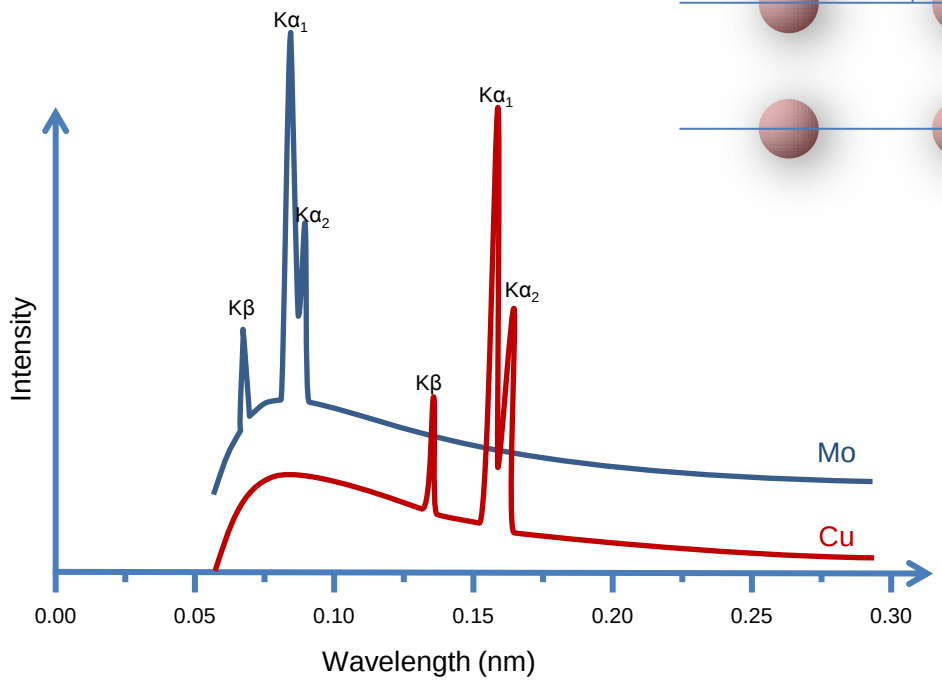
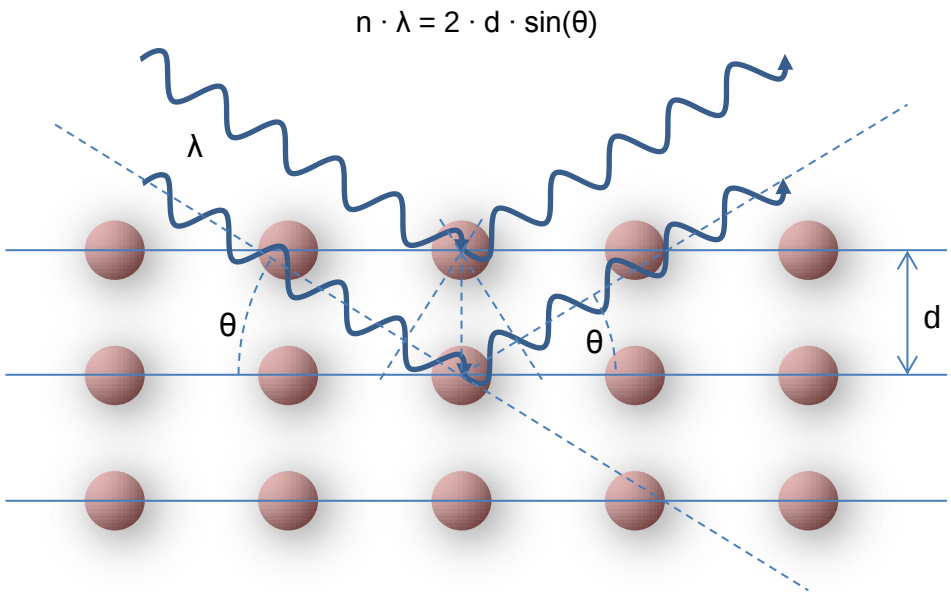
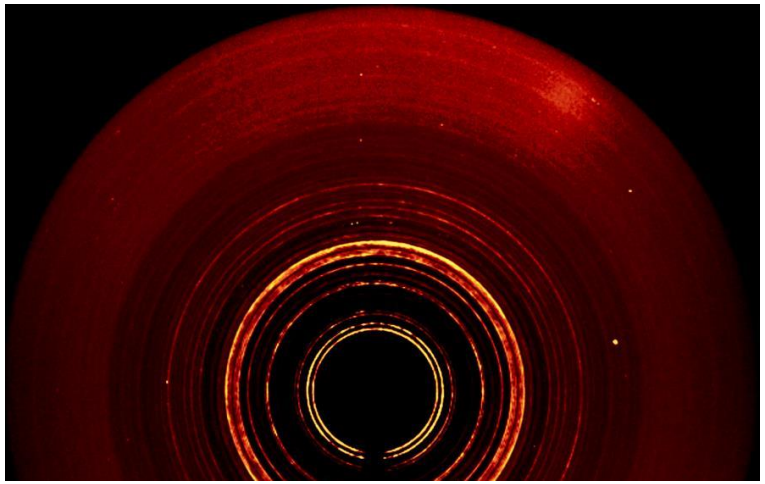
Lesson 4
Phase Identification

Nicola Döbelin
RMS Foundation, Bettlach, Switzerland

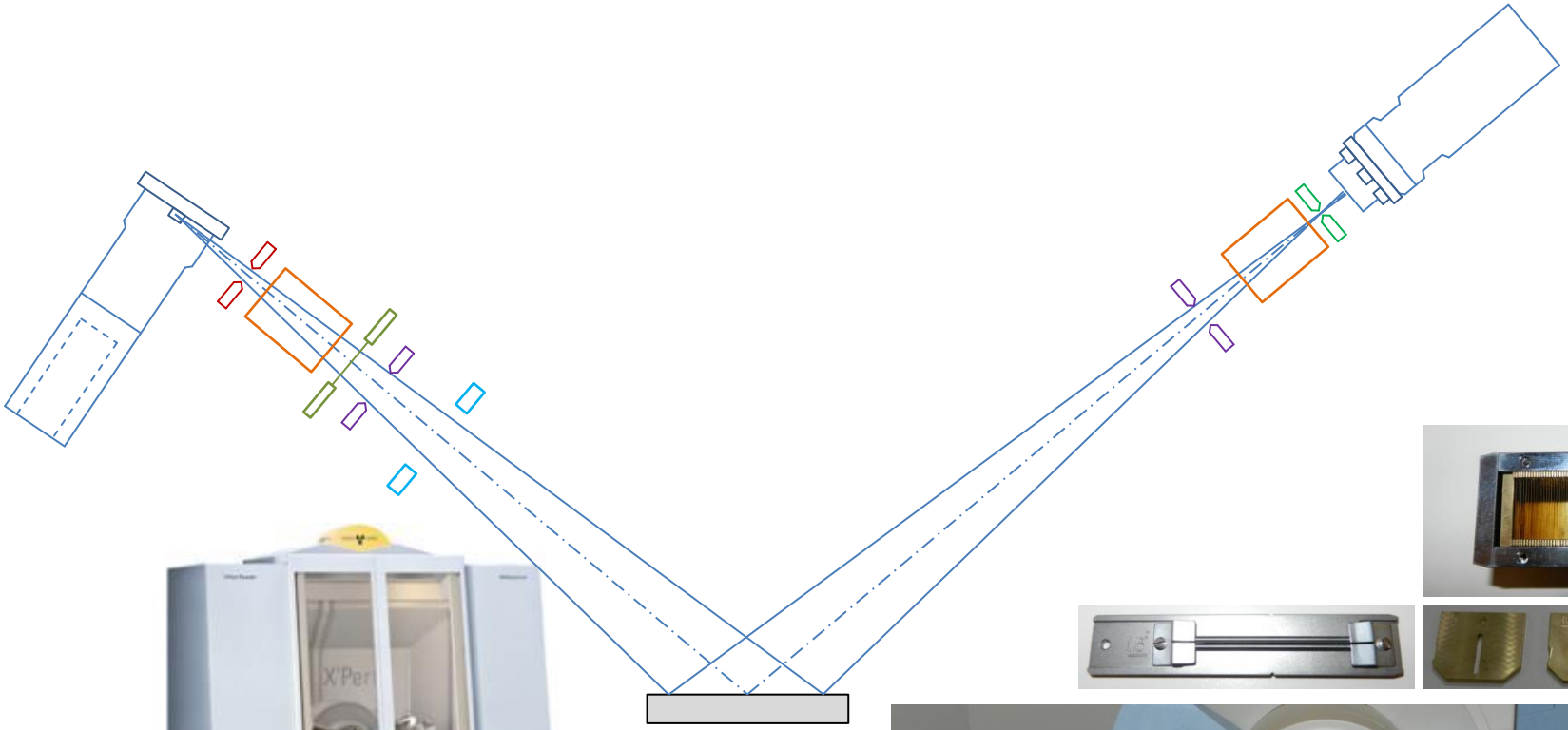
Repetition: X-Rays and Diffraction

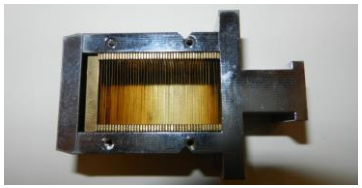


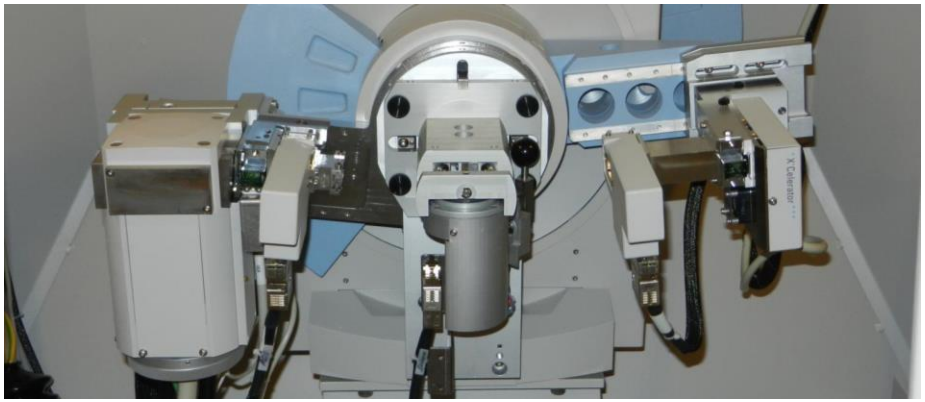




Repetition: Bragg-Brentano Diffractometer Setup



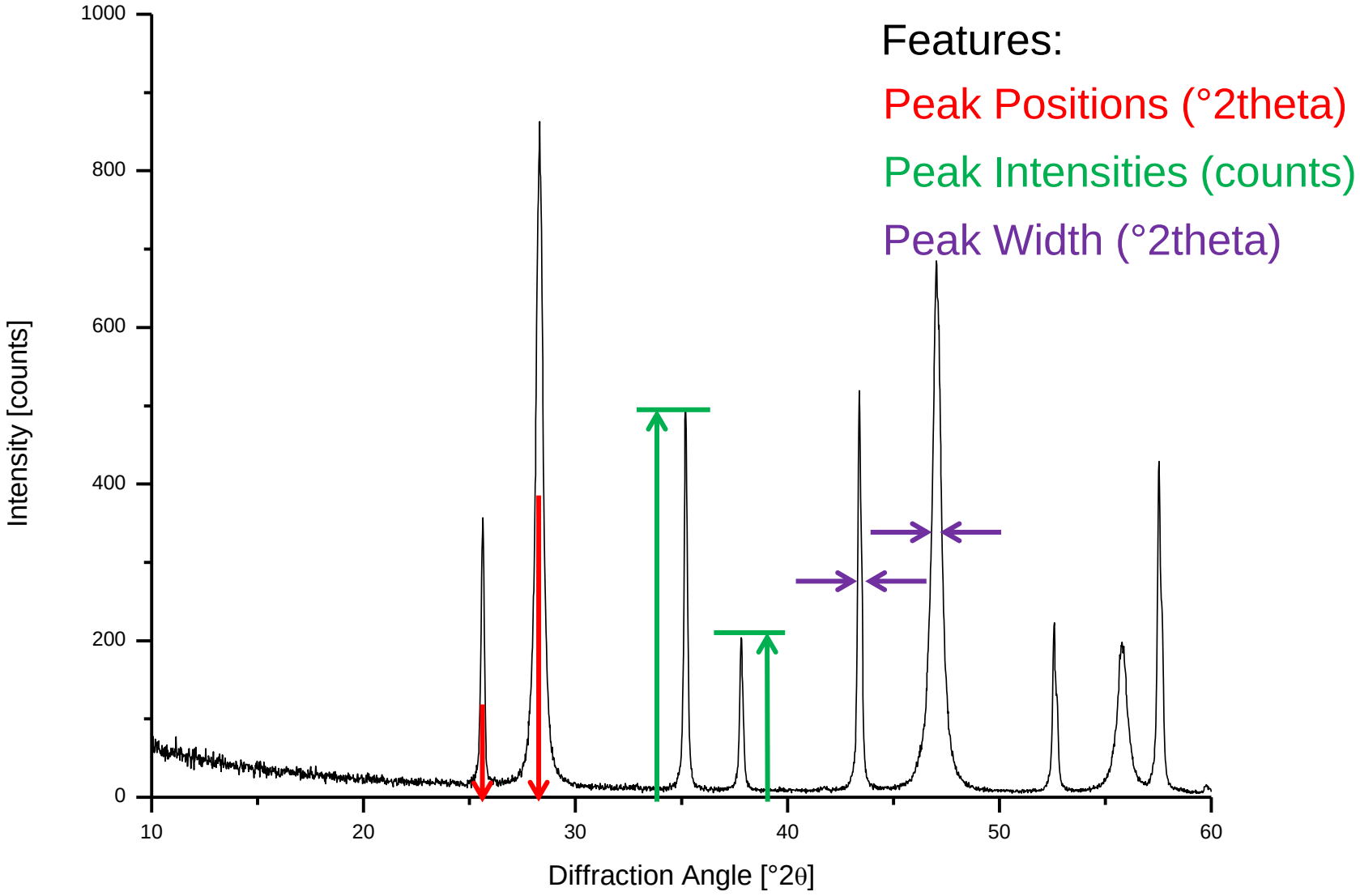




Repetition: Sample Preparation

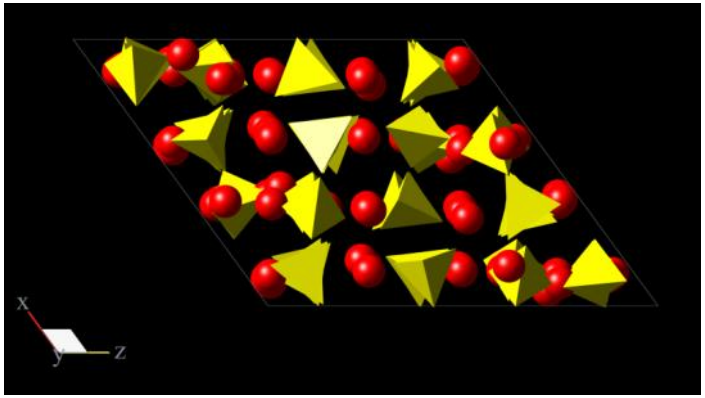
- Graininess
- Micro-absorption
- Texture
- Sample height displacement
- Surface roughness
- Sample transparency

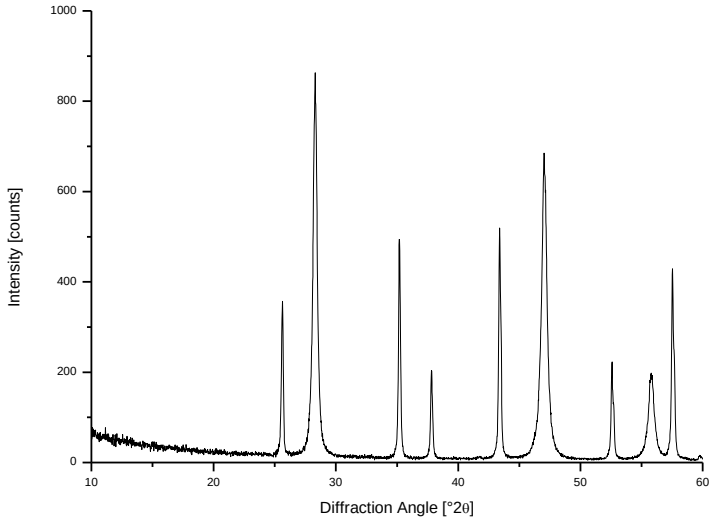
Diffraction Pattern



Phase Identification

«Pattern Features» originate from crystallographic properties

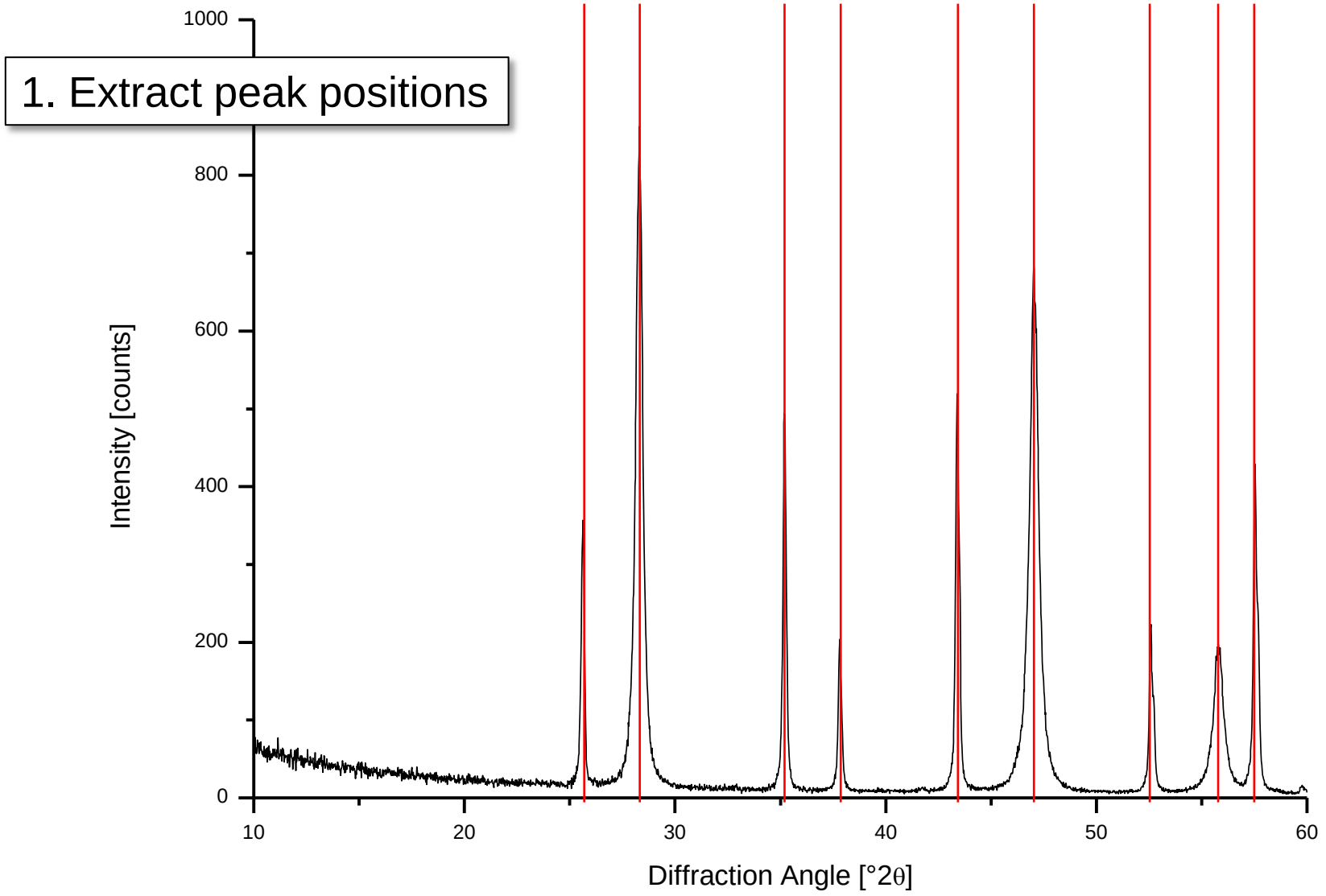




Usually sufficient for identification

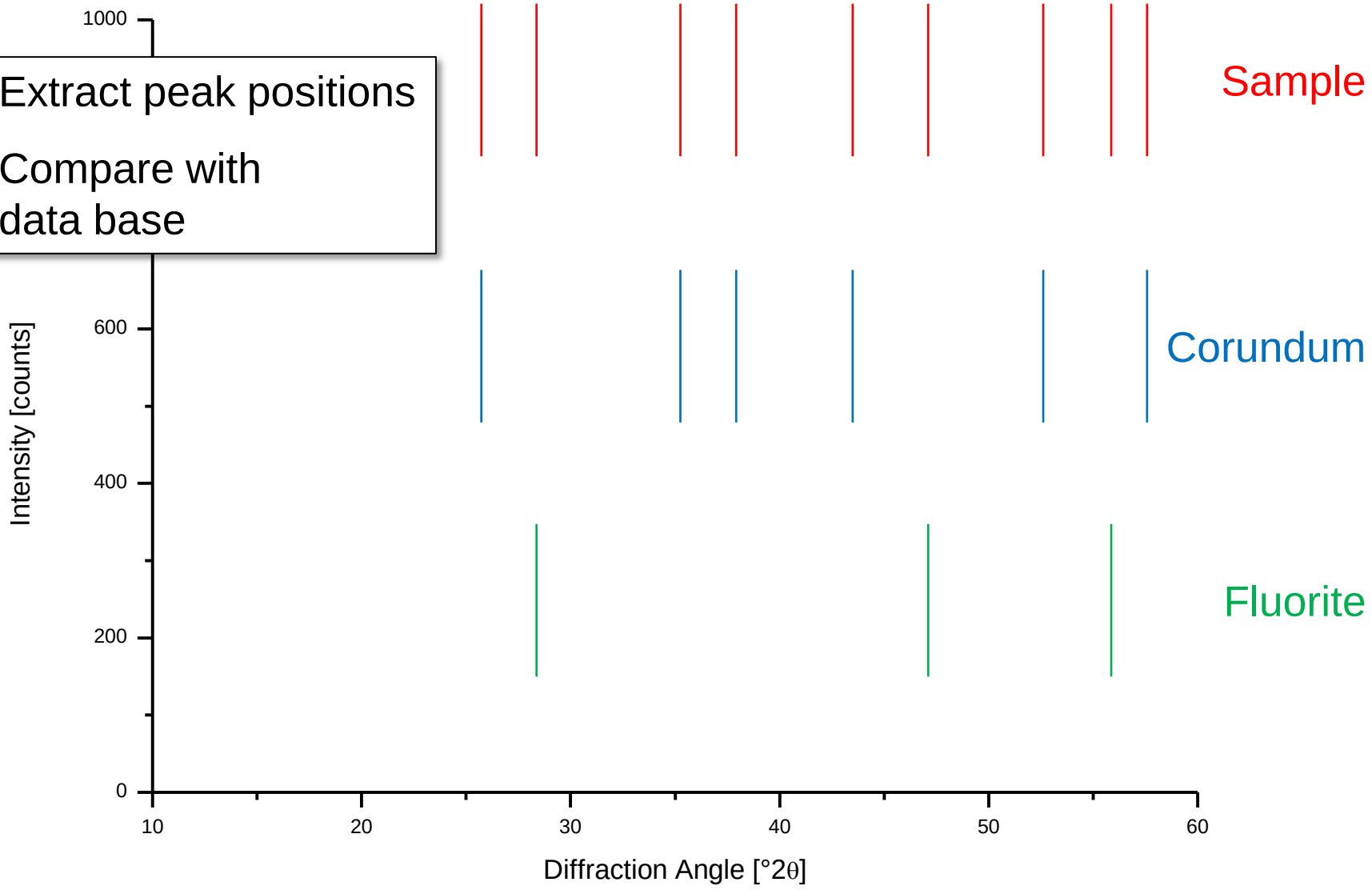
Feature	Origin
Peak positions	- Symmetry of the unit cell (space group) - Dimensions of the unit cell
Relative peak intensities	- Coordinates of atoms in unit cell - Species of atoms
Absolute peak intensities	- Abundance of phase
Peak width	- Crystallite size - Stress/Strain in crystal lattice

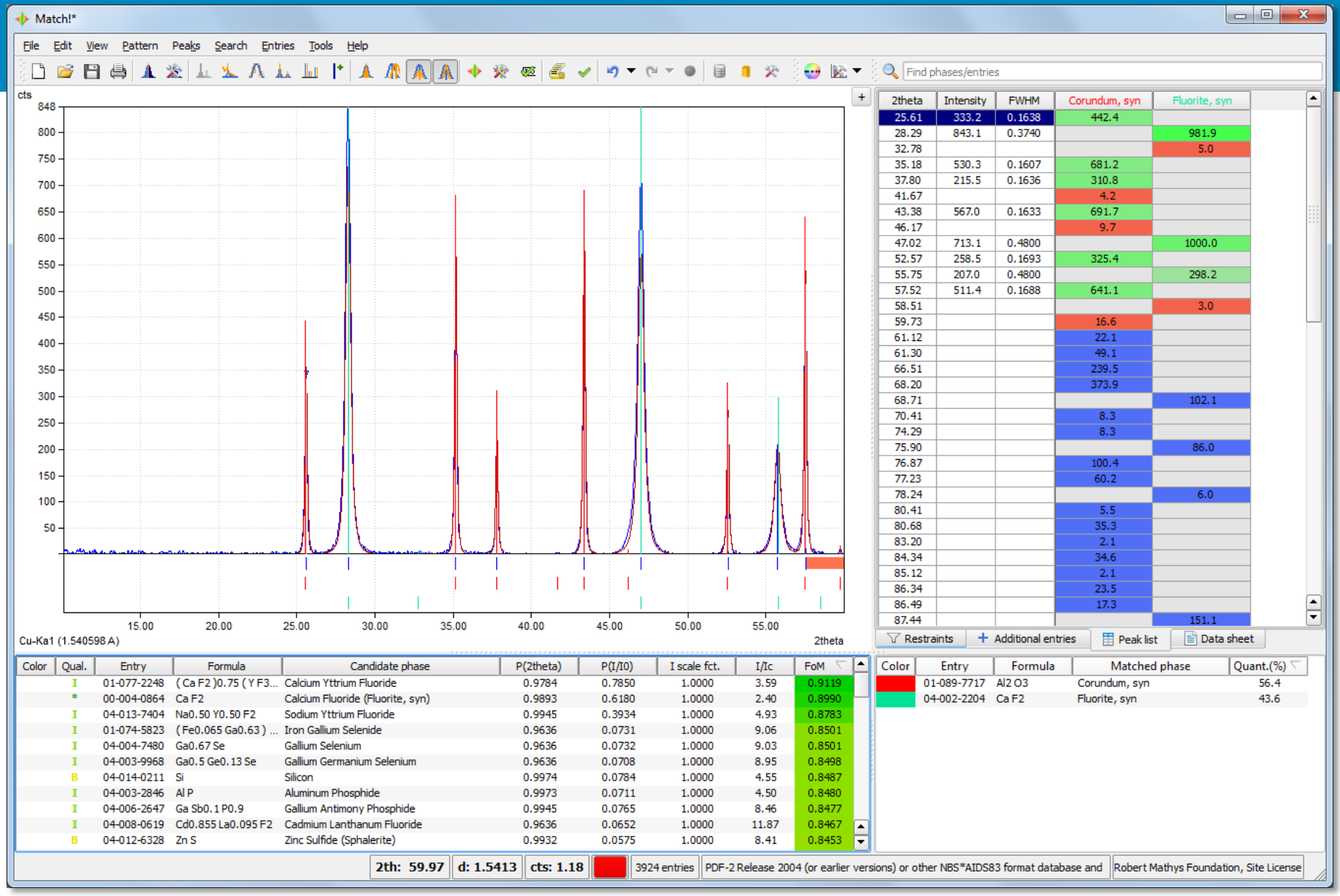
Phase Identification



Phase Identification

1. Extract peak positions
2. Compare with data base




Match!*
File Edit View Pattern Peaks Search Entries Tools Help
Find phases/entries
cts
848
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.00
55.00
Cu-Ka1 (1.540598 A)
2theta
2theta | Intensity | FWHM | Corundum, syn | Fluorite, syn
25.61 | 333.2 | 0.1638 | 442.4 |
28.29 | 843.1 | 0.3740 | | 981.9
32.78 | | | | 5.0
35.18 | 530.3 | 0.1607 | 681.2 |
37.80 | 215.5 | 0.1636 | 310.8 |
41.67 | | | 4.2 |
43.38 | 567.0 | 0.1633 | 691.7 |
46.17 | | | 9.7 |
47.02 | 713.1 | 0.4800 | | 1000.0
52.57 | 258.5 | 0.1693 | 325.4 |
55.75 | 207.0 | 0.4800 | | 298.2
57.52 | 511.4 | 0.1688 | 641.1 |
58.51 | | | | 3.0
59.73 | | | 16.6 |
61.12 | | | 22.1 |
61.30 | | | 49.1 |
66.51 | | | 239.5 |
68.20 | | | 373.9 |
68.71 | | | | 102.1
70.41 | | | 8.3 |
74.29 | | | 8.3 |
75.90 | | | | 86.0
76.87 | | | 100.4 |
77.23 | | | 60.2 |
78.24 | | | | 6.0
80.41 | | | 5.5 |
80.68 | | | 35.3 |
83.20 | | | 2.1 |
84.34 | | | 34.6 |
85.12 | | | 2.1 |
86.34 | | | 23.5 |
86.49 | | | 17.3 |
87.44 | | | | 151.1
Restraints
Additional entries
Peak list
Data sheet
Color | Qual. | Entry | Formula | Candidate phase | P(2theta) | P(I/I0) | I scale fct. | I/Ic | FoM
I | 01-077-2248 | (Ca F2)0.75 (Y F3... | Calcium Yttrium Fluoride | 0.9784 | 0.7850 | 1.0000 | 3.59 | 0.9119
* | 00-004-0864 | Ca F2 | Calcium Fluoride (Fluorite, syn) | 0.9893 | 0.6180 | 1.0000 | 2.40 | 0.8990
I | 04-013-7404 | Na0.50 Y0.50 F2 | Sodium Yttrium Fluoride | 0.9945 | 0.3934 | 1.0000 | 4.93 | 0.8783
I | 01-074-5823 | (Fe0.065 Ga0.63) ... | Iron Gallium Selenide | 0.9636 | 0.0731 | 1.0000 | 9.06 | 0.8501
I | 04-004-7480 | Ga0.67 Se | Gallium Selenium | 0.9636 | 0.0732 | 1.0000 | 9.03 | 0.8501
I | 04-003-9968 | Ga0.5 Ge0.13 Se | Gallium Germanium Selenium | 0.9636 | 0.0708 | 1.0000 | 8.95 | 0.8498
B | 04-014-0211 | Si | Silicon | 0.9974 | 0.0784 | 1.0000 | 4.55 | 0.8487
I | 04-003-2846 | Al P | Aluminum Phosphide | 0.9973 | 0.0711 | 1.0000 | 4.50 | 0.8480
I | 04-006-2647 | Ga Sb0.1 P0.9 | Gallium Antimony Phosphide | 0.9945 | 0.0765 | 1.0000 | 8.46 | 0.8477
I | 04-008-0619 | Cd0.855 La0.095 F2 | Cadmium Lanthanum Fluoride | 0.9636 | 0.0652 | 1.0000 | 11.87 | 0.8467
B | 04-012-6328 | Zn S | Zinc Sulfide (Sphalerite) | 0.9932 | 0.0575 | 1.0000 | 8.41 | 0.8453
Color | Entry | Formula | Matched phase | Quant.(%)
01-089-7717 | Al2 O3 | Corundum, syn | 56.4
04-002-2204 | Ca F2 | Fluorite, syn | 43.6
2th: 59.97
d: 1.5413
cts: 1.18
3924 entries
PDF-2 Release 2004 (or earlier versions) or other NBS*AIDS83 format database and
Robert Mathys Foundation, Site License

Databases

Databases containing powder diffraction data (line positions)

Database	Publisher	# of Entries*	Data sets
PDF-2	ICDD (http://www.icdd.com)	291’119	All
PDF-4+	ICDD (http://www.icdd.com)	384’613	Inorganics
PDF-4/Minerals	ICDD (http://www.icdd.com)	44’341	Minerals (Subset of PDF-4+)
PDF-4/Organics	ICDD (http://www.icdd.com)	516’054	Organics
Crystallography Open Database	COD http://www.crystallography.net	366’977**	All (excl. biopolymers)

Commercial

Open Access

* September 2016

**2013: 215’708

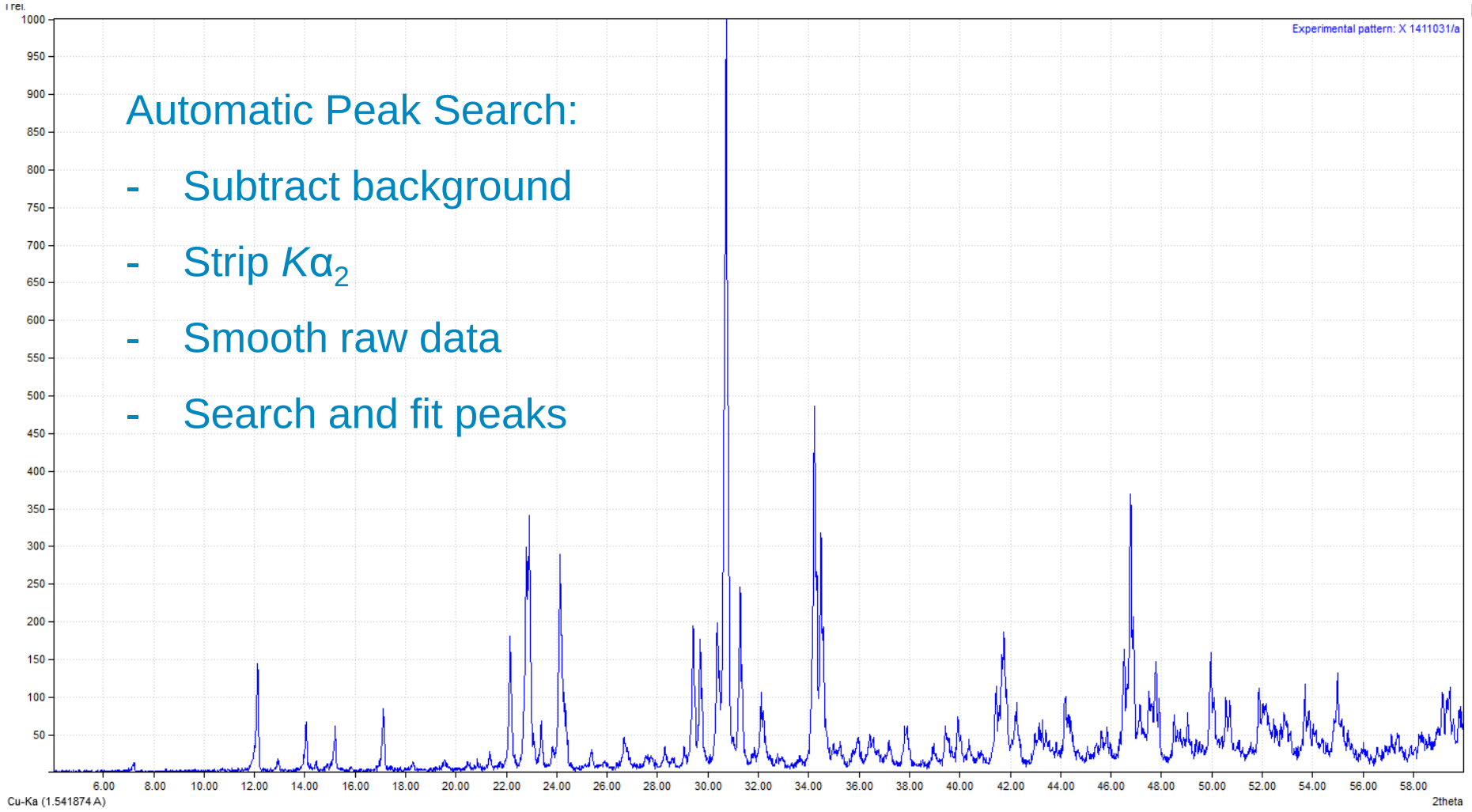
Programmes for Search / Match

Programme	Publisher	Supported Databases*
HighScore	PANalytical	PDF-2/4 COD
EVA Search/Match	Bruker	PDF-2/4 COD
PDXL2	Rigaku	PDF-2 COD
RayfleX	GE	PDF-2/4
Sleve	ICDD	PDF-2/4
Match!	Crystal Impact	PDF-2/4 COD
CSM	Oxford Cryosystems	PDF-2/4
Jade	MDI	PDF-2/4

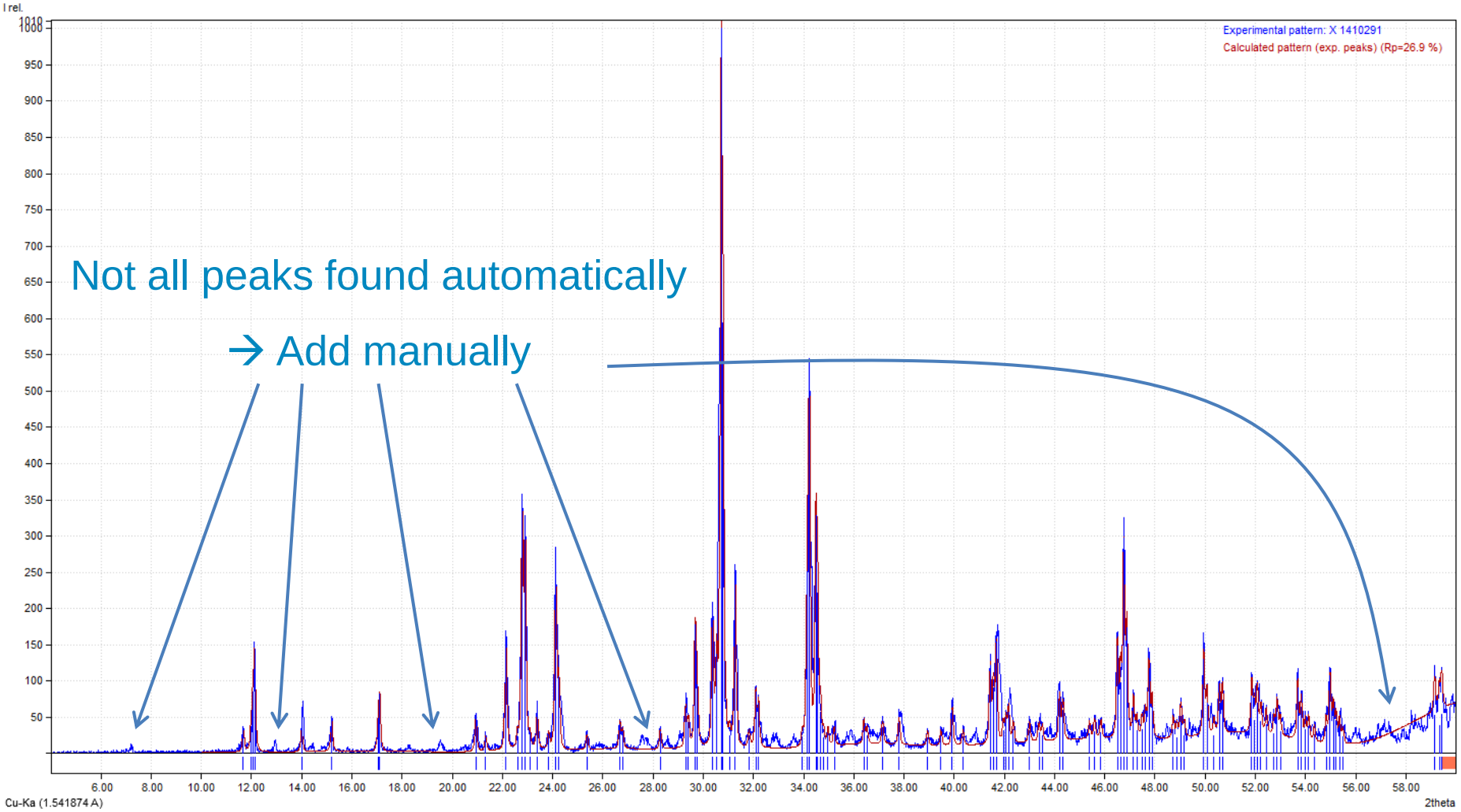
+ many more
(see http://www.ccp14.ac.uk/solution/search-match.htm)

*incomprehensive

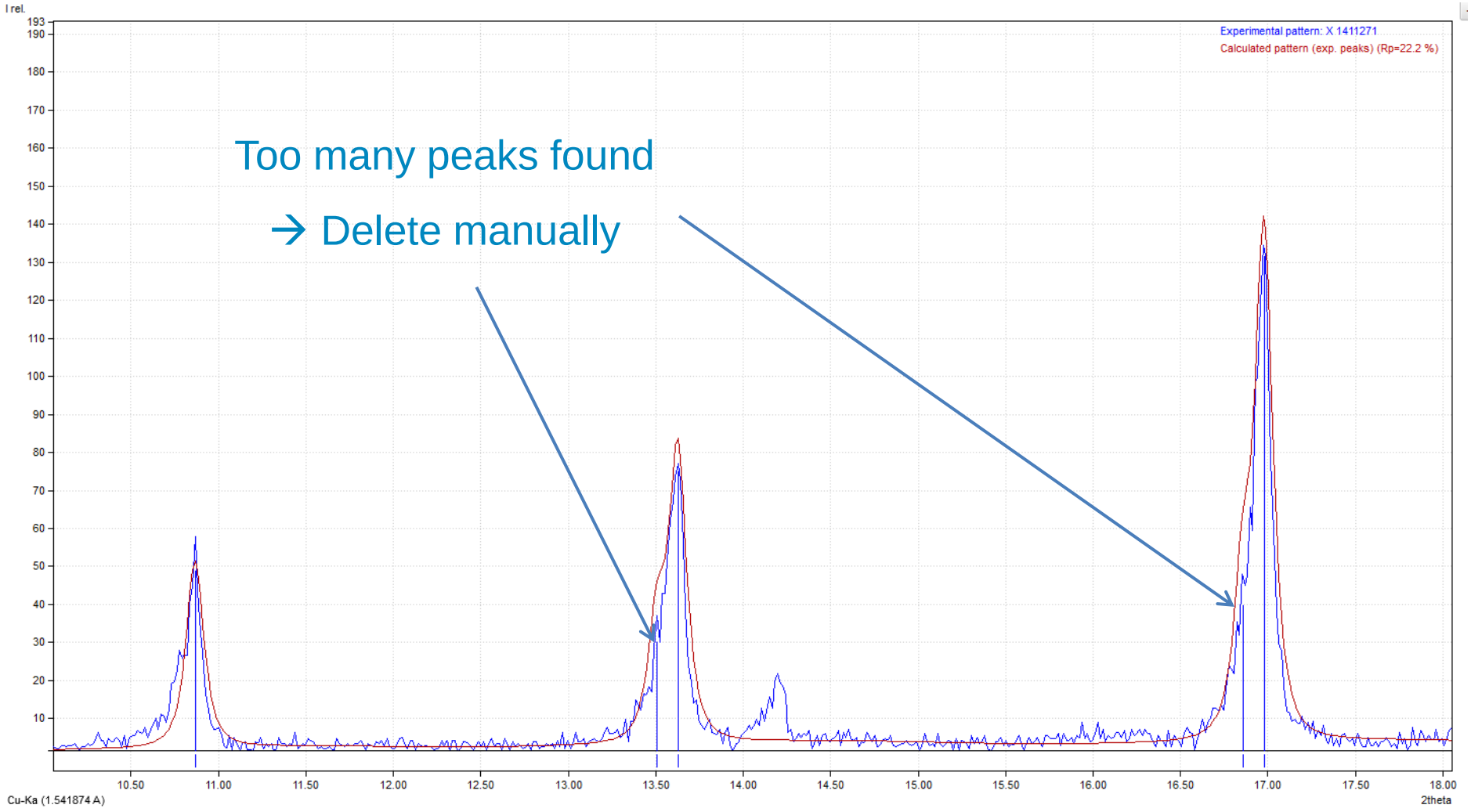
Search / Match: Peak Search



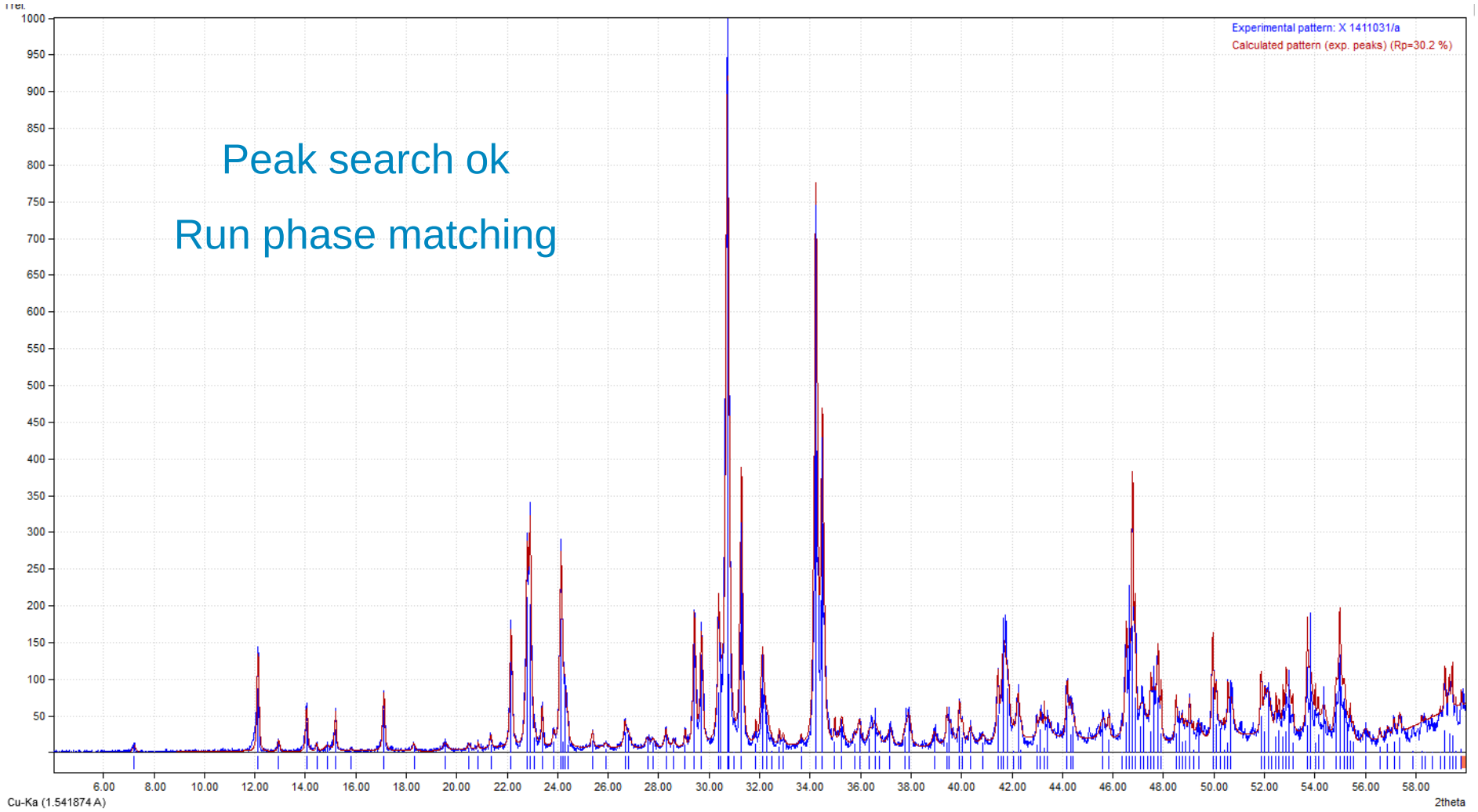
Search / Match: Peak Search



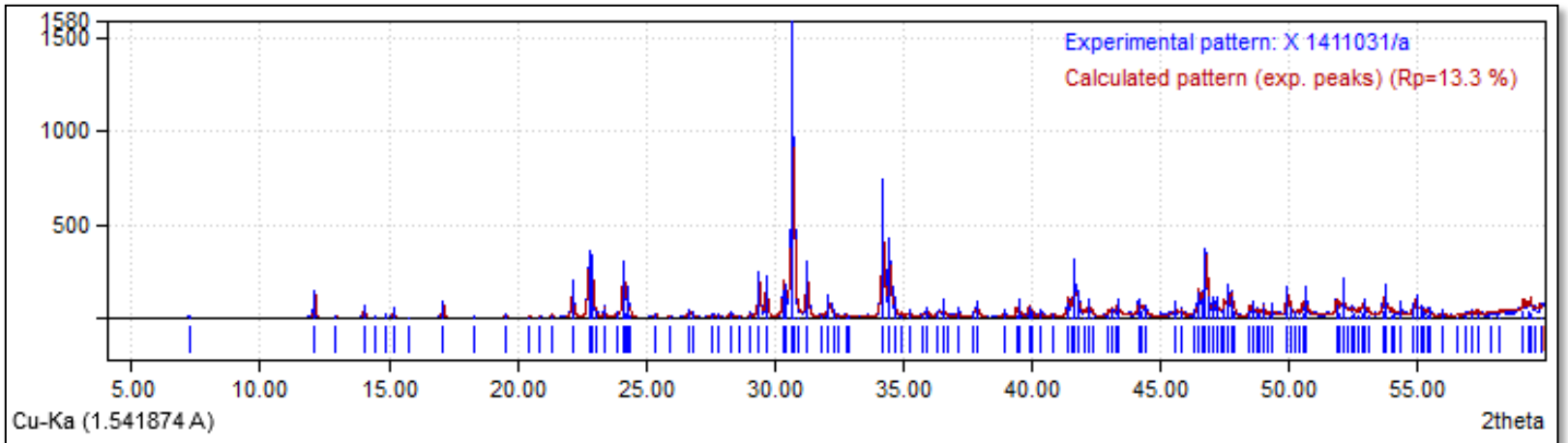
Search / Match: Peak Search



Search / Match: Phase Matching



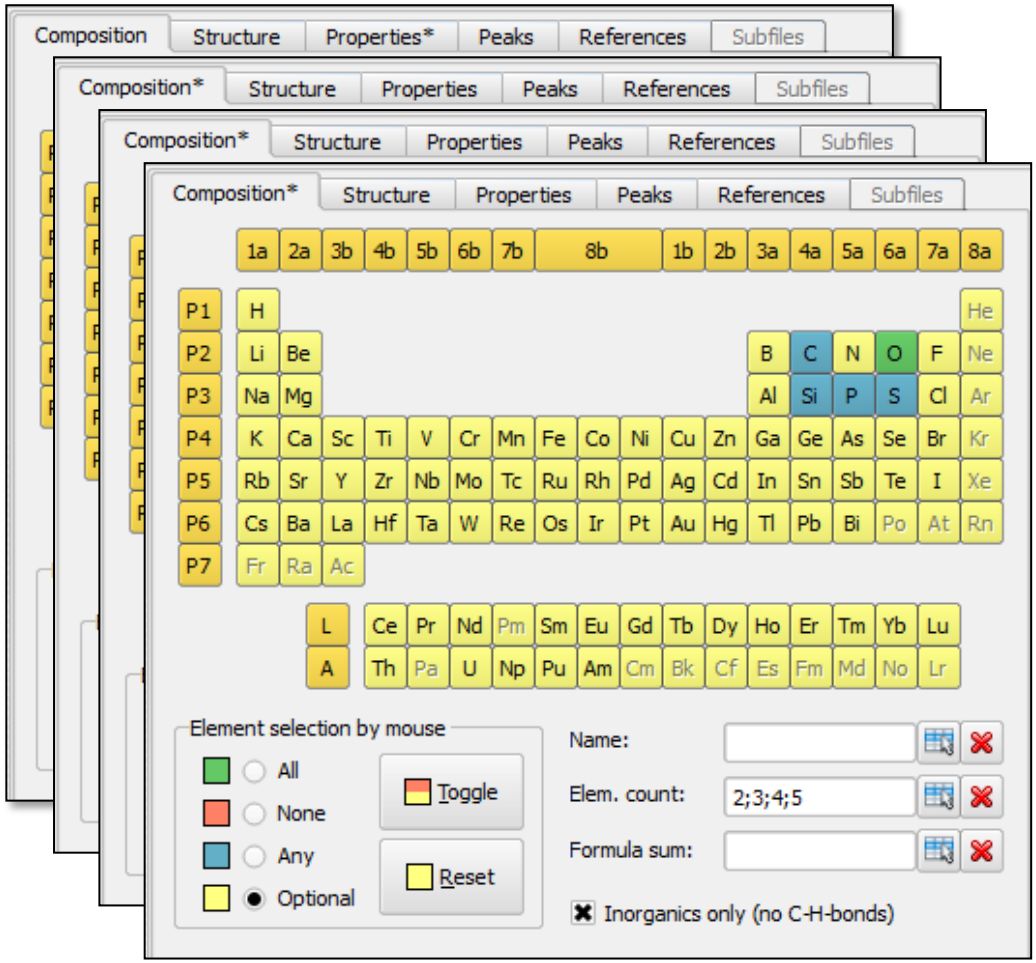
Search / Match: False Positives



Color	Qual.	Entry	Formula	Candidate phase	P(2theta)	P(I/I0)	I scale fct.	I/Ic	FoM
	C	96-200-2442	Ba In2 O4	Barium tetraoxodiindate	0.5909	0.8304	0.6448	6.66	0.8680
	C	96-210-4469	Ga6 O19 Sr10		0.4640	0.8239	0.7491	3.52	0.8627
	C	96-810-1307	Mo N4 Sr3	Tristrontium tetranitridomol...	0.5751	0.8112	0.3609	3.24	0.8620
	C	96-901-1958	Ca0.74 F Fe...	Lavenite	0.5289	0.8146	0.5950	2.21	0.8597
	C	96-901-3286	Fe0.015 Mg0...	Pyroxmangite	0.5497	0.4951	0.7240	0.89	0.8581
	C	96-900-5610	Ca3.27 Ce0....	Kochite	0.5510	0.6586	0.4102	0.79	0.8576
	C	96-210-5286	Ca6 O16 P4		0.5889	0.9690	0.1925	0.51	0.8573
	C	96-901-1846	Ca7 F4 Mn N...	Rosenbuschite	0.5289	0.7188	0.4101	1.03	0.8570
	C	96-411-6447	C4 Cl2 F N2 ...		0.5094	0.8784	0.3335	2.39	0.8568
	C	96-900-5693	Ca3.69 F2 N...	Cuspidine	0.5962	0.8322	0.3277	1.72	0.8558
	C	96-100-5054	B2 Ca9 Cl8	Nonacalcium octachloride bi...	0.5228	0.8931	0.5774	2.17	0.8542
	C	96-900-8997	B Cl		0.5101	0.8890	0.3917	1.37	0.8537
	C	96-200-2497	Ni O6 V2	Nickel divanadate	0.5655	0.8443	0.3996	1.50	0.8526
	C	96-210-2007	F Nb O2		0.9515	0.9781	0.3590	11.66	0.8510
	C	96-410-2357	Fe0.75 Pb3....	Iron Lead Antinony Selenid...	0.5207	0.8897	0.2499	4.93	0.8510
	C	96-430-6890	Ag0.77 Ge4 ...		0.5883	0.7484	0.2773	4.48	0.8495
	C	96-210-4211	Ga2 O9 Zn6		0.4985	0.9234	0.5158	3.85	0.8490
	C	96-100-1565	K O24 P7 V4	Potassium tecto-phosphato...	0.5324	0.7690	0.2748	1.18	0.8487

Search / Match: Restrictions

By chemical Composition



Use additional information from…

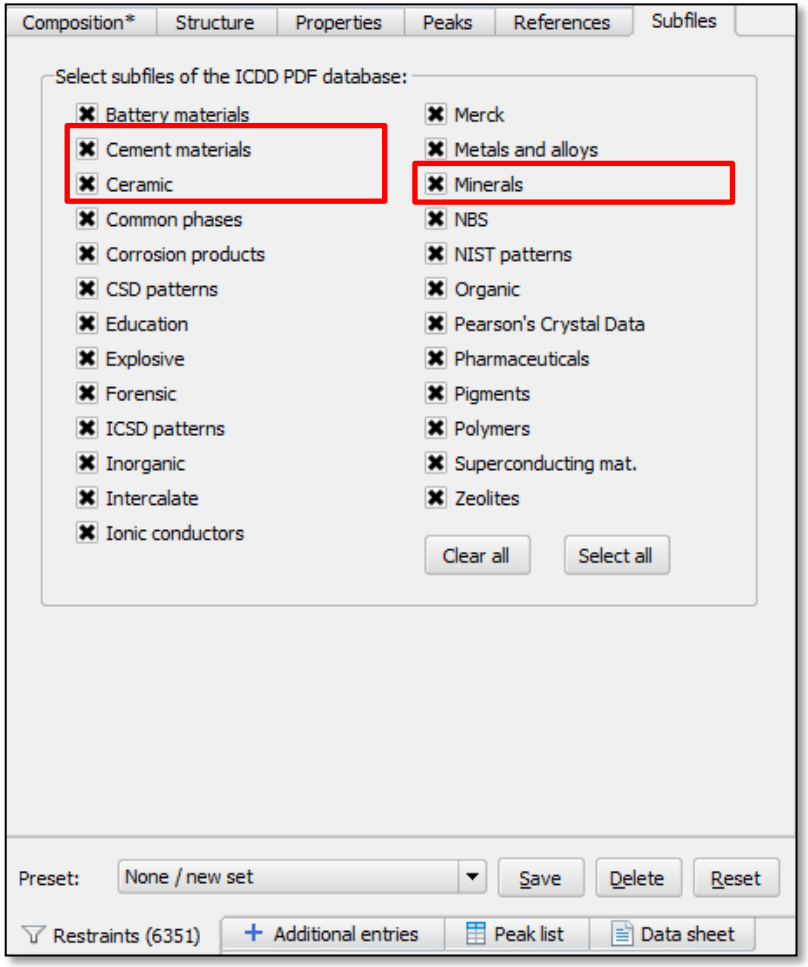
… synthesis

… chemical analysis

... geological situation

Search / Match: Restrictions

By Subfile



Only supported by PDF-2 and PDF-4+ database

No subfiles in COD database

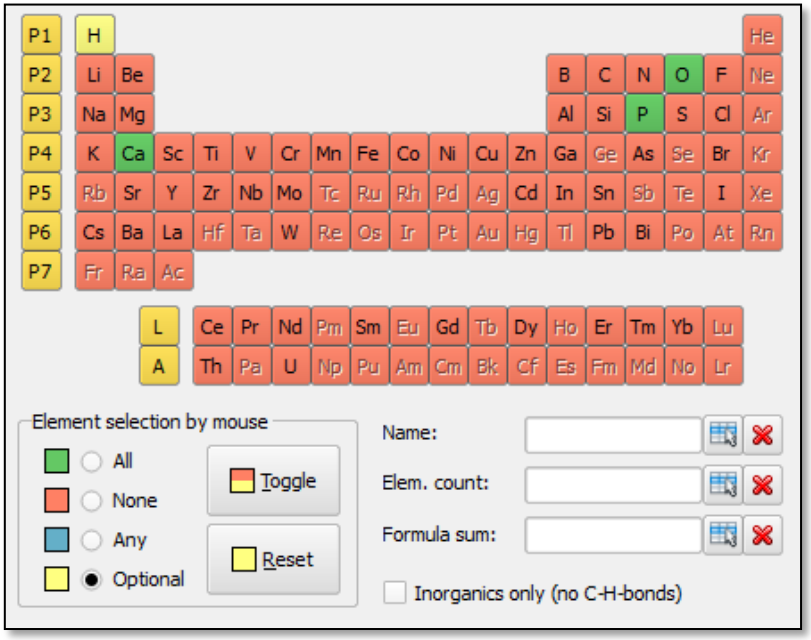
Search / Match: Restrictions

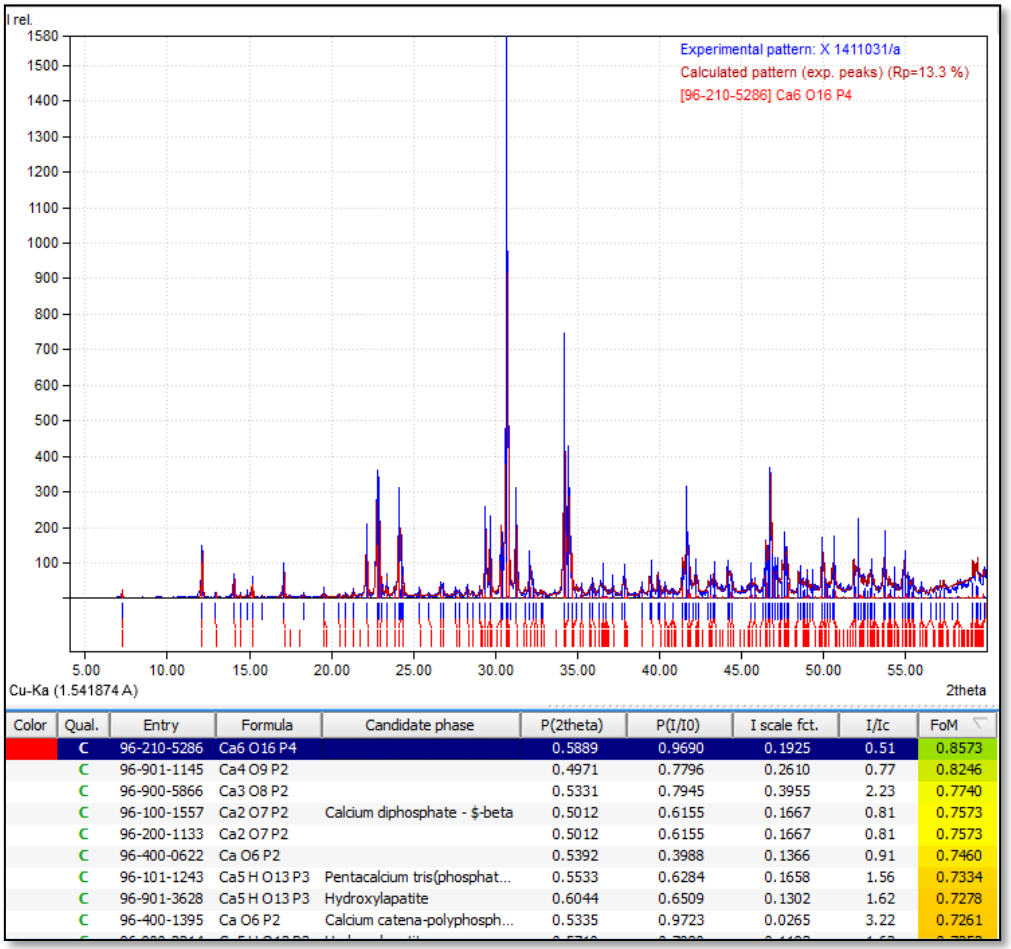
Known from synthesis: Sample = synthetic calcium phosphate

Chemical restrictions:

All: Calcium Phosphate

Optionally: hydrate or hydrogen phosphate

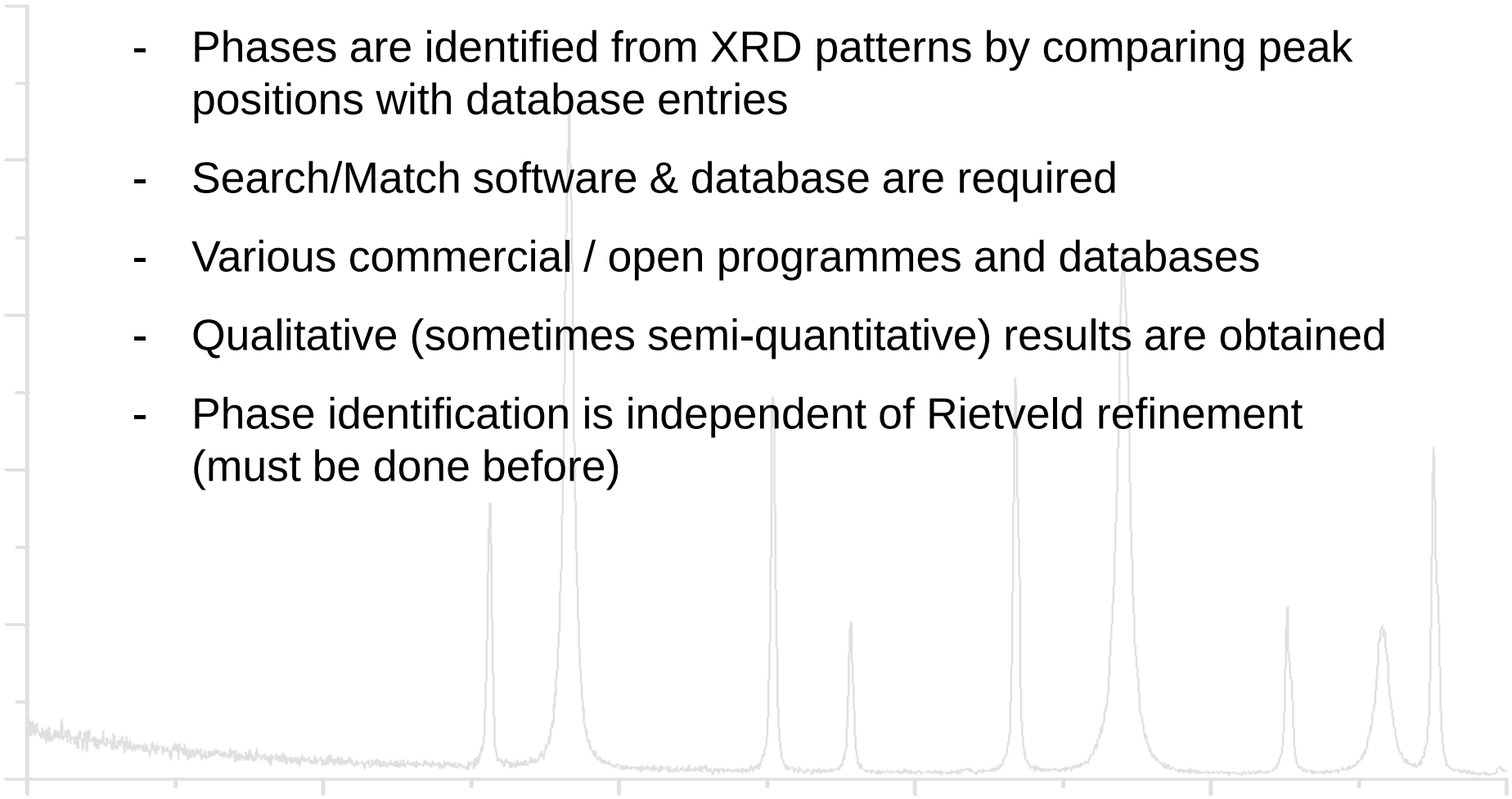




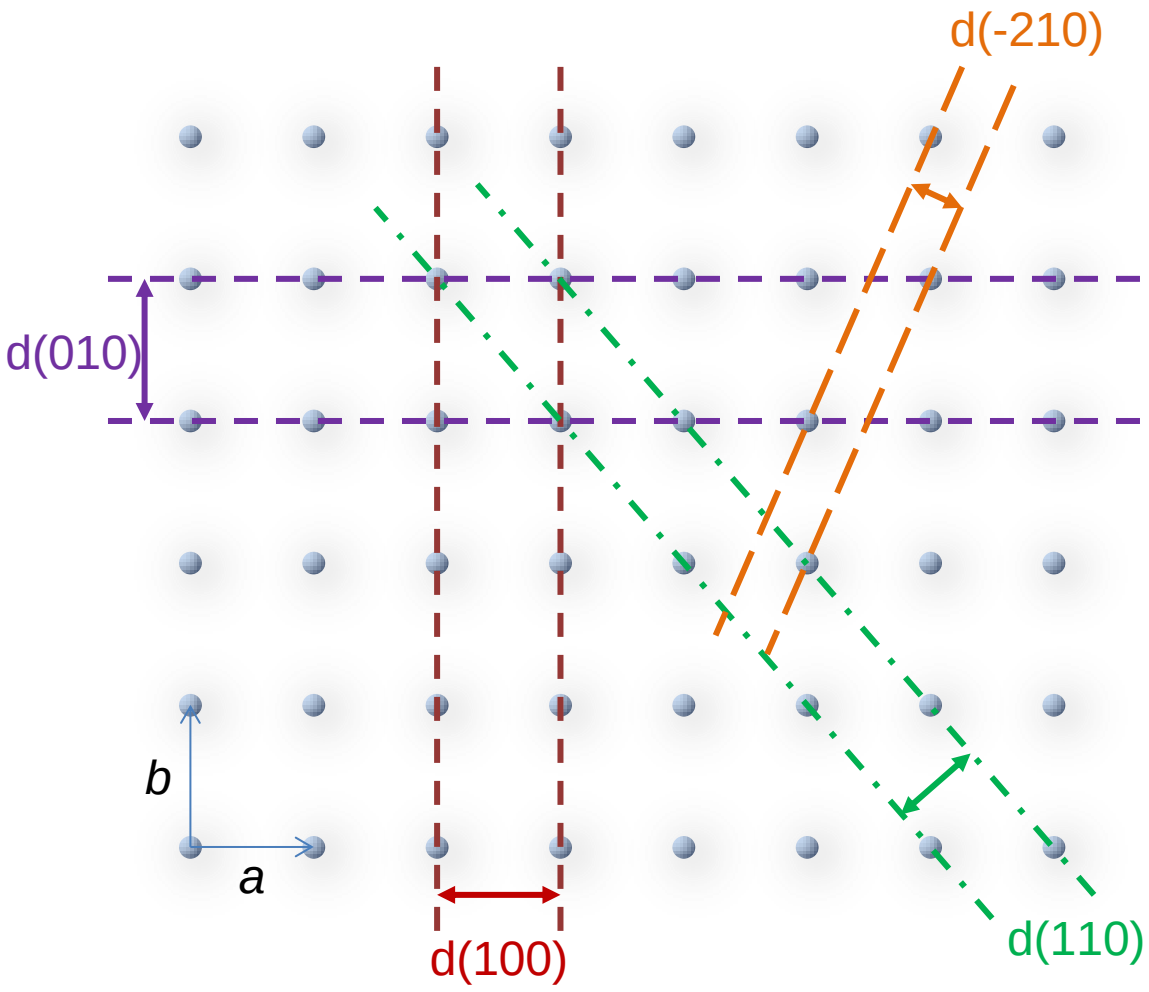
Color	Qual.	Entry	Formula	Candidate phase	P(2theta)	P(I/I0)	I scale fct.	I/Ic	FoM
	C	96-210-5286	Ca6 O16 P4		0.5889	0.9690	0.1925	0.51	0.8573
	C	96-901-1145	Ca4 O9 P2		0.4971	0.7796	0.2610	0.77	0.8246
	C	96-900-5866	Ca3 O8 P2		0.5331	0.7945	0.3955	2.23	0.7740
	C	96-100-1557	Ca2 O7 P2	Calcium diphosphate - $-beta	0.5012	0.6155	0.1667	0.81	0.7573
	C	96-200-1133	Ca2 O7 P2		0.5012	0.6155	0.1667	0.81	0.7573
	C	96-400-0622	Ca O6 P2		0.5392	0.3988	0.1366	0.91	0.7460
	C	96-101-1243	Ca5 H O13 P3	Pentacalcium tris(phosphat...	0.5533	0.6284	0.1658	1.56	0.7334
	C	96-901-3628	Ca5 H O13 P3	Hydroxylapatite	0.6044	0.6509	0.1302	1.62	0.7278
	C	96-400-1395	Ca O6 P2	Calcium catena-polyphosph...	0.5335	0.9723	0.0265	3.22	0.7261

Summary: Phase Identification I

- Phases are identified from XRD patterns by comparing peak positions with database entries
- Search/Match software & database are required
- Various commercial / open programmes and databases
- Qualitative (sometimes semi-quantitative) results are obtained
- Phase identification is independent of Rietveld refinement (must be done before)



Question I: Polytypes



Each set of lattice planes has a characteristic spacing *d*.

Diffraction angle θ depends on *d*:

$$\theta = \mathrm{asin}\left(\frac{\lambda}{2d}\right)$$

Moving atoms in the crystal lattice changes lattice plane spacings *d*.

Changes in *d* also changes diffraction angle θ.

Question I: Polytypes

Is powder XRD the ideal tool to distinguish and identify the following phases?

Phase	Composition	Space Group
Calcite	$CaCO_3$	R-3c
Magnesite	$MgCO_3$	R-3c
Siderite	$FeCO_3$	R-3c

Question II: Polymorphs

Is powder XRD the ideal tool to distinguish and identify the following phases?

Phase	Composition	Space Group
Calcite	$CaCO_3$	R-3c
Vaterite	$CaCO_3$	P63/mmc
Aragonite	$CaCO_3$	Pnam

Summary: Phase identification II

- XRD is mostly sensitive to structural differences
- Only little information on chemical differences
- Chemical analyses (XRF, ICP, EDX,…) provide complementary information
- Sometimes additional chemical information can be very helpful for phase identification (→ restrictions)
- For a comprehensive material characterization, combine XRD with chemical analysis