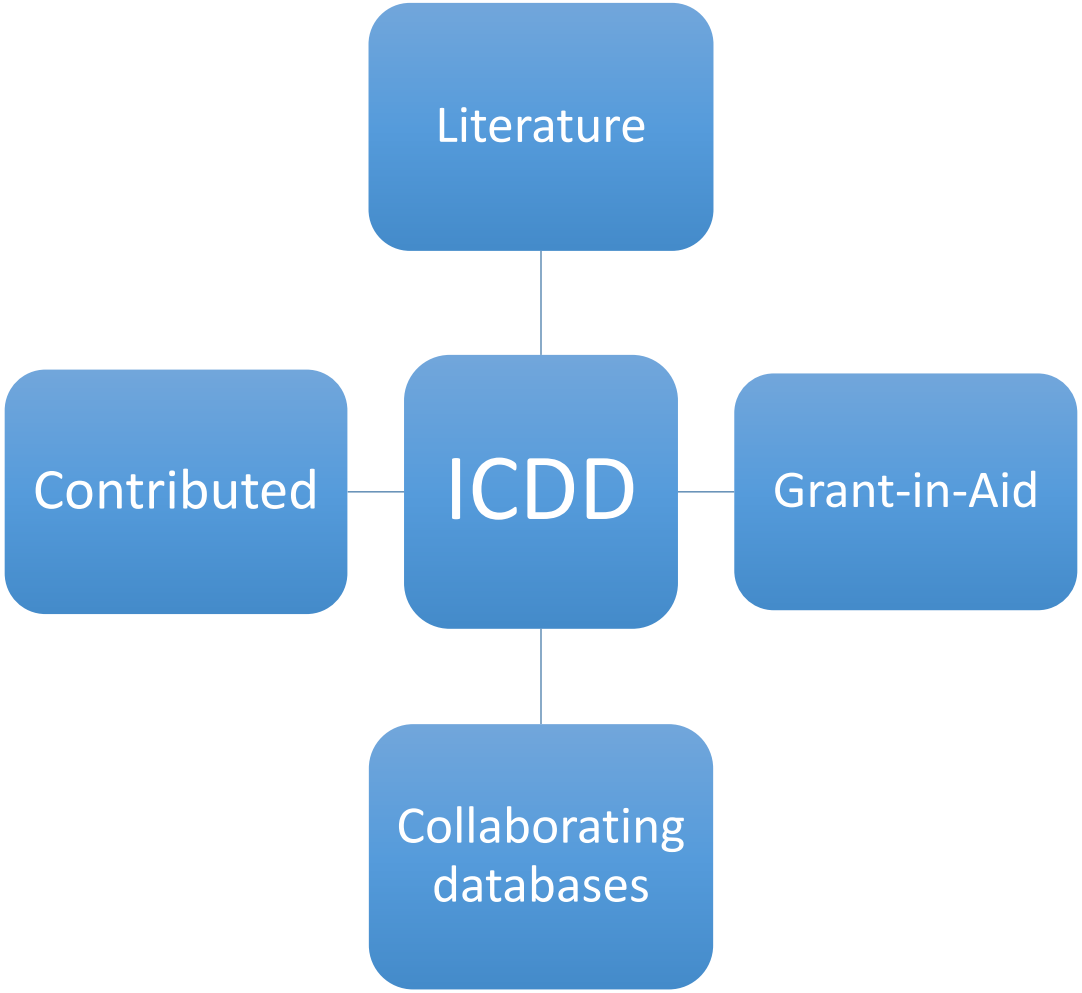
INTERNATIONAL CENTRE FOR DIFFRACTION DATA

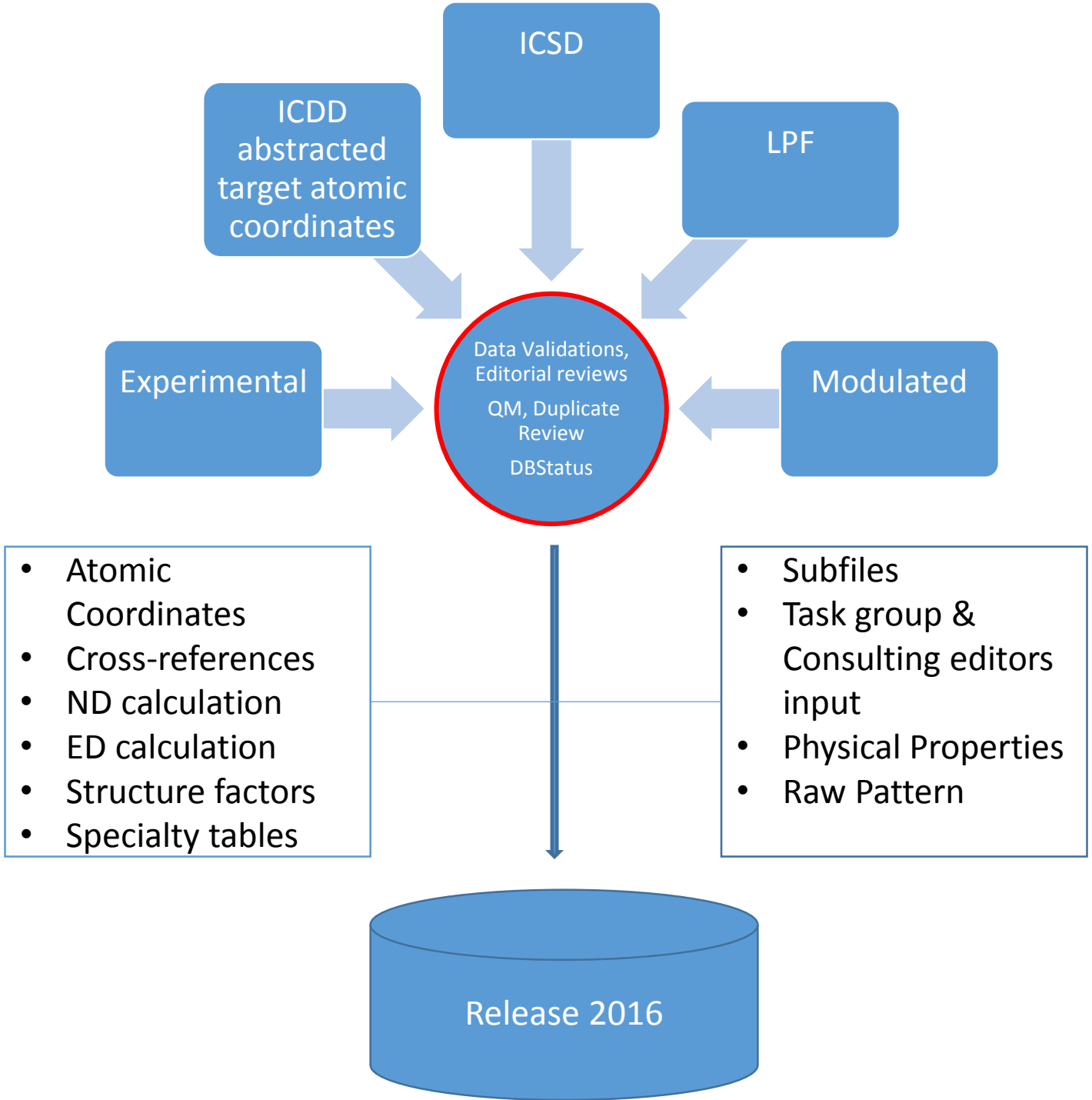
Database Overview

- Quality Marks
- Database Status of a given entry
- Subfile Classification
- Database Filters
- Structural Classification
- Raw Data Archival

Data Source



Celebrating 75 years 1941–2016 ICDD® International Centre for Diffraction Data


ICSD
ICDD abstracted target atomic coordinates
LPF
Experimental
Data Validations, Editorial reviews
QM, Duplicate Review
DBStatus
Modulated
Atomic Coordinates
Cross-references
ND calculation
ED calculation
Structure factors
Specialty tables
Subfiles
Task group & Consulting editors input
Physical Properties
Raw Pattern
Release 2016

Quality Marks (QM)

- Upcoming release of Powder Diffraction File will have **848,757** entries (Inorganic+Organic)
- Quality marks are essential while working with larger database with similar diffraction patterns
- Data validation and the quality mark assignments is the most important step in the editorial process
- Every entry in Powder Diffraction File has quality mark
- If an entry does not meet the condition for star pattern, editorial comment(s) describing the reason will be added

QM for Experimental Patterns

- **Star** (Well characterized chemically and crystallographyically, No unindexed lines,Δ2ɵ≤0.03º)
- **R** (d values from whole pattern fitting, like Rietveld, Le Bail refinement)
- **I** (Well characterized chemically No unindexed strong lines,Δ2ɵ≤0.06º)
- **B** (Do not meet the criteria for *, I)
- **O** (Poorly characterized, with editorial comment explaining the reason)
- **C** (author calculated d values)
- **H** (Hypothetical)
- M (Minimally acceptable non crystalline pattern)
- G (Good non crystalline pattern, usually has additional characterization other than XRD)

QM for Experimental Patterns

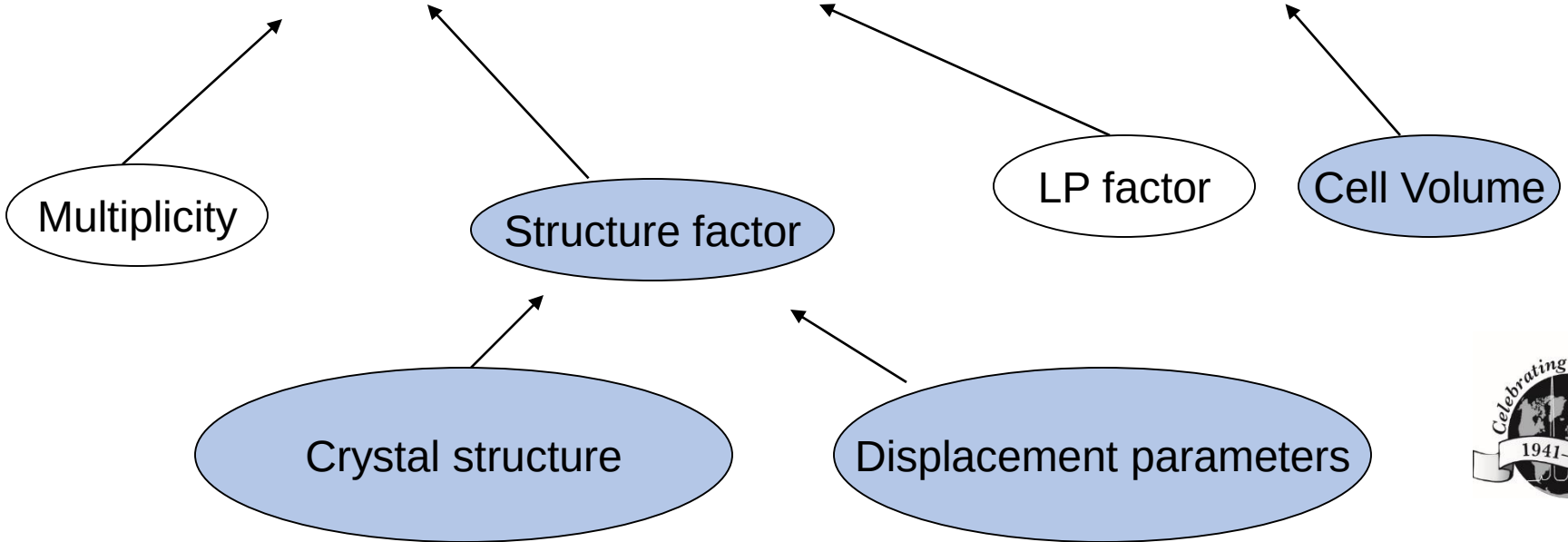
- Each and every pattern editorially reviewed including visual comparison of raw data vs d-I list
- Undergoes more than 100 data validation checks before gets published

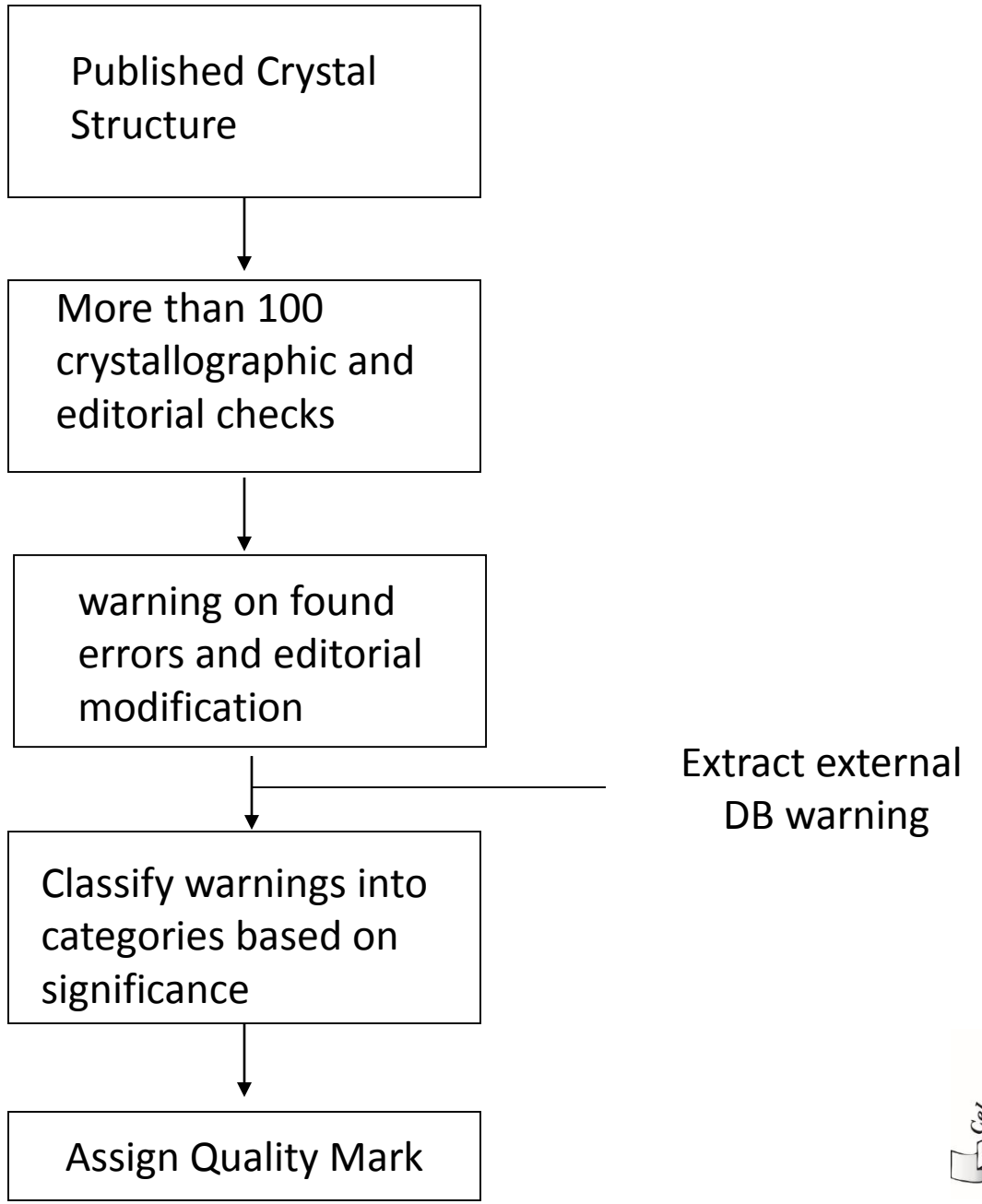
Calculated Patterns QM

If we know the crystal structure, we can calculate the diffraction pattern using the equation

It is extremely important to make sure that the crystal structure used for the calculation is correct. In fact it is the rate determining step in the editorial process

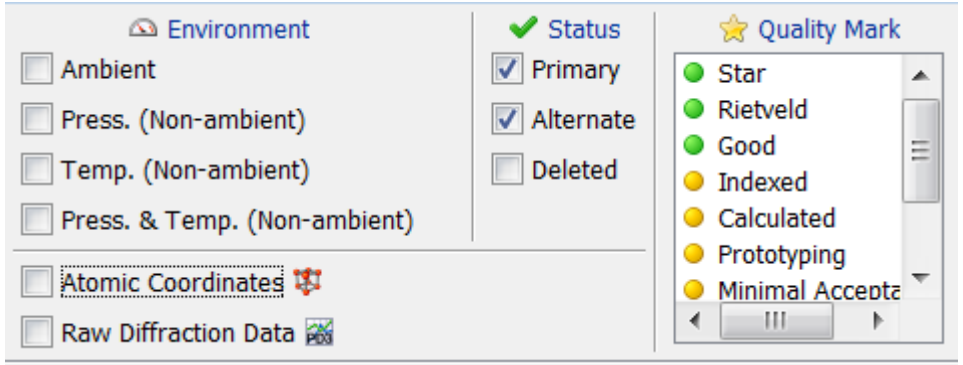
$$I_{hkl} = M_{hkl}\left|F_{hkl}\right|^2\left(1+\cos^2(2\theta)\cos^2(2\theta_m)/\sin^2\theta\cos\theta\right)_{hkl}/V^2$$



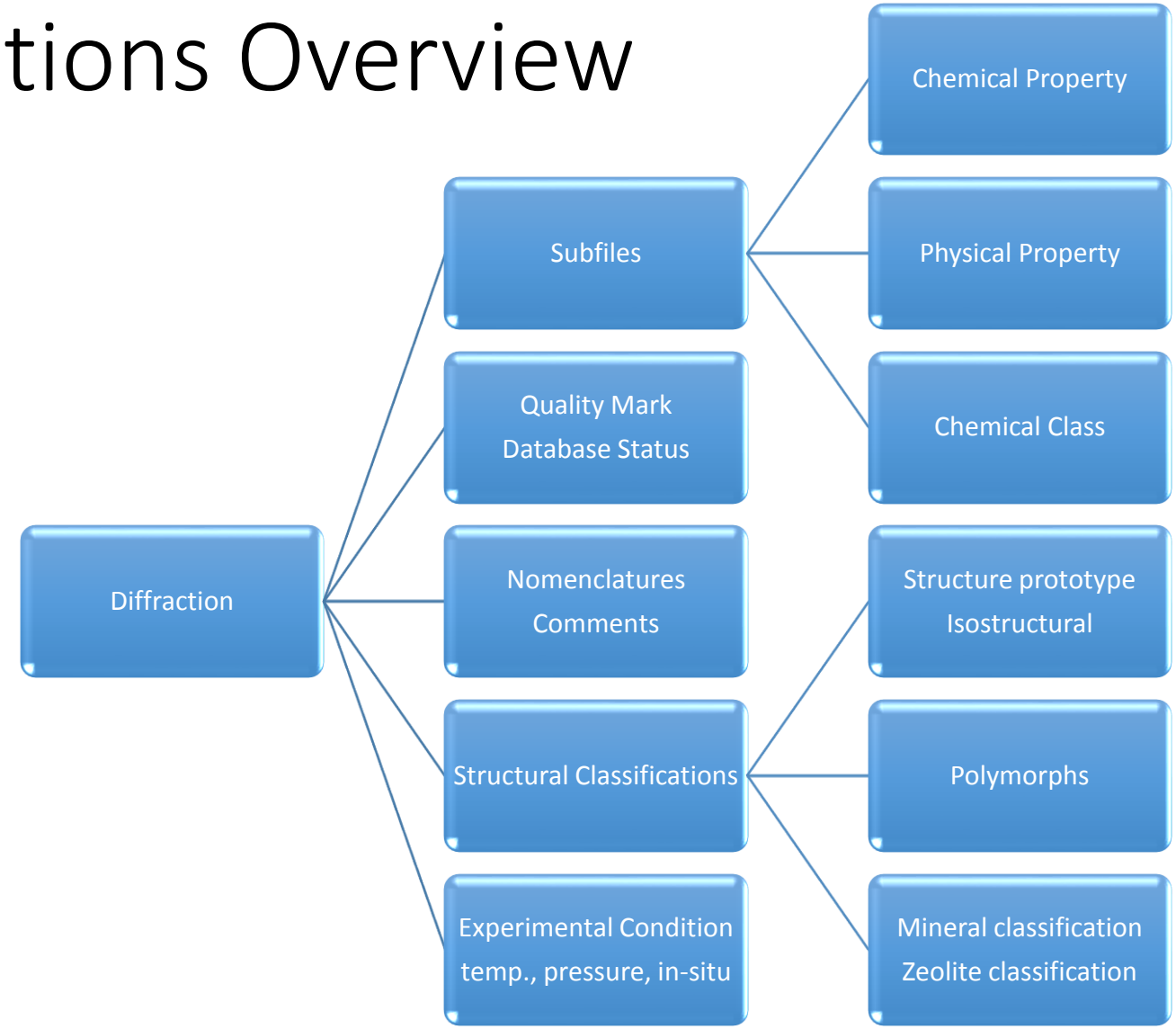

Published Crystal Structure
More than 100 crystallographic and editorial checks
warning on found errors and editorial modification
Extract external DB warning
Classify warnings into categories based on significance
Assign Quality Mark

Database status

- When multiple entries are available, database status is assigned editorially to avoid nearly duplicate result set
- Primary
  - Primary pattern for a given phase usually best quality, room temperature data
- Alternate
  - Alternate to primary. Not necessarily mean of poor quality
- Deleted
  - Unresolved errors
  - Duplicated entry



Classifications Overview



PDF databases: subfiles

Comprehensive data collections - classified and edited by experts

PDF-4+ 2016	384,613
PDF-4/Organics 2017	516,054 Entries

Edited subfiles, unique to the Powder Diffraction File

31 Subfiles
17 Subclasses
---
48 Collections

<u>Chemistry</u>
Minerals
Metals & Alloys

<u>Application</u>
Forensic
Cements

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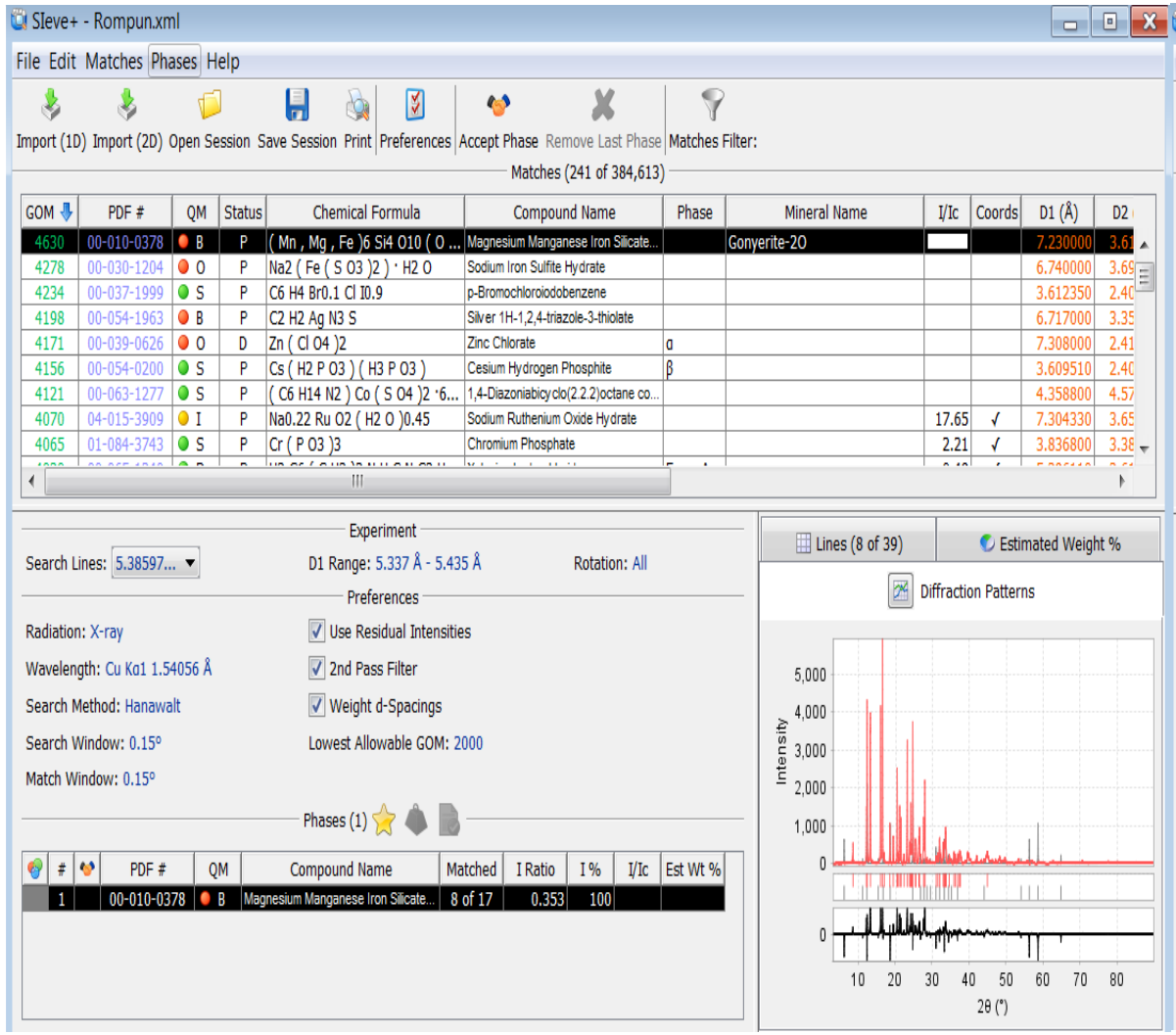
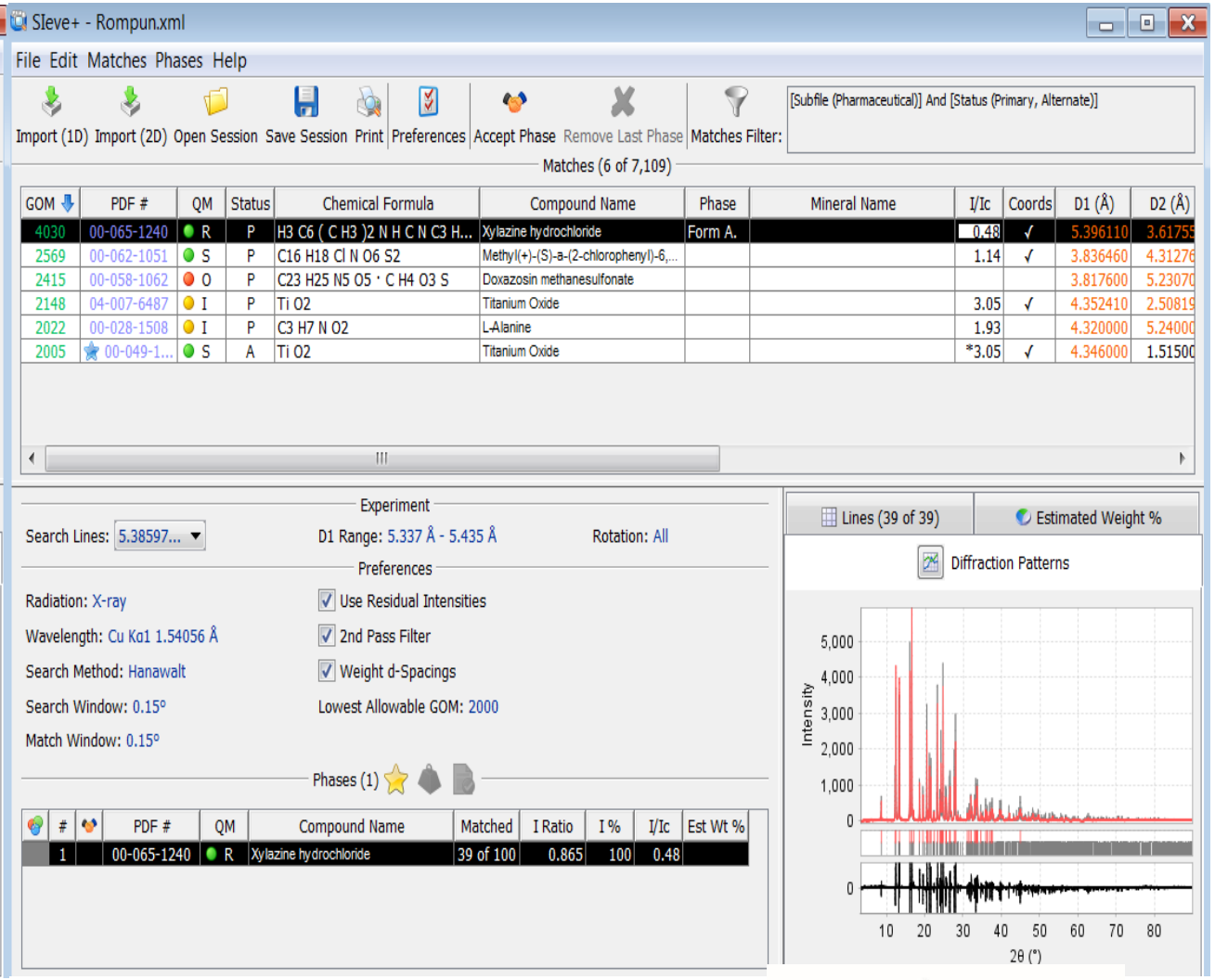
Subfiles

- Classified into various categories based on chemistry, properties and application
- Very useful in minimizing false positives while performing search/match using a large database
- Each subfile is defined by set of rules approved by the concerned subcommittee
- Subcommittee members review the file and continuously improvise it
- Library database gets updated frequently based on subcommittee's input
- Examples: Cement, Pharmaceutical, Ion Conductor, Forensic etc

Application of subfile in search/match





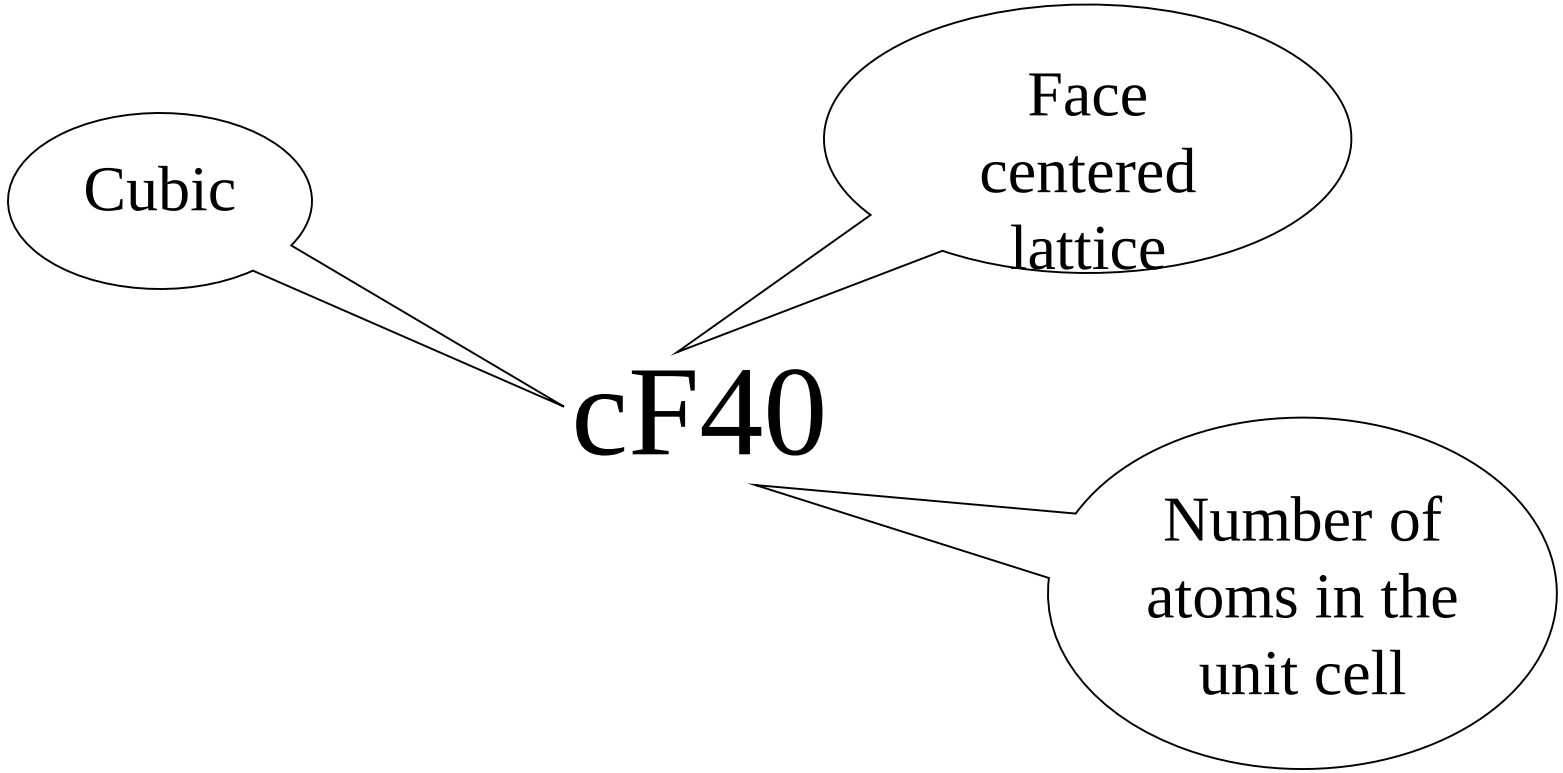
Without subfile filter
False positive

Correct answer using
subfile filter

Structural Classifications

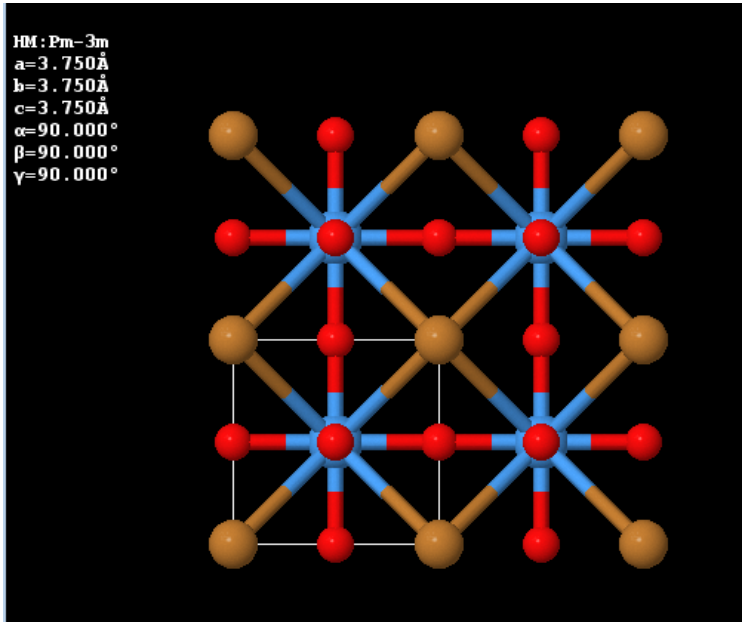
- Pearson Symbol Code (PSC)
- Traditional Structure Type Notations
- ANX Formula
- Long descriptive Notation following Parthe's method
- Mineral Classification
- Zeolite Classification

Pearson Symbol Code



Pearson Symbol Code Types

- Filled
  - Do not distinguish partially occupied site from fully occupied one
  - Example cP5
- Actual
  - Actual site occupation (true to the composition)
  - Example cP4.50
- Without hydrogen



Ca0.5 Ta O3

Atom	Num	Wyckoff	Symmetry	x	y	z	SOF	IDP	AET
Cu	1	1a	m-3m	0.0	0.0	0.0	0.5		12-b
Ta	2	1b	m-3m	0.5	0.5	0.5	1.0		6-a
O	3	3c	4/mm.	0.0	0.5	0.5	1.0		2#b

ANX Formula

ANX formula is a type of structural classification based on type of atoms (cations, anions) and their site occupation

- Coordinate of all the atoms in the structure must be defined to apply this classification successfully
- Atoms occupying same site are treated as one single atom type
- All the sites occupied by the same atom type is combined except when oxidation state is different
- Symbols used : Cations (A-M), Neutral (N-R), anions (X,Y,Z, S-W)
    - **Example**
        - **Ca Ti O3 is of ABX3 type**
        - **Fe3O4 is of AB2X4 type**

Long descriptive Notation

- Structure Type Formula, Pearson Symbol, Space group number
- Examples: Cu3 Au,cP4,221; Cu3 As,cI64,220; NaCl,cF8,225

Structure type requirements

- Must crystallize in the same space group
- Similar cell parameter ratio
- Same Wyckoff positions (Wyckoff sequence)
- When all the above 3 conditions satisfy, we have similar atomic environments

Standardization of Crystal Structure

- First proposed by Parthe and Gelato (*Acta Cryst. (1984), A40, 169-183*)
- The method calculated standardization parameter τ based on
  - Shift of origin
  - Rotation of the coordinate system
  - Inversion of the basis vectors

  The smallest τ represents the standard description

$$\Gamma = \sum_{i=1}^{N} \left(x_i^2 + y_i^2 + z_i^2 \right)^{1/2}$$

N is number of atom sites, x,y,z are fractional coordinates

Why standardized data for comparison?

CeCu2, Imma, a=4.425,b=7.057, c=7.475

Cu (8h) 0 0.051 0.1648

Ce (4e) 0 0.25 0.5377

Standardization

CeCu2, Imma, a=4.425,b=7.057, c=7.475

Cu (8h) 0 0.051 0.1648

Ce (4e) 0 0.25 0.5377

KHg2, Imma, a=8.10,b=5.16, c=8.77

Hg (8i) 0.190 0.25 0.087

K (4e) 0 0.25 0.703

Standardization

KHg2, Imma, a=5.16,b=8.10, c=8.77

Hg (8h) 0 0.06 0.163

K (4e) 0 0.25 0.547

Structure Type Applications

- Deriving Starting Model for Rietveld Refinements
  - Traditionally starting model for Rietveld refinements was developed based on chemical/crystallographic intuition. In other words it is individual's knowledge of structure types
  - Databases with Structure Type information can make seminal contributions to this effort. Powder Diffraction File in particular is advantageous as one can perform search match based on their diffraction pattern to explore the possible models.

Structure Type Applications

- Structural chemistry information
  - Database search results can also be sorted based on their structural chemistry
  - Can be used to explore the database from the materials design point of view
  - 3D crystalline structure related properties
    - Ferrolectric, Piezoelectric, Non Linear Optics,Transport

Mineral Classifications

Family
- Related by partial structural similarities
- Examples: Double chain (Amphiboles), Sheet (Mica)

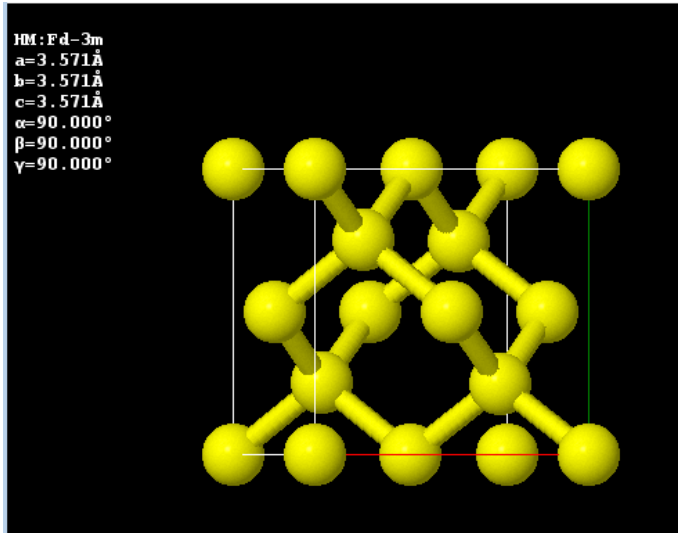
Subfamily
- Collection within the families based on specific similarties
- Homologus (humite), Homeotype (perovskite)

Supergroup
- Highest symmetry phase where structure arrangement remains unchanged
- Example: Diamond

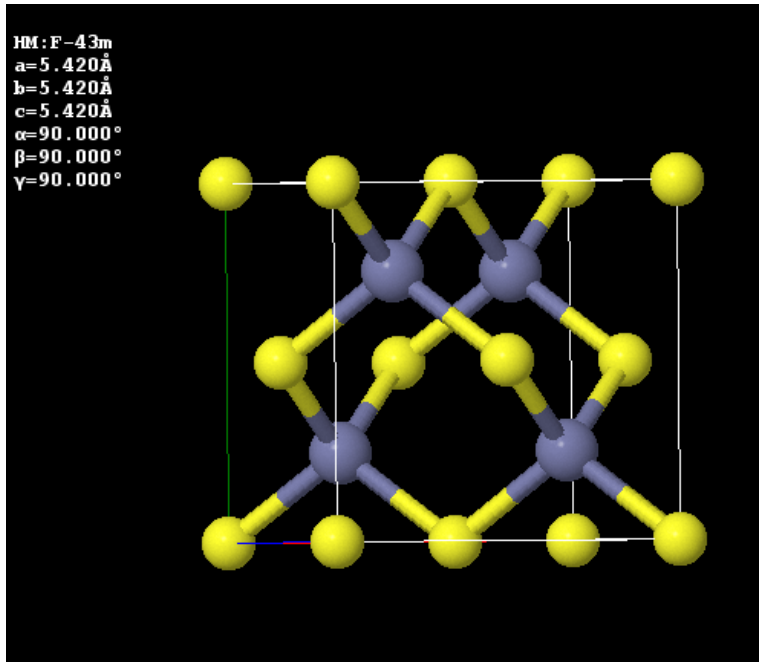
Group
- Composed of isostructural phases
- cF8 NaCl group

Subgroup
- Subsets of group based on chemistry (halides, oxides etc)

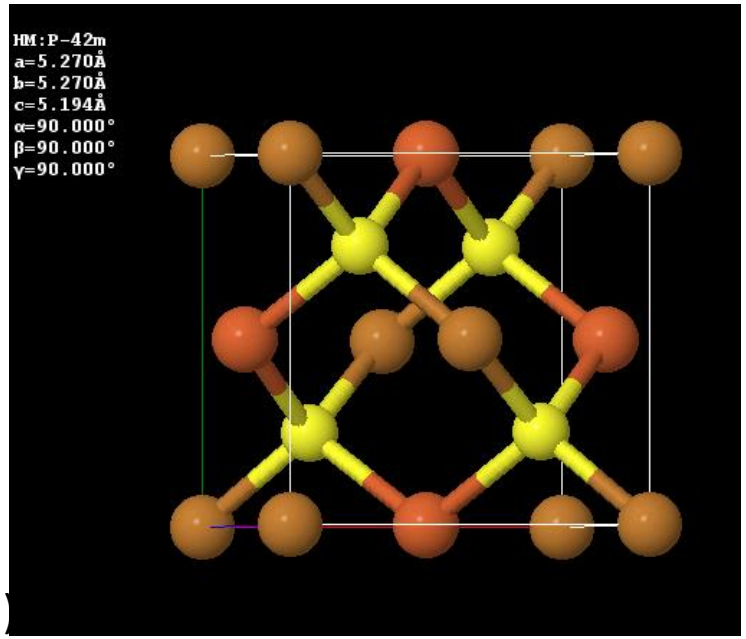
Advances in X-ray Analysis **41**, 606-613 (1997)



Supergroup, Diamond cF8 Fd-3m

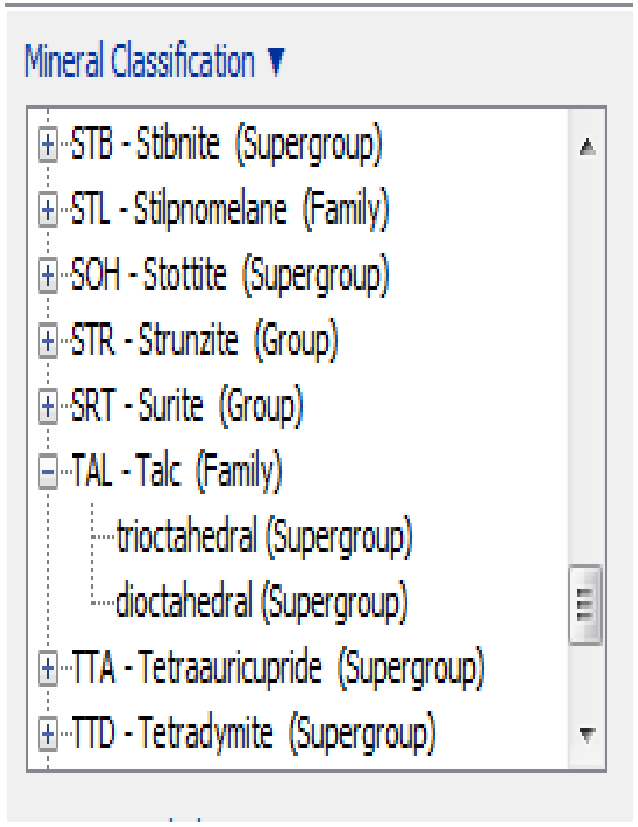


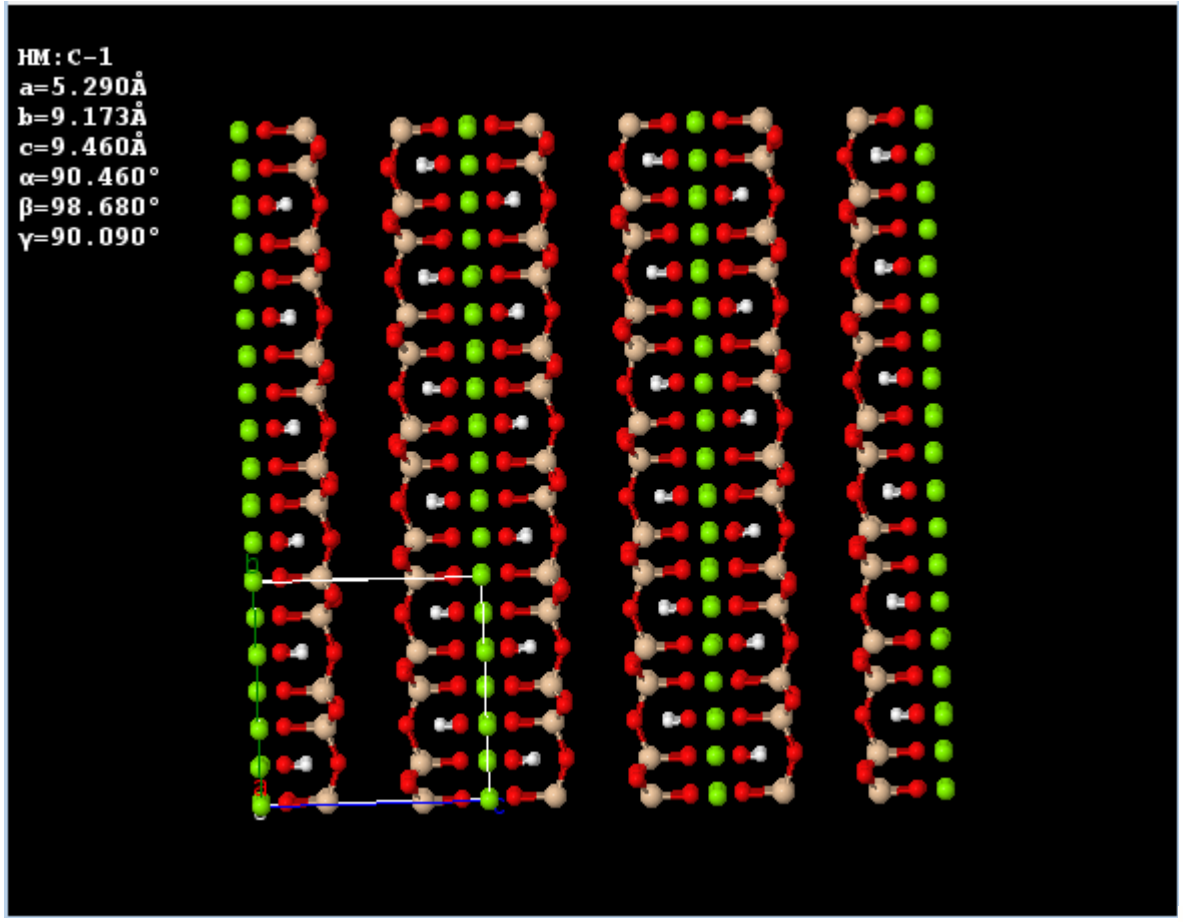
Group, Sphalerite (ZnS) cF8 F-43m



Subgroup, Chalcopyrite (CuFeS2)

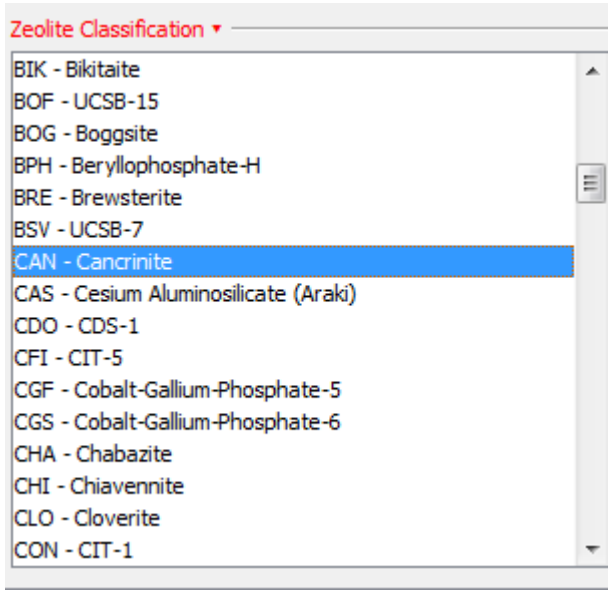
Search Based on Mineral Classification

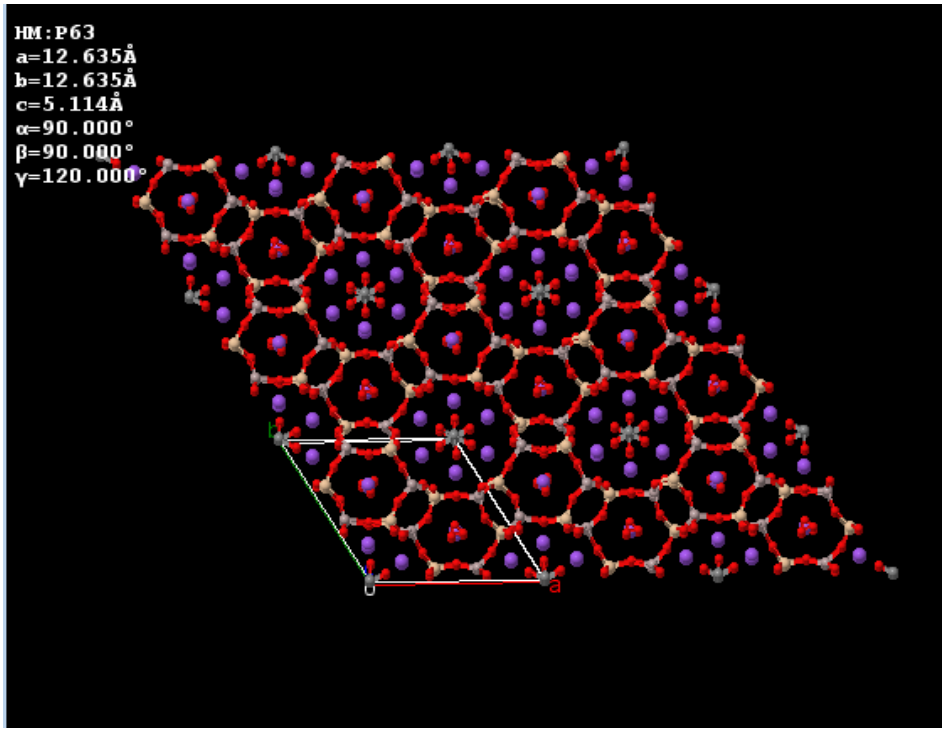


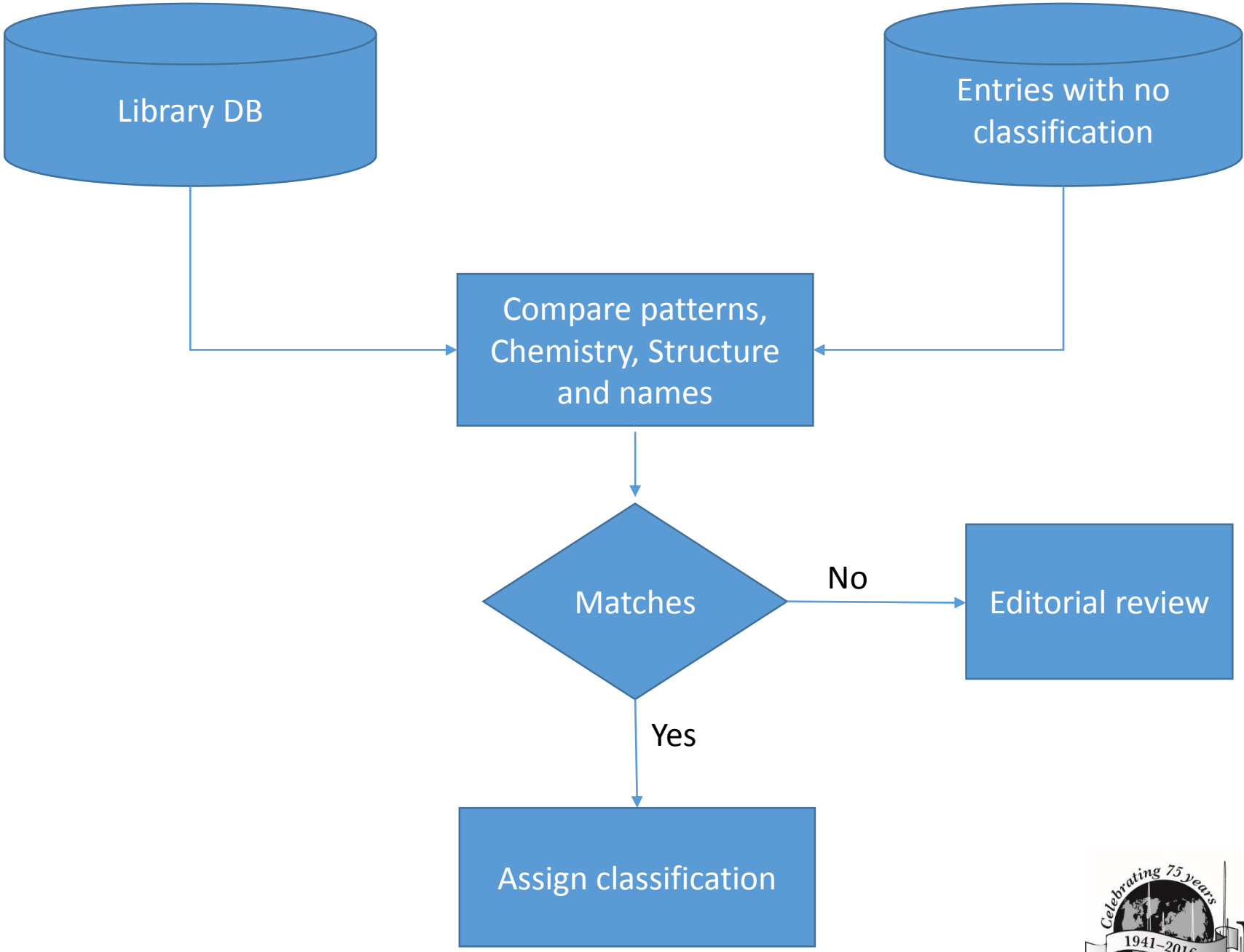


Zeolite Classification

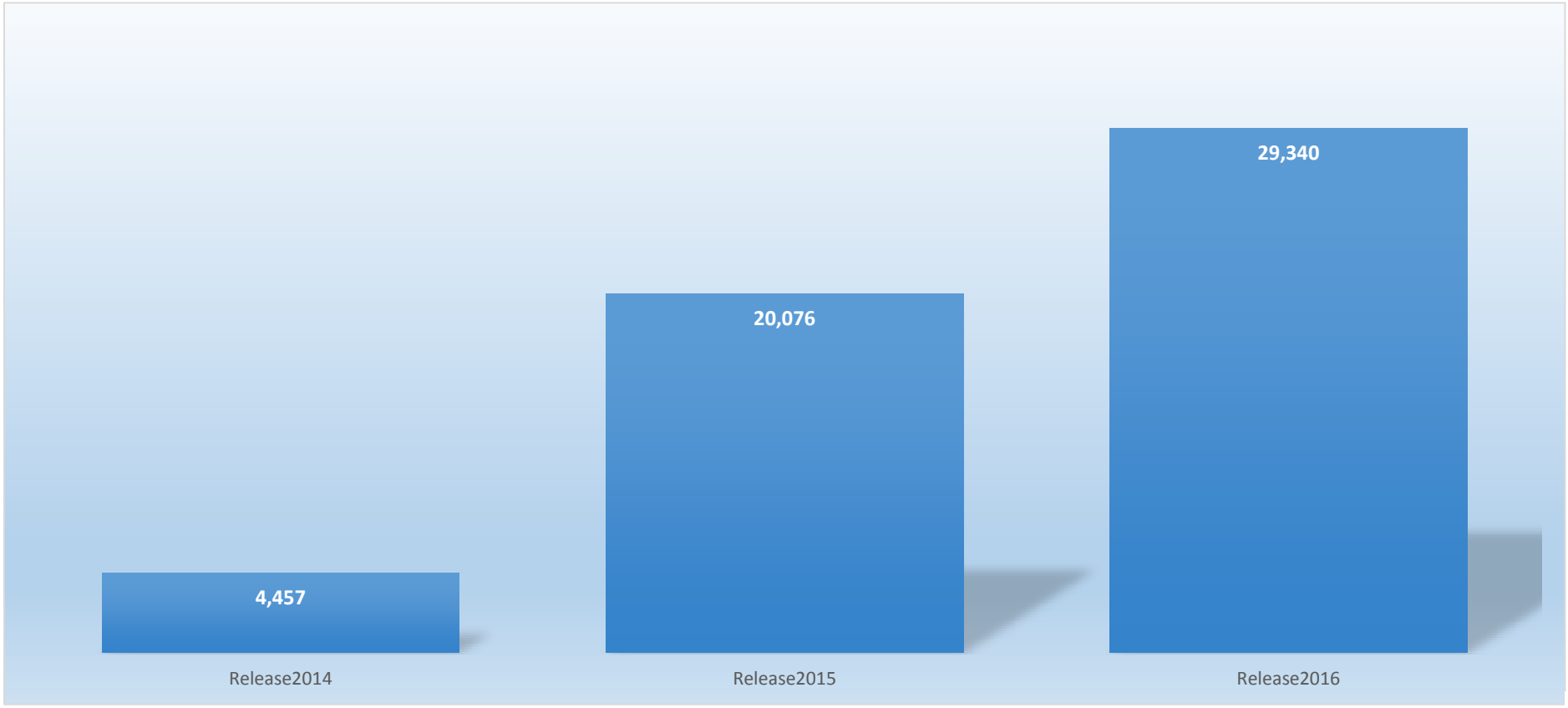
- Zeolite classification based on framework type
- These are noted by a three capital letter code describing network of corner sharing tetrahedrally coordinated framework atoms.






Library DB
Entries with no classification
Compare patterns, Chemistry, Structure and names
Matches
No
Editorial review
Yes
Assign classification

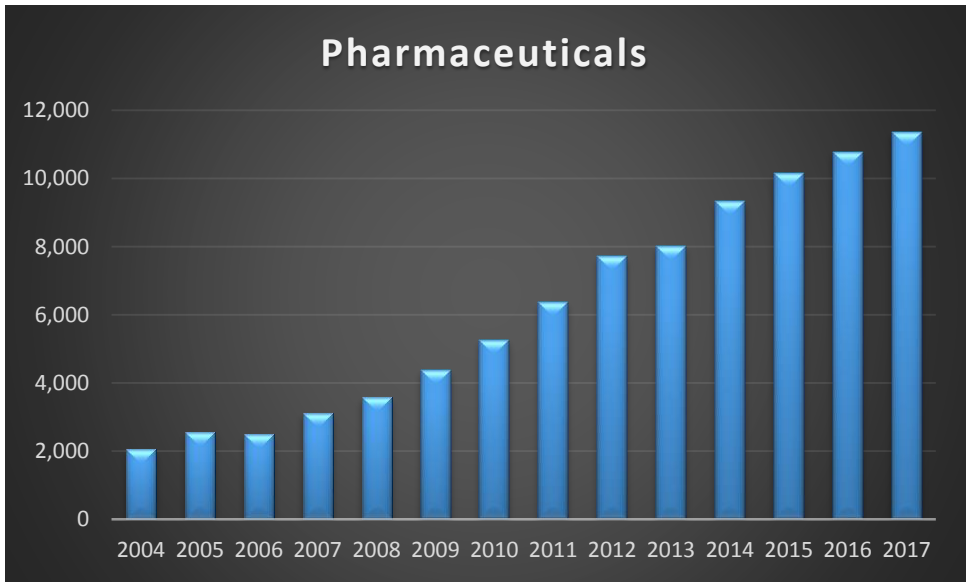
Entries with Mineral Classification

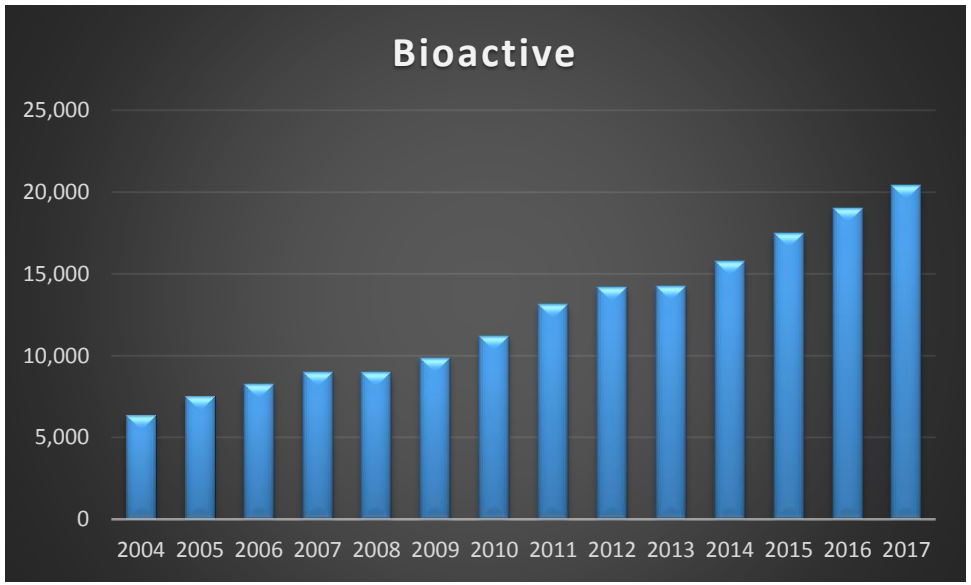


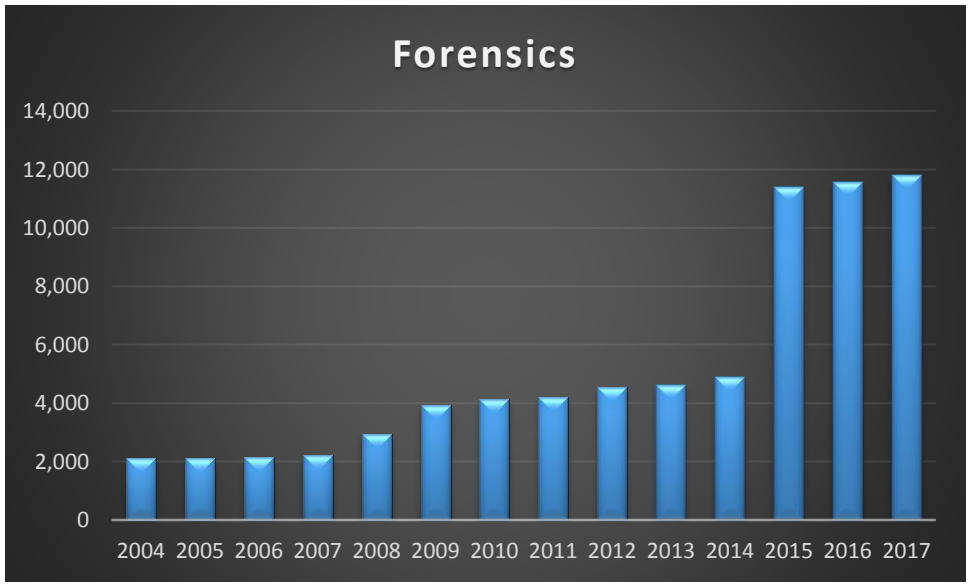
Subfiles in Powder Diffraction File

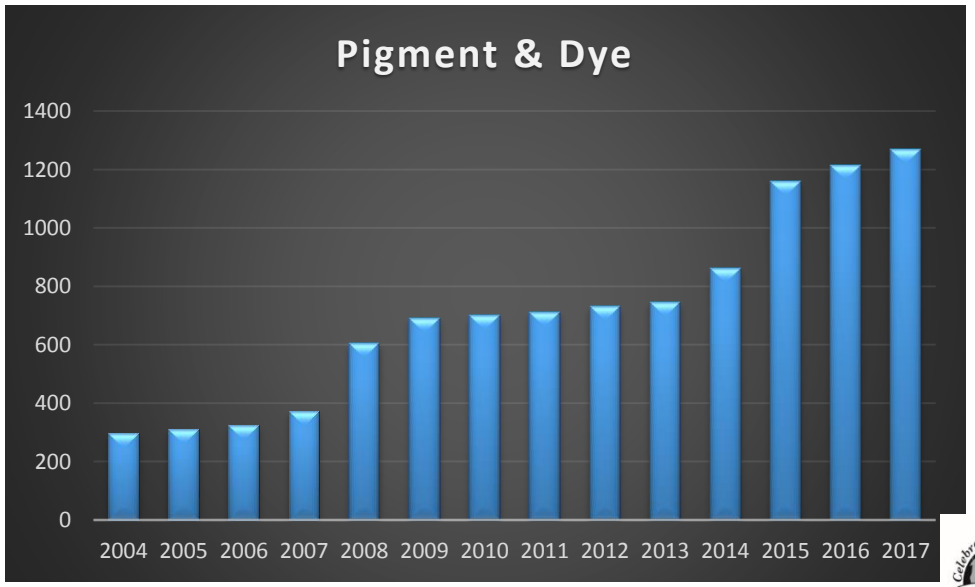
- Custom PDF Set
- Alkaloids
- Amino Acids, Peptides & Complexes
- Battery Material
- Bioactivity
  - No Subclass
  - Narcotic
  - Psychotropic
- Carbohydrate
- Cement & Hydration Product
- Ceramic
  - No Subclass
  - Bioceramic
  - Ferroelectric
  - Microwave
  - Perovskite
  - Semiconductor
- Common Phase
- Education
- Explosive
- Forensic
- Hydrogen Storage Materials
- Inorganic
- Intercalate
- Ionic Conductors
- Merck
- Metals & Alloys
- Micro & Mesoporous
  - No Subclass
  - Clathrate
  - Metal-Organic Framework
  - Zeolite
- Mineral Related
  - No Subclass
  - Mineral
  - Gem
  - Natural
  - Synthetic
- Modulated Structure
- NBS
- Nucleosides & Nucleotides
- Organics
- Pharmaceutical
  - No Subclass
  - Excipient
- Pigment & Dye
- Polymer
- Porphyrins, Corrins & Complexes
- Steroids
- Superconducting Material
  - No Subclass
  - Conventional Superconductor
  - Superconductor Reaction Product
  - Superconductor Related Materials
  - High Tc Superconductor
- Terpenes
- Thermoelectric Material

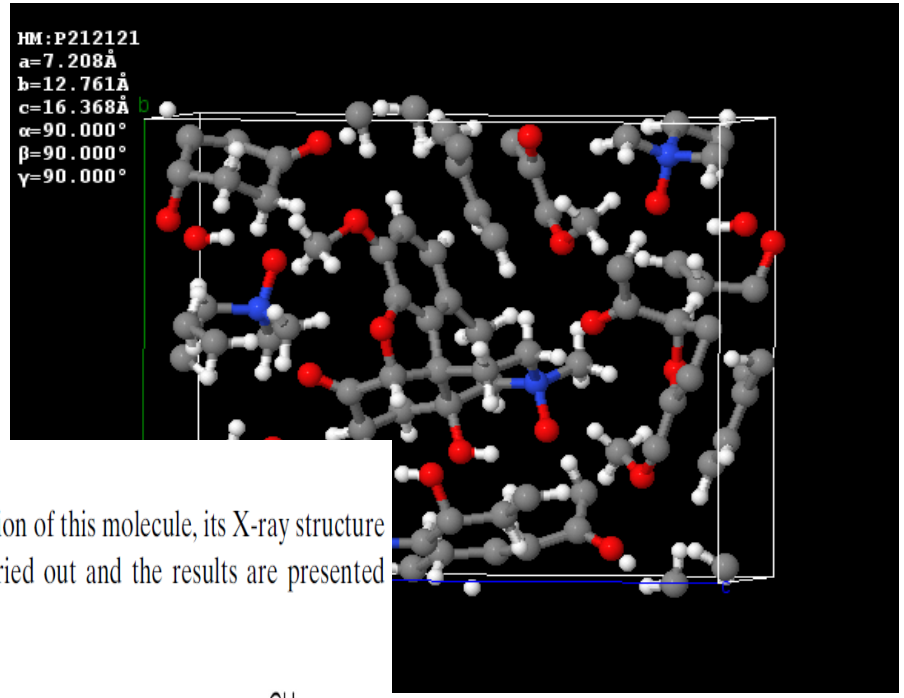
Subfile Growth by Release year











C18 H21 N O5 - 05-006-3720

File Edit Plots Window Help

Save Print Preferences Temperature Series Toolbox Property Sheet 2D 3D Bonds SAED EBSD Ring Simulated Profile Raw Diffraction Data

Cu Kα1 1.54056 Å ☑ Simulated Profile (Calc)

Fixed Slit Intensity ☐ Raw Diffraction Data (PD3)

1,000
800

2θ (°)	d (Å)	I	h	k	l	*
8.7794	10.063800	71	0	1	1	
10.8016	**8.183800**	564	0	0	2	
12.8399	6.888890	57	0	1	2	
13.4112	6.596660	62	1	0	1	
13.8677	6.380550	54	0	2	0	
14.0998	6.276030	4	1	1	0	
15.1064	**5.860000**	999	1	1	1	
16.3740	**5.409090**	516	1	0	2	

PDF

Experimental
Physical
Crystal
Optical
Structure
Classifications
Cross-references
References
Comments

Status: Primary QM:
Phase:
Chemical Formula: C18 H21 N O5
Structural Formula:
Empirical Formula: C18 H21 N O5
Weight %: C65.24 H6.39 N4.23 O
Atomic %: C40.00 H46.67 N2.22
Compound Name: (5R,9R,13S,14S,17R)
Mineral Name:
Common Name: Oxycodone N-oxide
CAS:
Entry Date: 09/01/2015
Last Modification Date:
Last Modifications:

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Crystal Structure Communications
ISSN 0108-2701

Oxycodone *N*-oxide

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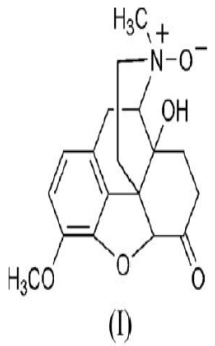
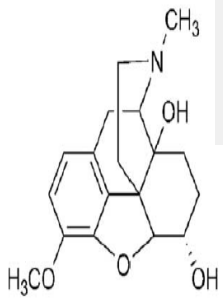
Correspondence e-mail: pacrooks@uams.edu

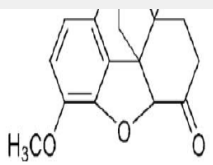
Received 24 August 2012
Accepted 22 September 2012
Online 18 October 2012

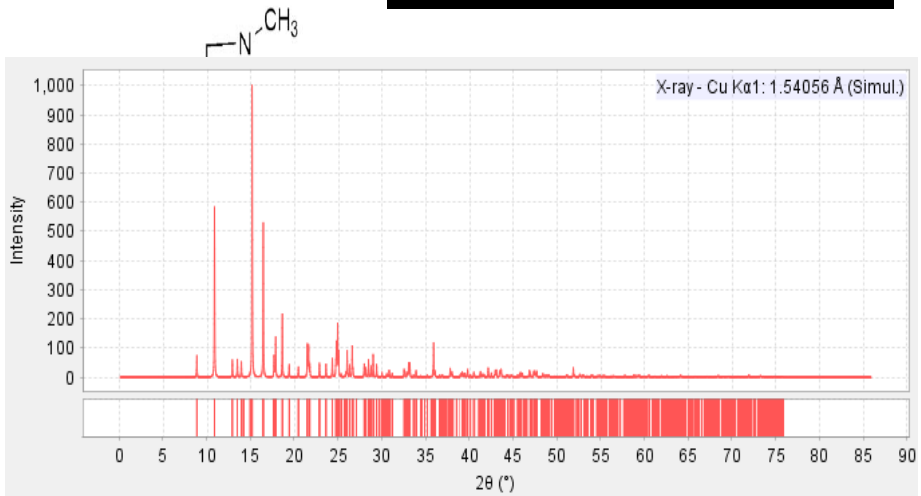
the detailed conformation of this molecule, its X-ray structure determination was carried out and the results are presented here.



(I)







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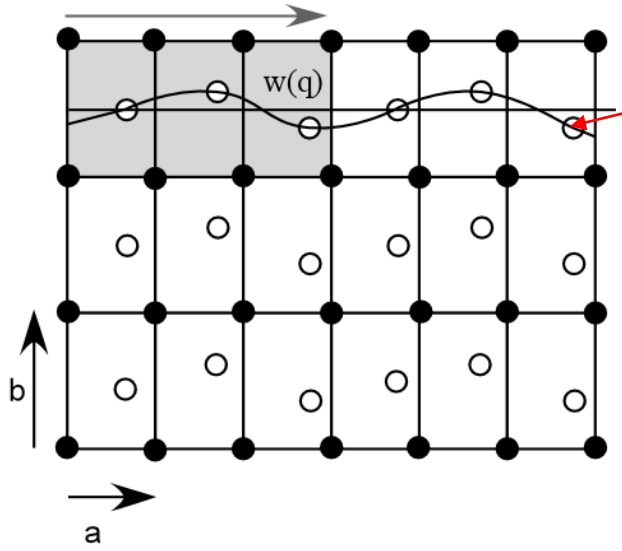
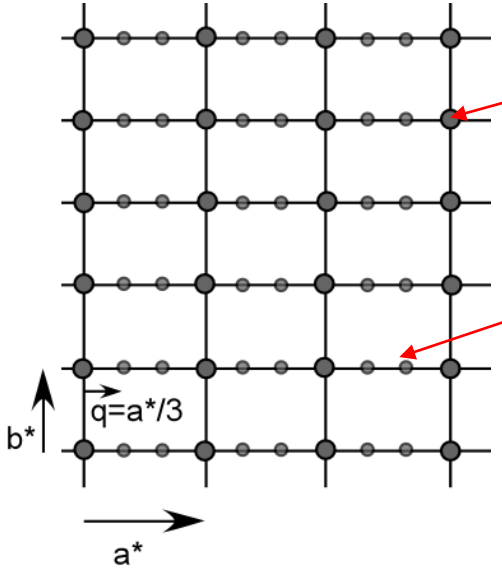
Modulated Structures

- Modulated structures form on account of perturbation in atomic position, occupation and/or thermal motion
- If period of fluctuation matches that of the 3D unit cell then a superstructure results otherwise an incommensurate modulated structure is obtained
- We can explain their symmetry in higher dimension 3+d (Super Space)

Schematic Representation



Modulation on White atoms



Main reflection

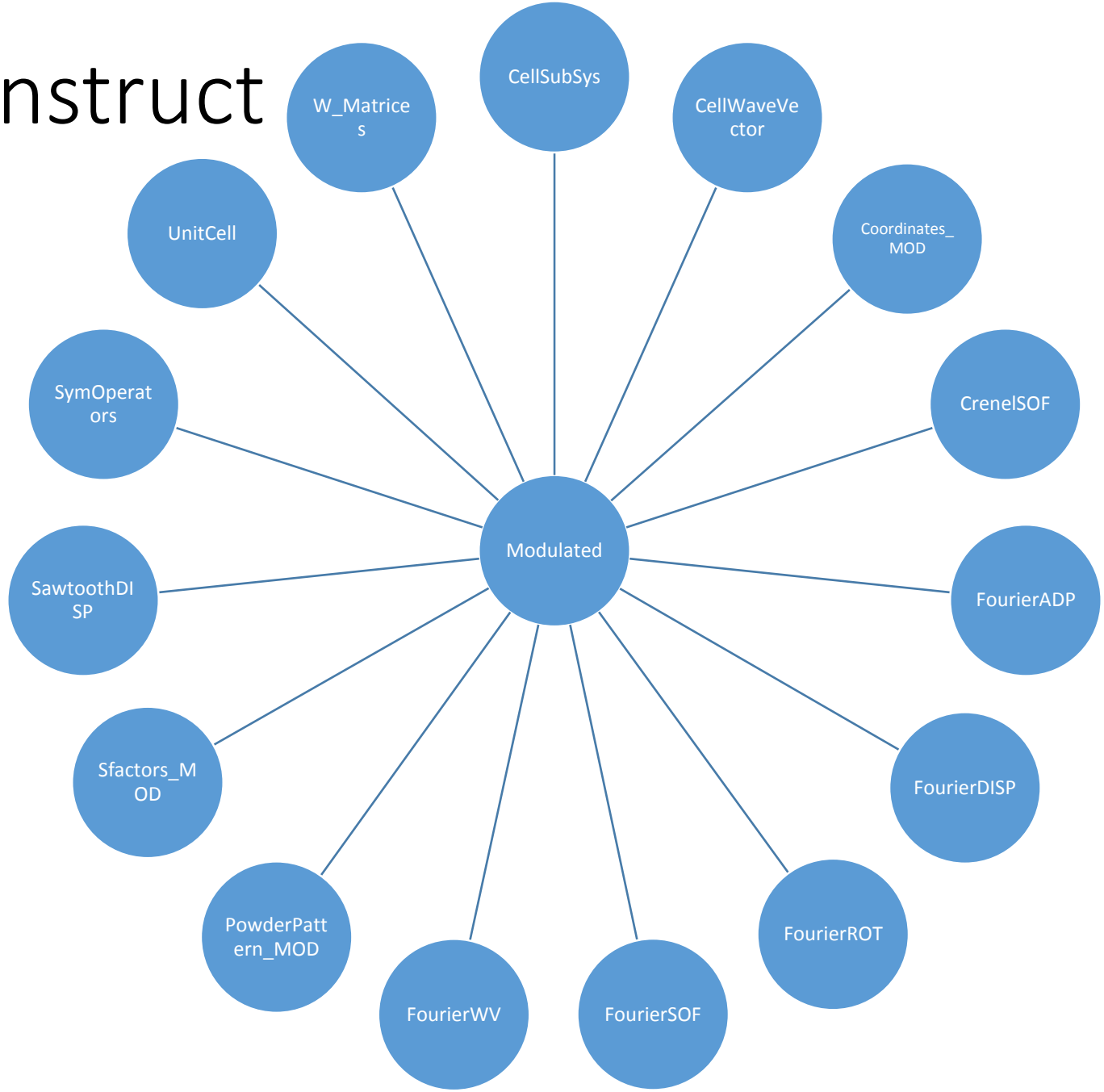
Satellite reflections

We can not index these satellite reflections in a regular 3D cell. It can be indexed by using a modulation vector q

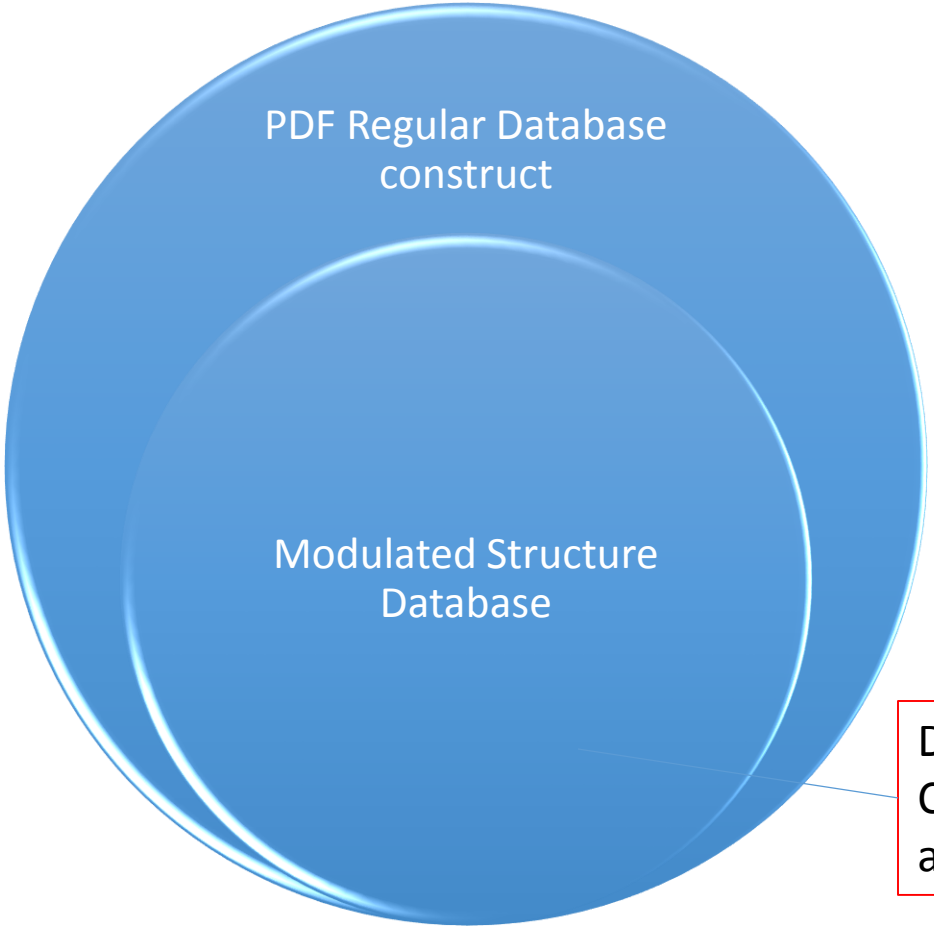
$$\mathbf{Q} = h\mathbf{a}_1^* + k\mathbf{a}_2^* + l\mathbf{a}_3^* + m\mathbf{q}$$

$$\mathbf{q} = q_1\mathbf{a}_1^* + q_2\mathbf{a}_2^* + q_3\mathbf{a}_3^*$$

Database Construct

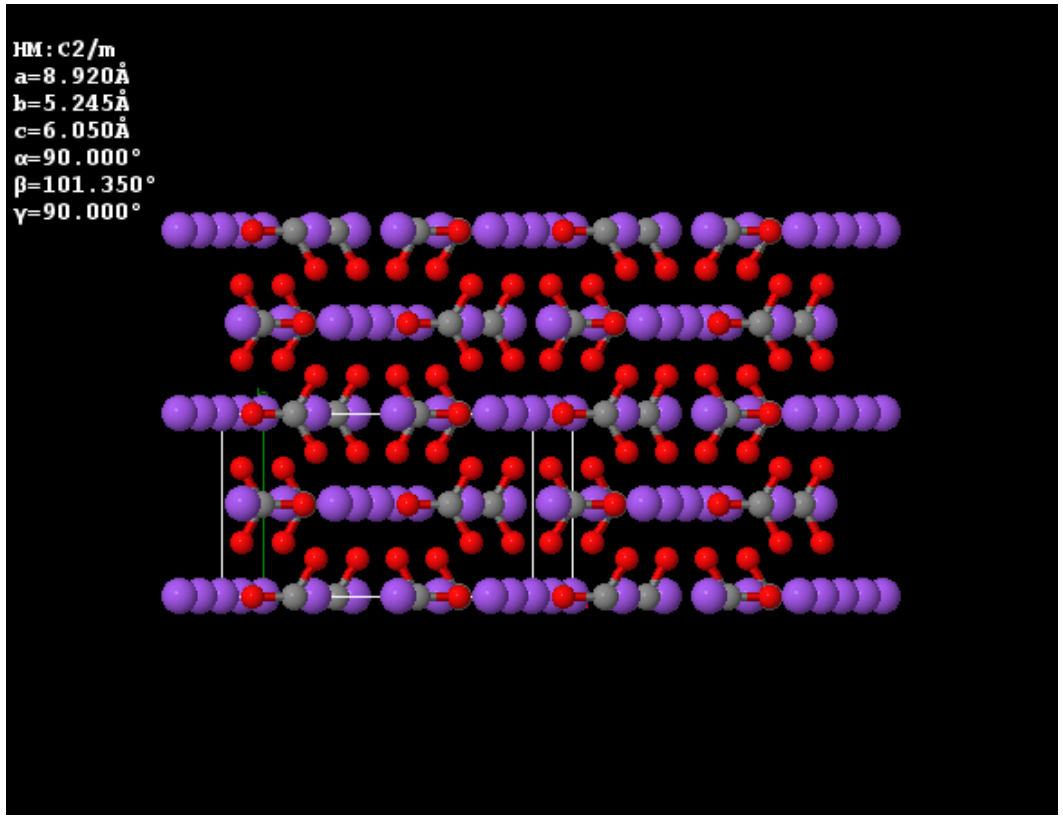


Database Construct

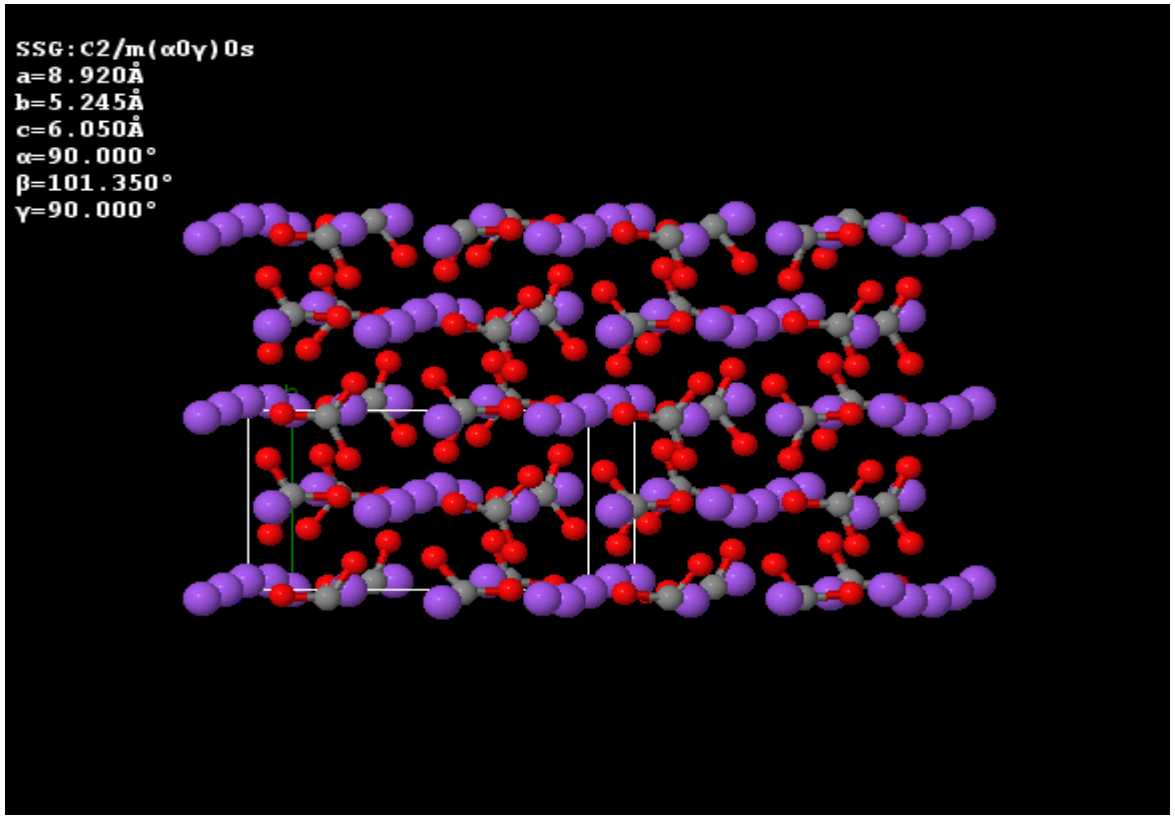


Describes superspace. Can handle (3+1), (3+2) and (3+3) D cases

NaCO3 in average and modulated structure representation



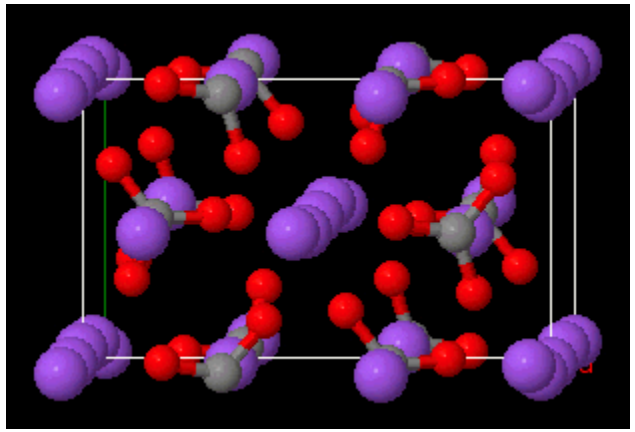
Average Structure



Incommensurately Modulated Structure

$$q_1 = (0.182)a^* + (0.322)c^*$$

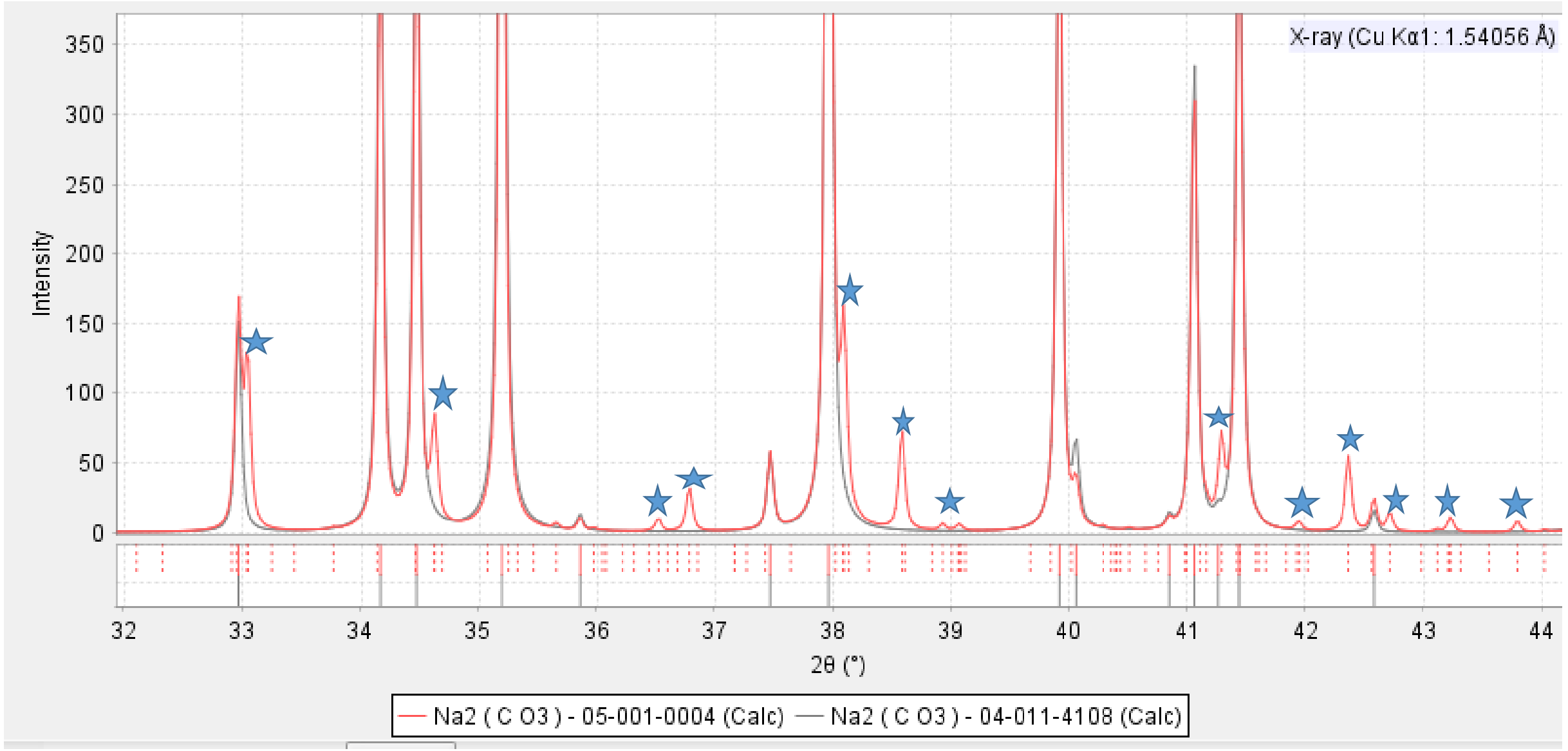
γ $NaCO_3$



Incommensurately Modulated Structure

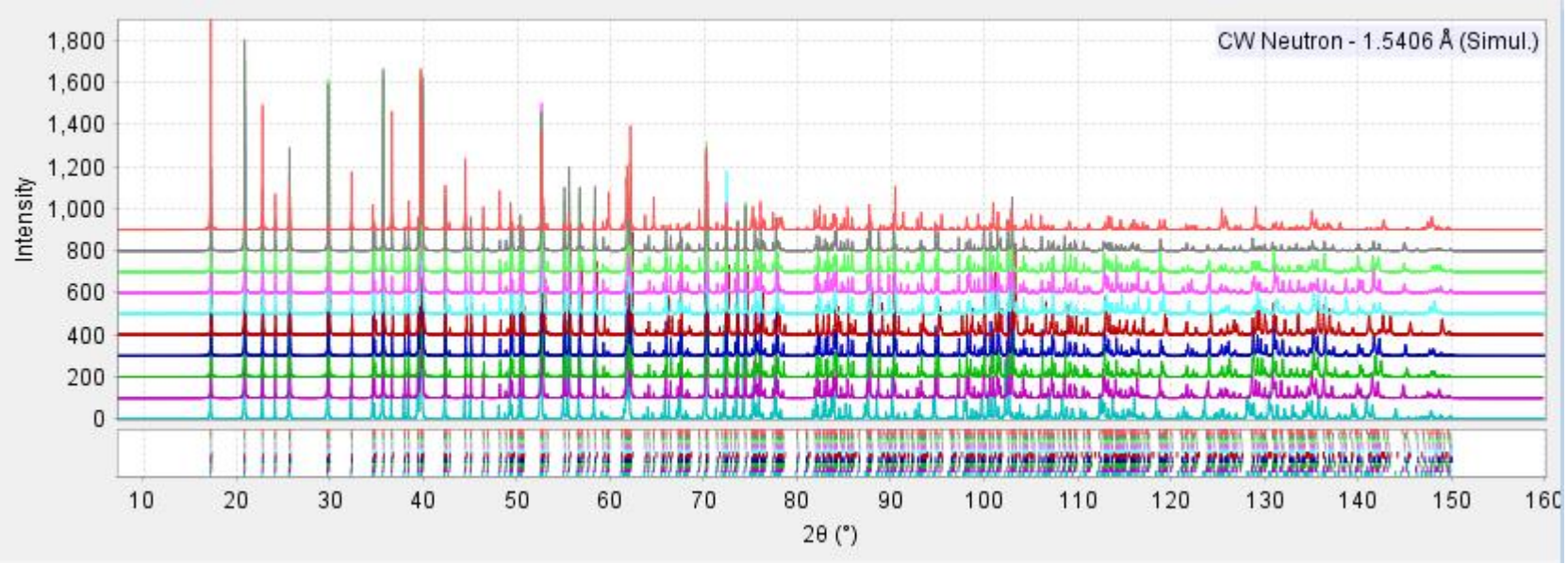
$$q_1 = (0.182)a^* + (0.322)c^*$$

Comparison of Powder X-ray Diffraction Patterns



Neutron Diffraction Database

- As a part of PDF4+ database, first released in 2014 enabling search/match using CW neutron diffraction pattern
- More than 272,000 neutron diffraction entries in release 2016
- RIR based on neutron diffraction intensities for semi-quantitative phase analysis



Oilivine type LiFePO4 battery material

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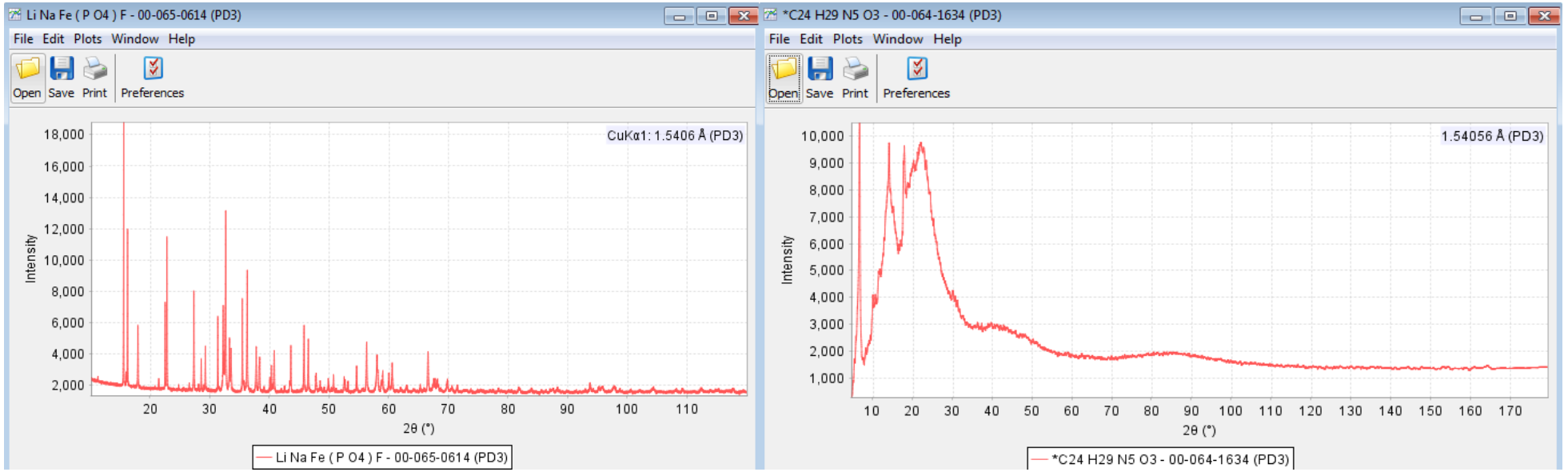
Raw Data Archival

- There are 11,284 raw powder diffraction data in release 2016 including crystalline, amorphous, nano materials
- This data can be exported out for analysis
- In future this feature will be extended to TOF and CW neutron patterns



Example of usage of raw data

TECHNICAL ARTICLE

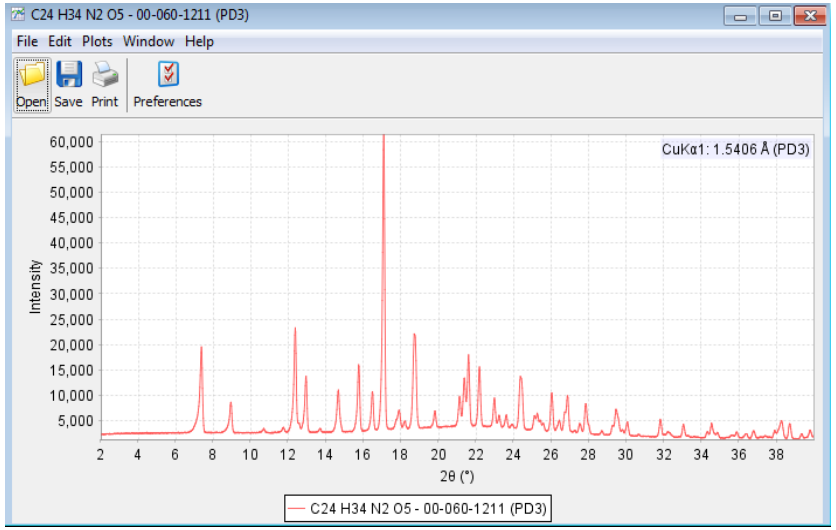
The crystal structure of trandolapril, $C_{24}H_{34}N_2O_5$: an example of the utility of raw data deposition in the powder diffraction file

Joel W. Reid,[1,a] James A. Kaduk,[2] and Martin Vickers[3]
[1]*Canadian Light Source, 44 Innovation Boulevard, Saskatoon, SK, S7N 2V3, Canada*
[2]*Illinois Institute of Technology, 3101 S. Dearborn St., Chicago, Illinois 60616*
[3]*Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK*

(Received 3 February 2016; accepted 13 April 2016)

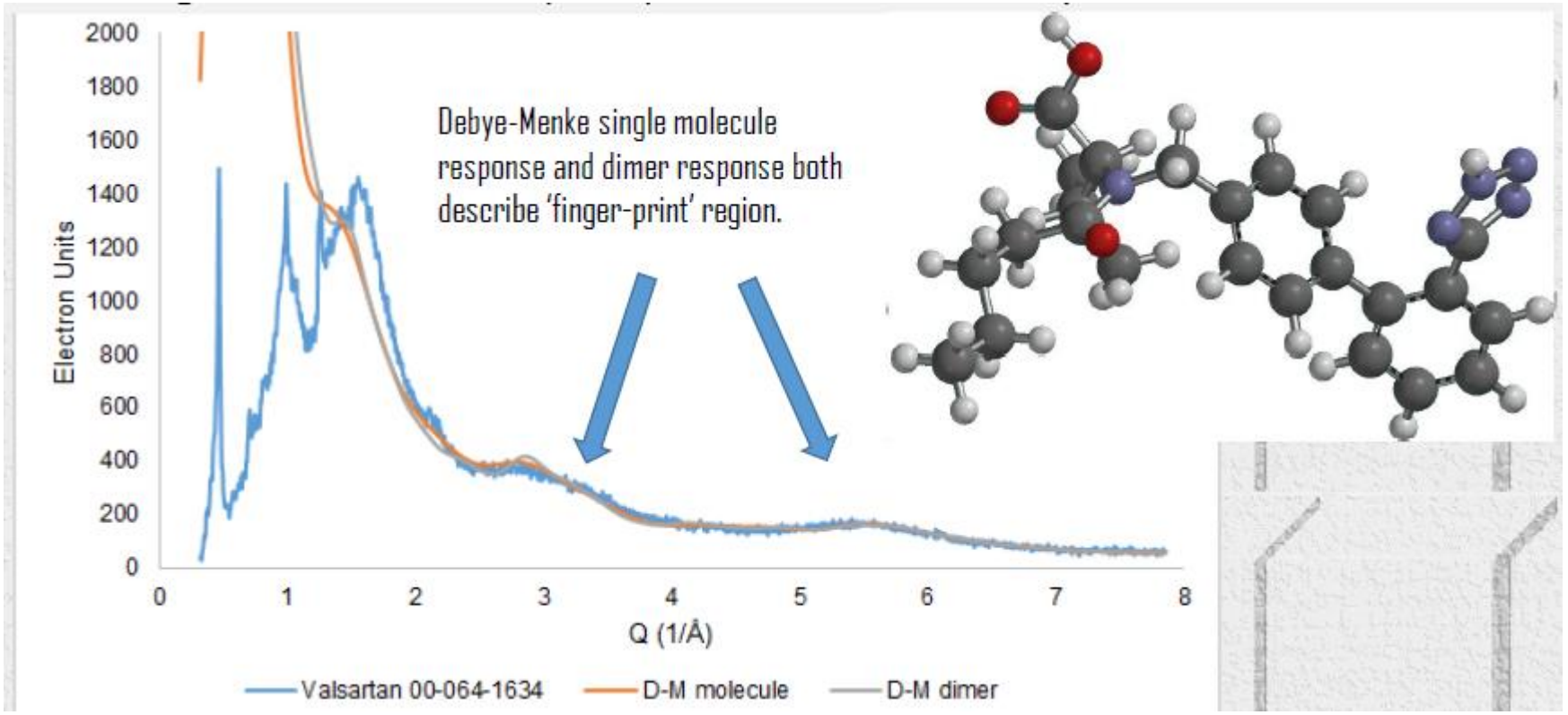
The crystal structure of trandolapril has been solved by parallel tempering using the FOX software package with laboratory powder diffraction data submitted to and published in the Powder Diffraction File. Rietveld refinement was performed with the software package GSAS yielding orthorhombic lattice parameters of $a = 19.7685(4)$, $b = 15.0697(4)$, and $c = 7.6704(2)$ Å ($C_{24}H_{34}N_2O_5$, $Z = 4$, space group $P2_12_12_1$). The Rietveld refinement results were compared with density functional theory (DFT) calculations performed with CRYSTAL14. While the structures are similar, discrepancies are observed in the configuration of the octahydroindole ring between the Rietveld and DFT structures, suggesting the refined and calculated molecules are diastereomers. © *2016 International Centre for Diffraction Data*. [doi:10.1017/S0885715616000294]

Key words: trandolapril, powder diffraction, structure solution, density functional theory



Powder Diff. (2016) **31**(3),p 205-210

Debye-Menke Model: Valsartan ICDD: 00-0641634



Courtesy: Simon Bates, Triclinc Lab, Lafayette, IN: Presented at Denver X-ray Conference, Chicago August 1-5, 2016

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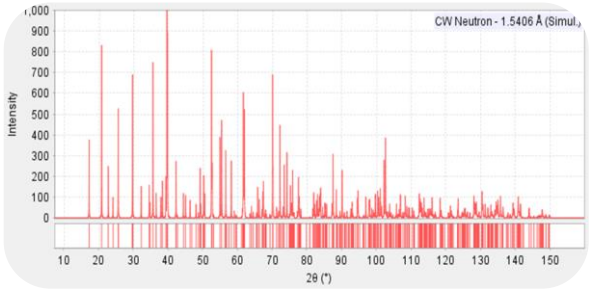
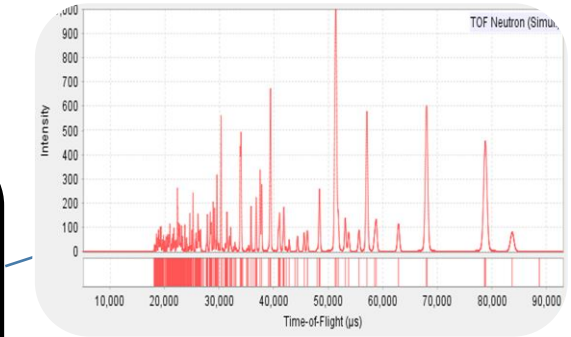
On the Fly Simulations

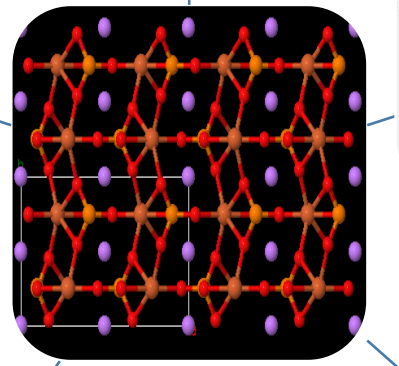


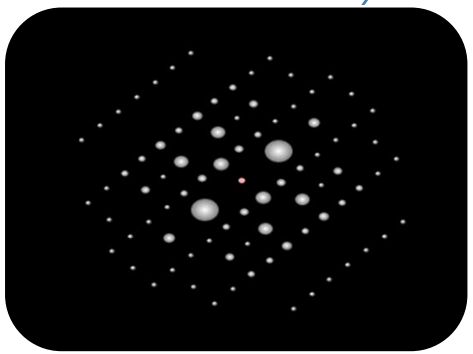
CW Neutron

Neutron TOF

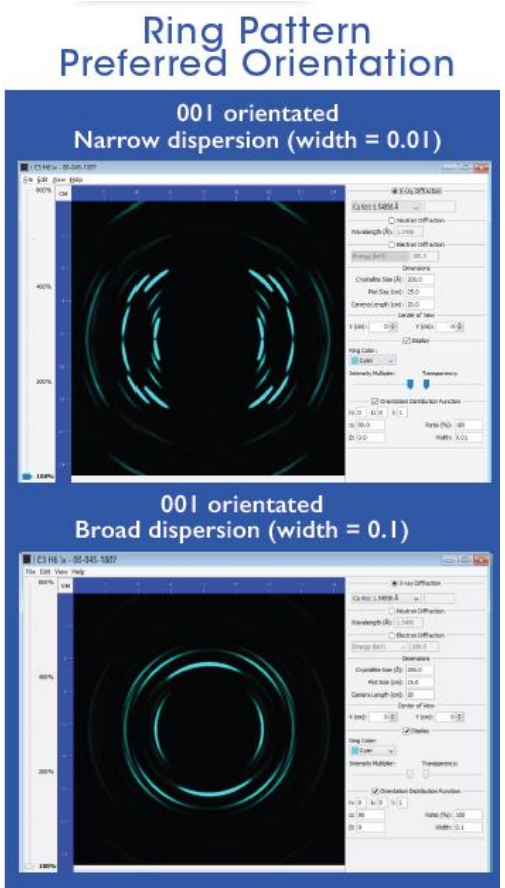


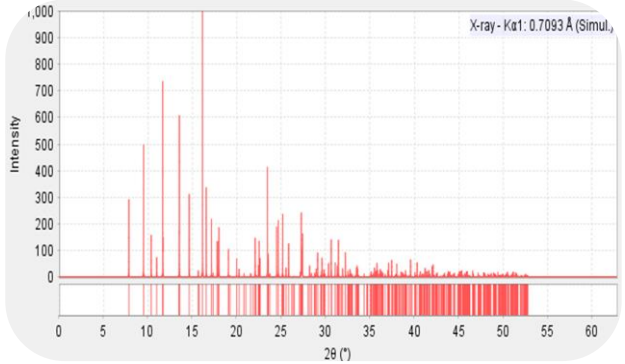
EBSD





SAED





Synchrotron

Conclusions

- In recent years there were several developments in Powder Diffraction File, including
  - Targeted subfiles
  - Enhancing classifications
  - Modulated structures
  - Neutron diffraction
  - Electron diffraction
  - Raw diffraction patterns
- Quality mark and editorial comments are useful while selecting a database entry
- Subfiles are very useful when performing search/match with a large database to minimize false positives

Thank you

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