Queen Mary
University of London

Advanced Methods in Structure Analysis

Lecture 3
Powder Diffraction

Dr. I. Abrahams
Queen Mary University of London

BRITISH COUNCIL

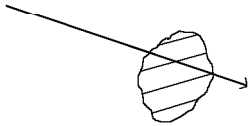
Part of a series of lectures sponsored by the British Council

Powder Diffraction

In order to observe a diffracted X-ray beam from a single crystal, the crystal must be rotated with respect to the incident X-ray beam so that a particular set of *hkl* planes makes the correct angle θ_{hkl} with the incident beam so as to satisfy Bragg's law.

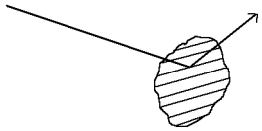
Crystalline powders contain large numbers of small crystallites, each of which is randomly orientated. Therefore at any one time all the allowed *hkl* planes will be correctly orientated in the X-ray beam. i.e for every possible *hkl* some crystals will make the correct θ_{hkl} for diffraction to occur.

1



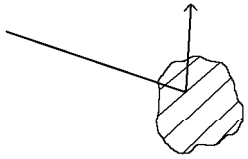
Crystal 1 shows the (002) sets of planes but is not correctly aligned with the incident beam

2



2 shows the same crystal with the parallel set of (001) planes which are correctly aligned, so diffraction occurs

3



3 shows another crystal where the (002) planes are correctly aligned so diffraction occurs.

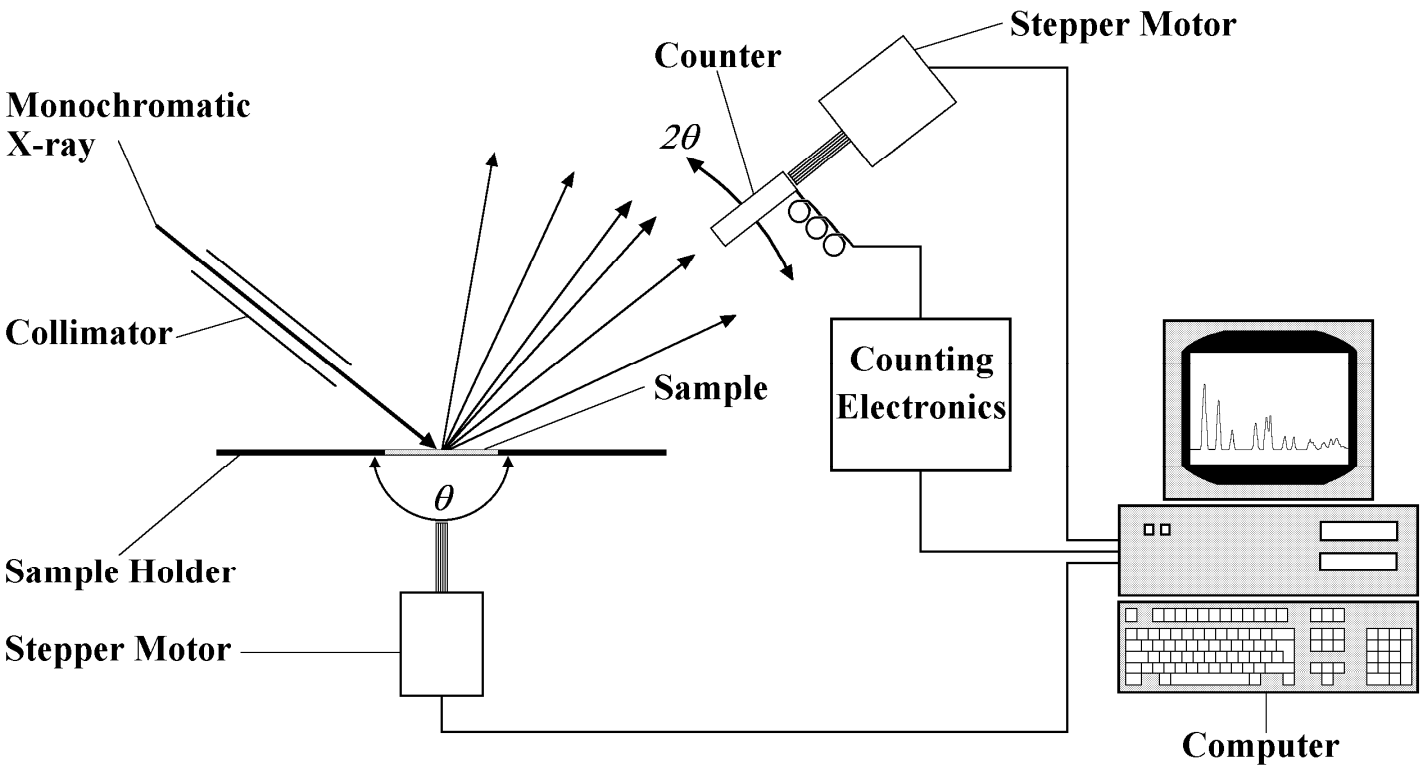
Powder Diffractometer

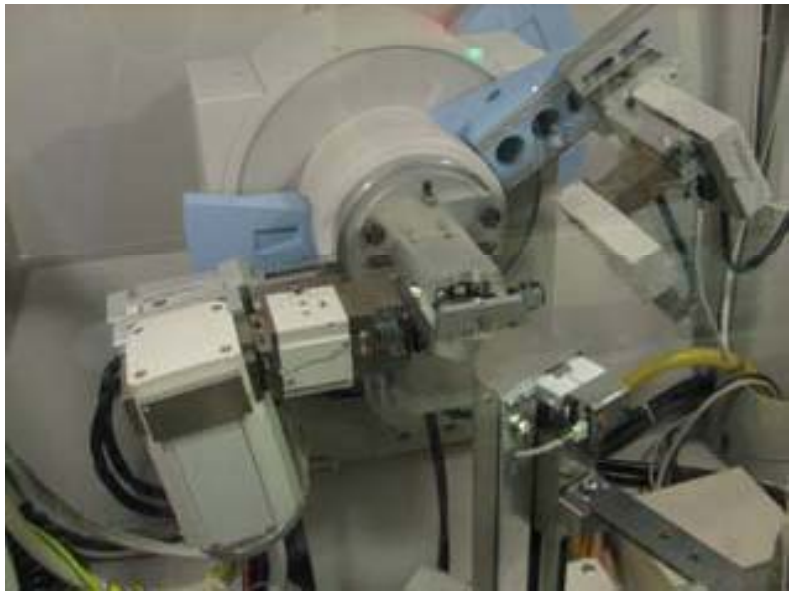
In the laboratory X-ray powder method a single wavelength of collimated X-ray beam is incident to the powder. The diffracted beams are subsequently observed by radiation detectors.

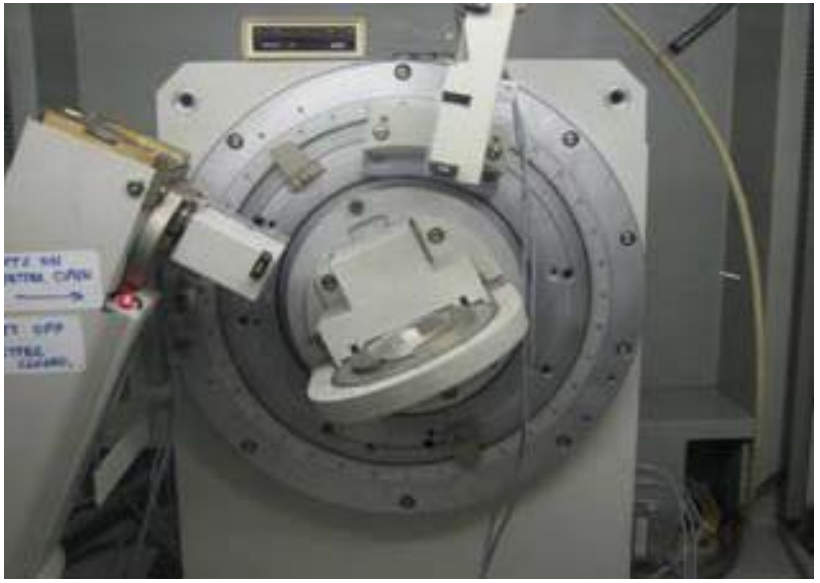
The resulting diffracted beams can be measured and the corresponding *d*-spacings calculated. The final results are essentially intensity versus *d*-spacings (or 2θ).

Modern diffractometers are computer controlled and allow for fast and efficient data collection and subsequent analysis.

Powder Diffractometer

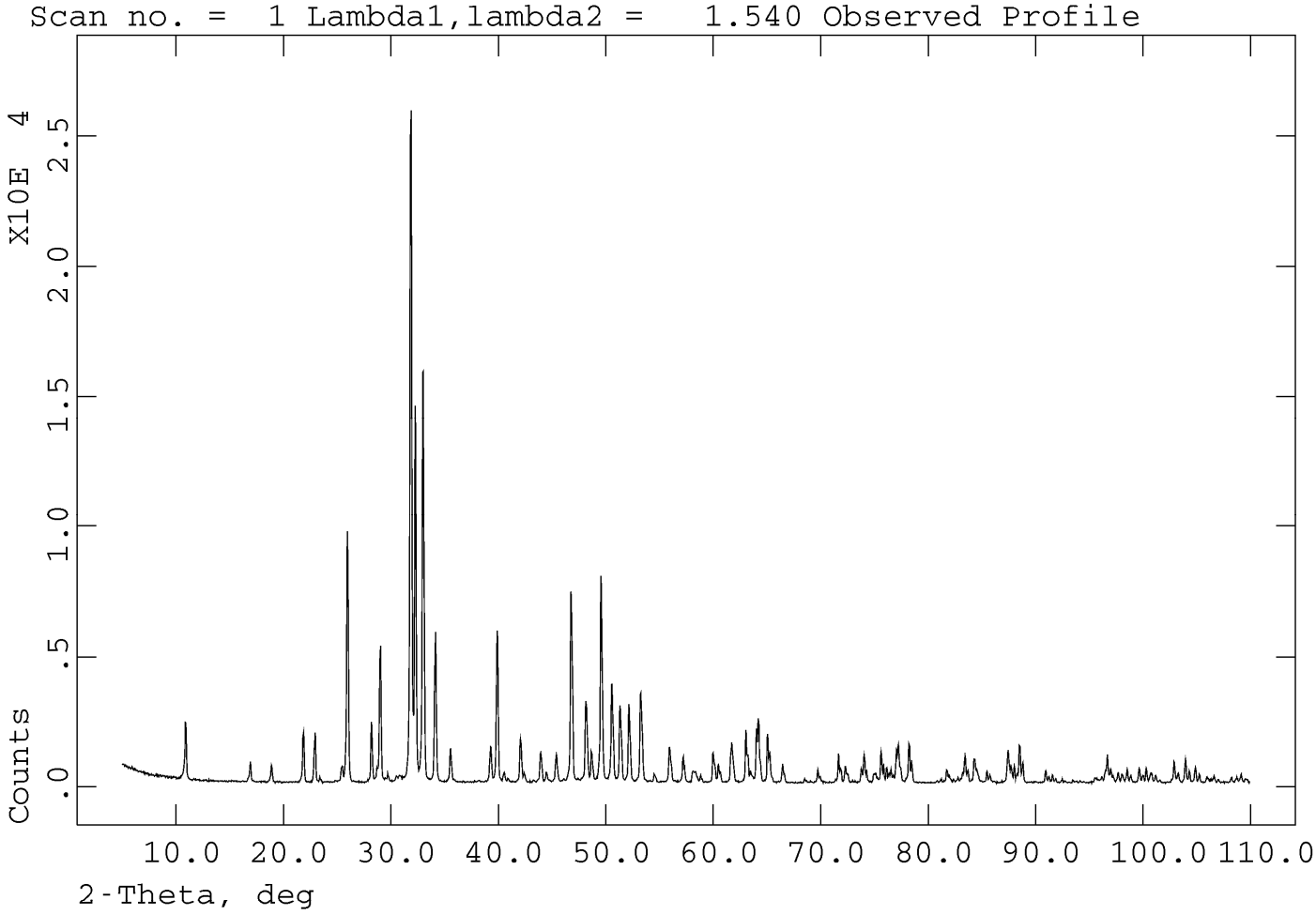






Modern PanAlytical X’Pert Pro diffractometer with Bragg-Brentano θ/θ focusing geometry.

Sintered HA


Scan no. = 1 Lambda1,lambda2 = 1.540 Observed Profile
X10E 4
2.5
2.0
1.5
1.0
.5
.0
Counts
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
2-Theta, deg

Multiplicities

In powder diffraction because three-dimensional space is reduced to one dimension in the powder pattern then if two sets of planes have the same *d*-spacing they will both contribute to the same peak.

e.g. For cubic crystals

$$d_{001} = d_{010} = d_{100} = d_{00\bar{1}} = d_{0\bar{1}0} = d_{\bar{1}00}$$

Therefore multiplicity = 6

Two different reflections (not *hkl* permutations) may also have the same *d*-spacing

e.g. In cubic crystals

$$d_{511} = d_{333}$$

Characterisation of Materials by Powder Diffraction

X-ray powder diffraction is a fundamental tool for materials characterisation.

e.g.

(1) Qualitative analysis
(2) Unit cell refinement
(3) Structure refinement
(4) Structure determination
(5) Quantitative analysis
(6) Phase transition studies
(7) Superlattice identification
(8) Kinetic studies
(9) Crystallite size determination
(10) Strain analysis
(11) Preferred orientation (Texture)

Qualitative Analysis

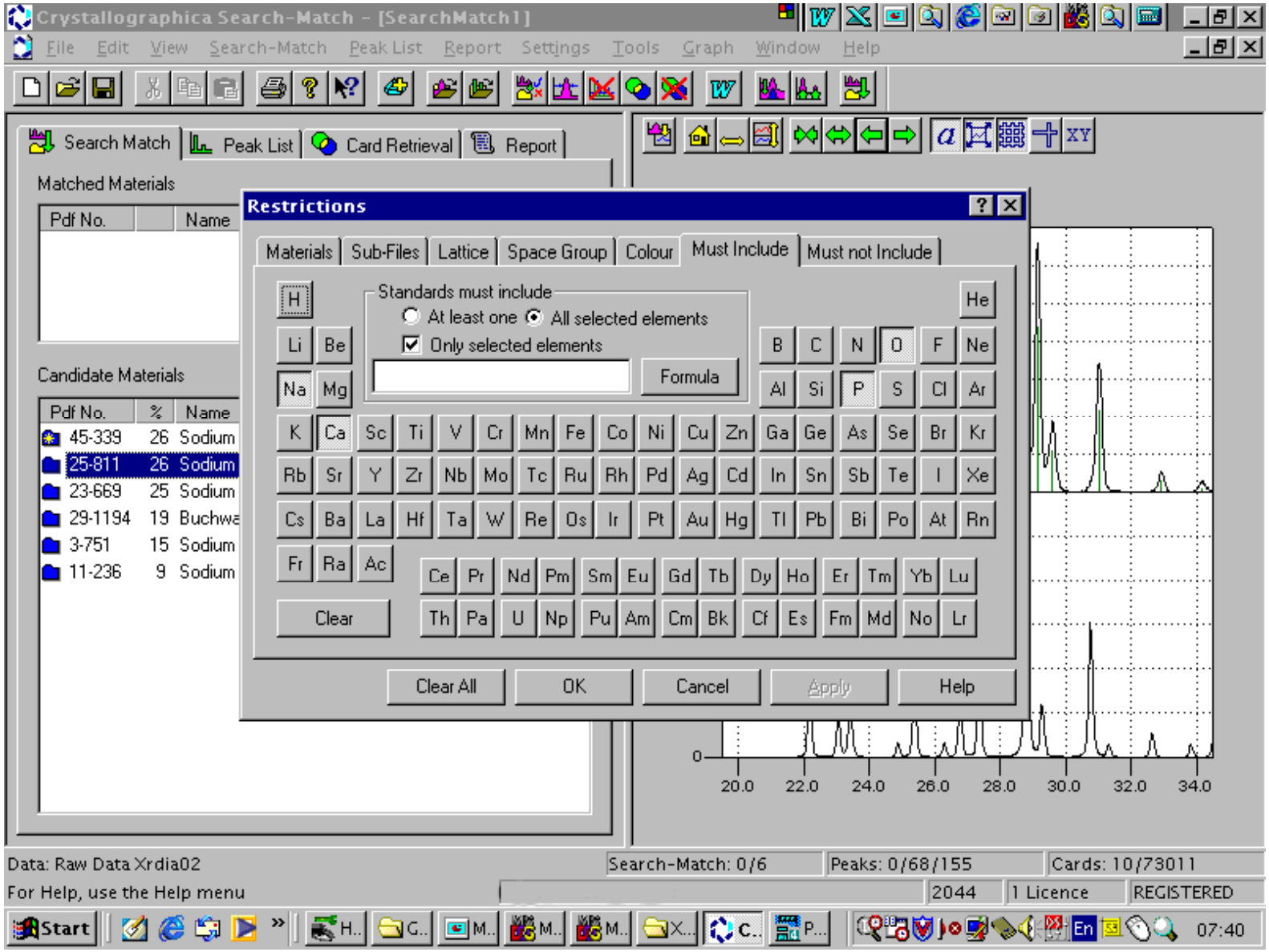
The primary role of the majority of X-ray powder diffractometers is phase identification. This relies on the fact that every unique crystal structure has its own unique powder pattern, *i.e*. its own fingerprint.

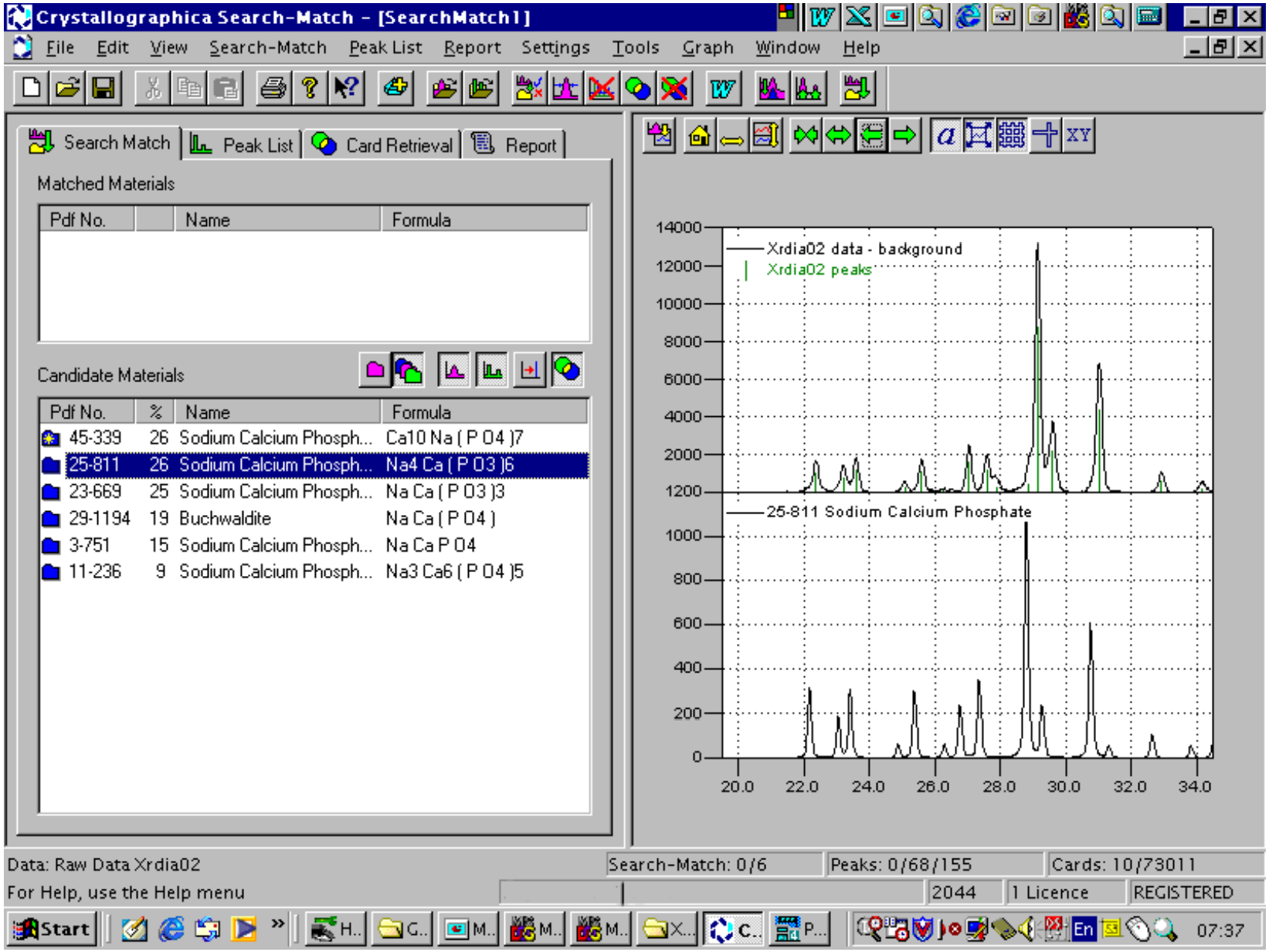
PDF

The Powder Diffraction File (PDF-2 or PDF-4) represents the most complete database of powder diffraction data. The database can be searched in a number of ways by a variety of commercial search engines.

A typical search would involve the loading of a powder pattern and automatic measurement of the diffraction peaks. These would then be compared to those in the database and matches ranked according to how good the match is.

To narrow the search it is advisable to restrict the search to compounds containing only those elements you know were in the reaction mixture.


Crystallographica Search-Match - [SearchMatch1]
File Edit View Search-Match Peak List Report Settings Tools Graph Window Help
Search Match
Peak List
Card Retrieval
Report
Matched Materials
Pdf No.
Name
Candidate Materials
Pdf No. % Name
45-339 26 Sodium
25-811 26 Sodium
23-669 25 Sodium
29-1194 19 Buchwa
3-751 15 Sodium
11-236 9 Sodium
Restrictions
Materials
Sub-Files
Lattice
Space Group
Colour
Must Include
Must not Include
Standards must include
At least one
All selected elements
Only selected elements
Formula
H
He
Li Be
B C N O F Ne
Na Mg
Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Ac
Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr
Clear
Clear All
OK
Cancel
Apply
Help
0
20.0 22.0 24.0 26.0 28.0 30.0 32.0 34.0
Data: Raw Data Xrdia02
For Help, use the Help menu
Search-Match: 0/6
Peaks: 0/68/155
Cards: 10/73011
2044
1 Licence
REGISTERED
Start
07:40


Crystallographica Search-Match - [SearchMatch1]
File Edit View Search-Match Peak List Report Settings Tools Graph Window Help
Search Match
Peak List
Card Retrieval
Report
Matched Materials
Pdf No.
Name
Formula
Candidate Materials
Pdf No. % Name Formula
45-339 26 Sodium Calcium Phosph... Ca10 Na (P O4)7
25-811 26 Sodium Calcium Phosph... Na4 Ca (P O3)6
23-669 25 Sodium Calcium Phosph... Na Ca (P O3)3
29-1194 19 Buchwaldite Na Ca (P O4)
3-751 15 Sodium Calcium Phosph... Na Ca P O4
11-236 9 Sodium Calcium Phosph... Na3 Ca6 (P O4)5
Xrdia02 data - background
Xrdia02 peaks
25-811 Sodium Calcium Phosphate
14000
12000
10000
8000
6000
4000
2000
1200
1000
800
600
400
200
0
20.0
22.0
24.0
26.0
28.0
30.0
32.0
34.0
Data: Raw Data Xrdia02
Search-Match: 0/6
Peaks: 0/68/155
Cards: 10/73011
For Help, use the Help menu
2044
1 Licence
REGISTERED
Start
07:37

Card Information

Names:	Sodium Calcium Phosphate
Formula:	$Na_4 Ca (P O_3)_6$
PDF Number:	25-811
Quality:	indexed
Subfiles:	inorganic

Cell and Symmetry Information

System:	monoclinic	Space Group:	C*/c (no. 15)		
a:	13.248	b:	8.120	c:	14.384
b:	94.65				
Density (Dx):	2.609	Z:	4		

Instrument Information

Wavelength:	0

Literature References

General:	Grenier et al. *Bull. Soc. Fr. Mineral. Cristallogr.* 93 52 (1970)
Unit Cell:	Ibid. *Bull. Soc. Fr. Mineral. Cristallogr.* ( )

Peak Data

PeakList

h	k	l	d	I
0	0	2	7.1800	20
1	1	0	6.9300	5
2	0	0	6.6300	5
-1	1	1	6.3100	5
1	1	1	6.1400	5
-2	0	2	5.0600	45
2	0	2	4.6700	15
-1	1	3	4.0100	25
1	1	3	3.8600	15
-3	1	1	3.8000	25
0	0	4	3.5800	5
-3	1	2	3.5100	25
-2	2	1	3.3900	5
2	2	1	3.3300	20
-2	0	4	3.2600	30
-4	0	2	3.1000	100
2	0	4	3.0500	20
3	1	3	2.9060	55
-2	2	3	2.8560	5
2	2	3	2.7430	10
1	3	0	2.6490	5
1	3	1	2.5970	10

Crystallographic Databases

ICSD Inorganic Crystal Structure Database *ca*. 50,000 Inorganic compounds

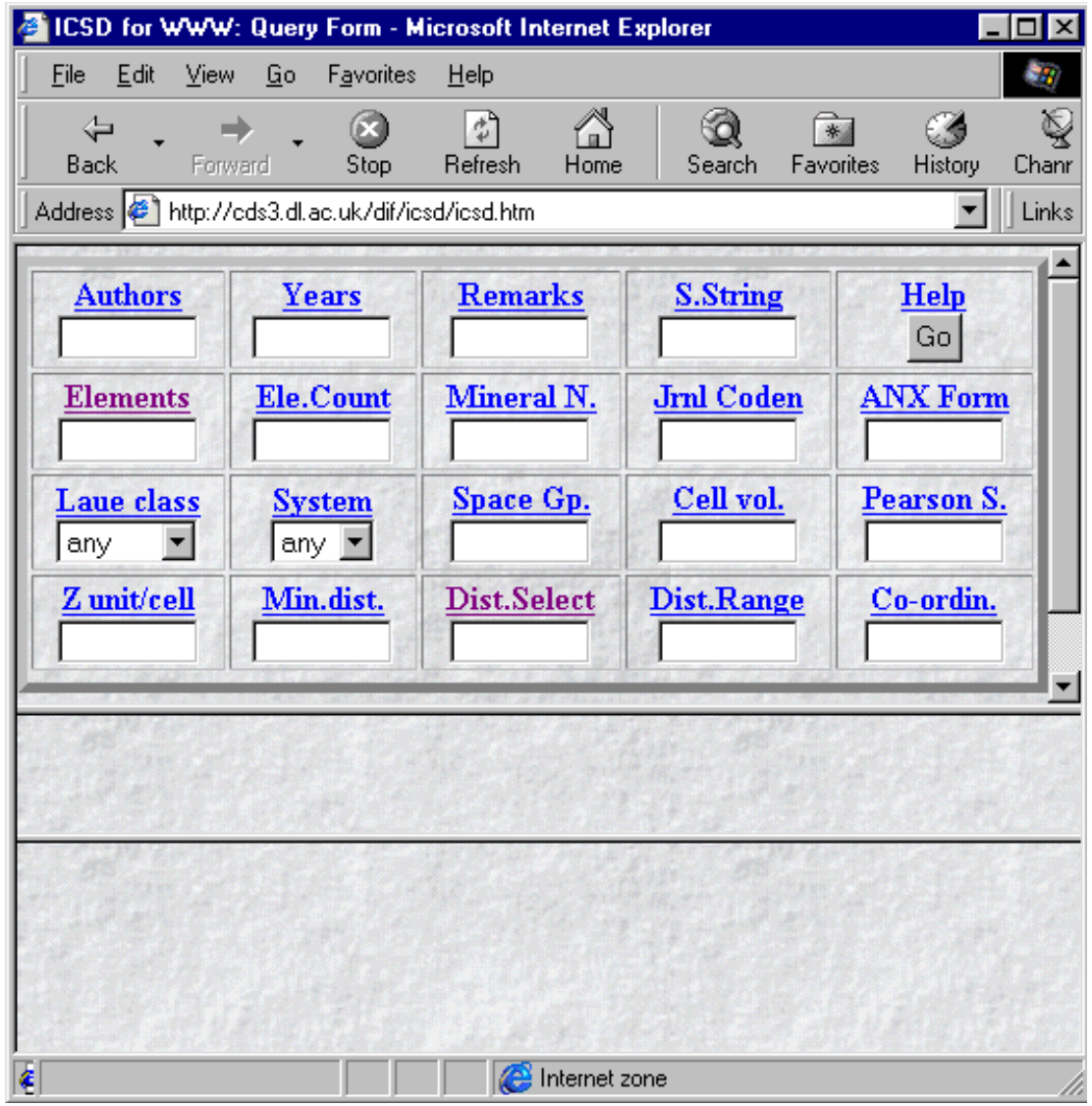
CSD Cambridge Structural Database, Organic/Organometallic Structures > 100,000 compounds

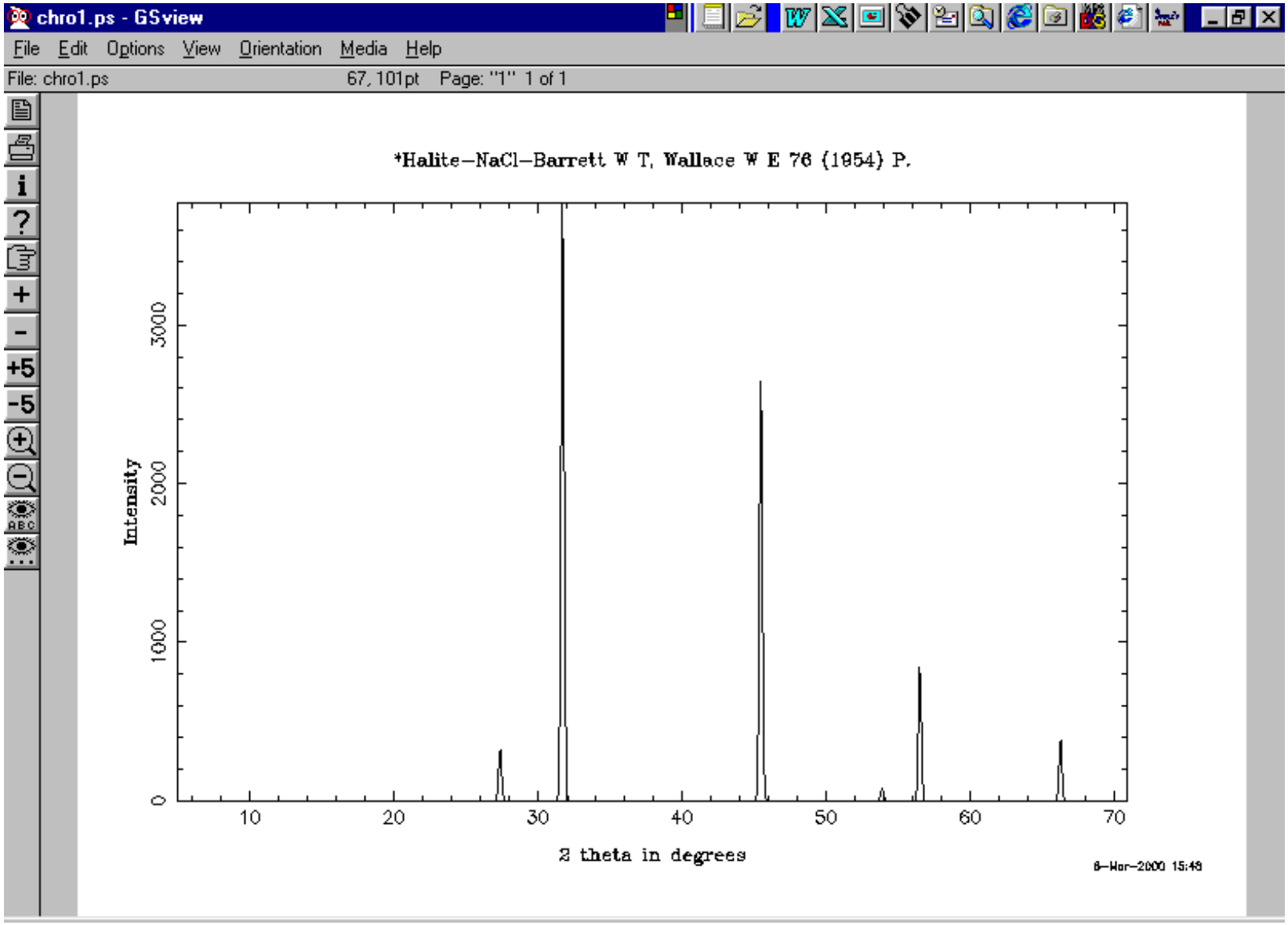
CDIF Crystal class and unit cell data

PDB Protein database

MDF Metals Data file

ICSD on the Web



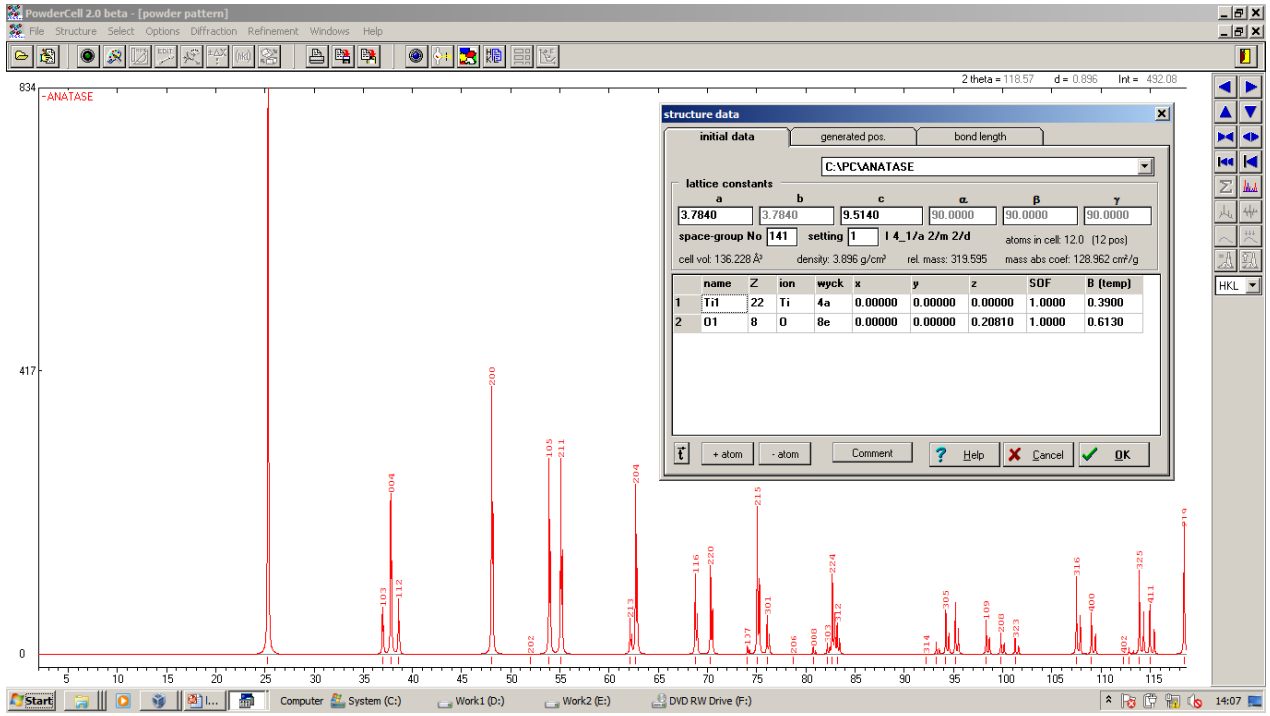

chro1.ps - GSview
File Edit Options View Orientation Media Help
File: chro1.ps 67, 101pt Page: "1" 1 of 1
*Halite—NaCl—Barrett W T, Wallace W E 76 (1954) P.
Intensity
0
1000
2000
3000
10
20
30
40
50
60
70
2 theta in degrees
8—Mar—2000 15:48

Using crystallographic data powder diffraction patterns may be calculated using a variety of software:

e.g.

LAZY-PULVERIX

POWDER-CELL



Unit cell refinement

Assuming that you have been able to identify phases and index the powder pattern, it is often useful to refine unit cell dimensions. This is particularly important if you want to identify solid-solutions.

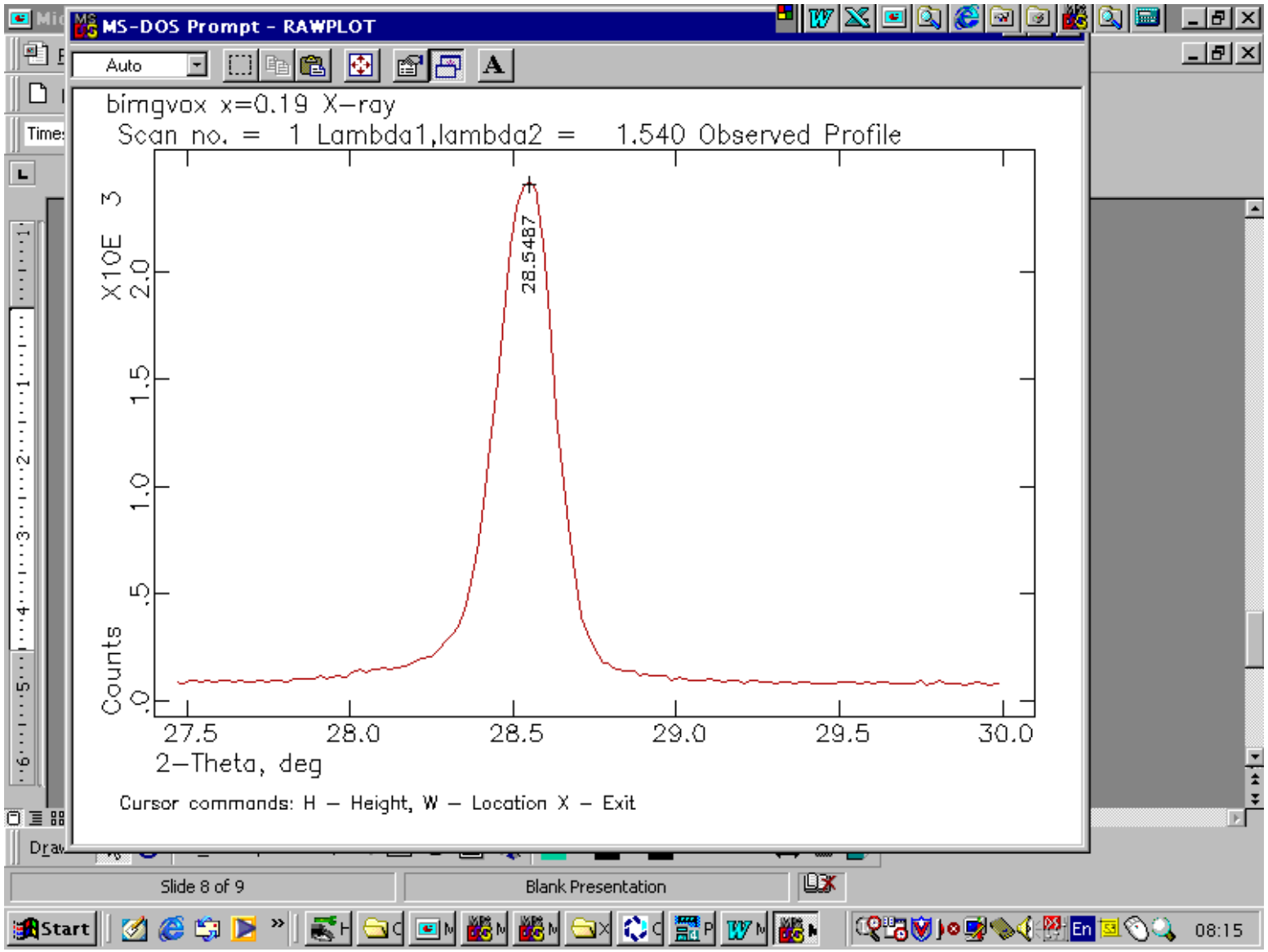
(1) Measure the peaks accurately

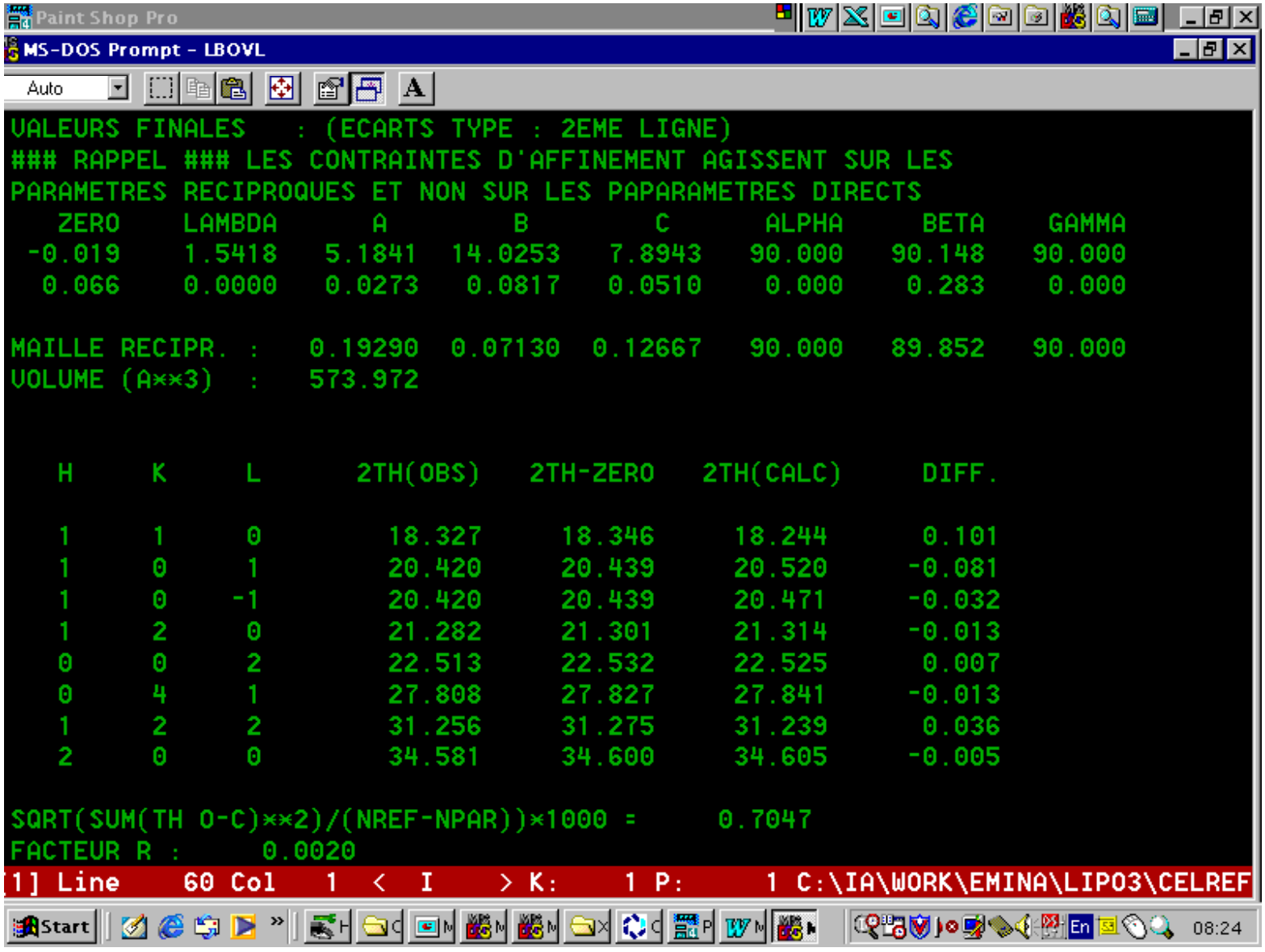
(2) Index the peaks

(3) Refine the unit cell dimensions and zero-point correction.

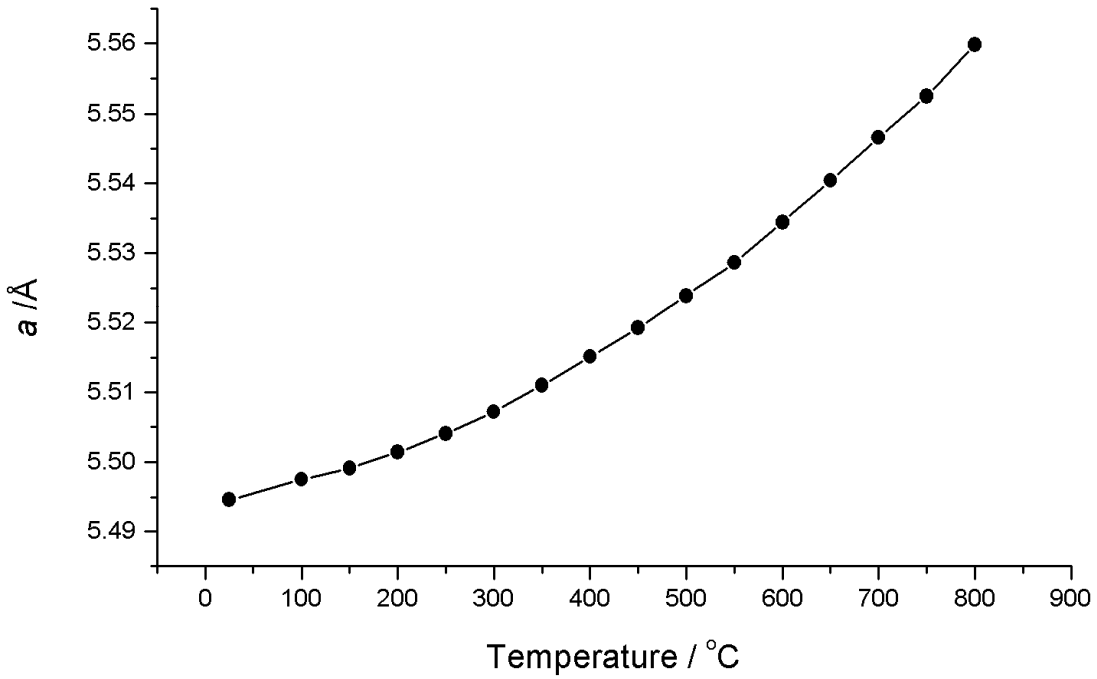
There are a number of programs available to do this. However they all rely on accurate peak measurement. Some incorporate automatic peak measurement

Often where the structure is known you are better off carrying out a Rietveld refinement. Alternatively a LeBail type fit can be carried out.


MS-DOS Prompt - RAWPLOT
Auto
bimgvox x=0.19 X-ray
Scan no. = 1 Lambda1,lambda2 = 1.540 Observed Profile
28.5487
X10E 3
2.0
1.5
1.0
.5
.0
Counts
27.5
28.0
28.5
29.0
29.5
30.0
2-Theta, deg
Cursor commands: H - Height, W - Location X - Exit
Slide 8 of 9
Blank Presentation
Start
08:15


Paint Shop Pro
MS-DOS Prompt - LBOVL
Auto
VALEURS FINALES : (ECARTS TYPE : 2EME LIGNE)
RAPPEL ### LES CONTRAINTES D'AFFINEMENT AGISSENT SUR LES
PARAMETRES RECIPROQUES ET NON SUR LES PAPARAMETRES DIRECTS
ZERO LAMBDA A B C ALPHA BETA GAMMA
-0.019 1.5418 5.1841 14.0253 7.8943 90.000 90.148 90.000
0.066 0.0000 0.0273 0.0817 0.0510 0.000 0.283 0.000
MAILLE RECIPR. : 0.19290 0.07130 0.12667 90.000 89.852 90.000
VOLUME (A**3) : 573.972
H K L 2TH(OBS) 2TH-ZERO 2TH(CALC) DIFF.
1 1 0 18.327 18.346 18.244 0.101
1 0 1 20.420 20.439 20.520 -0.081
1 0 -1 20.420 20.439 20.471 -0.032
1 2 0 21.282 21.301 21.314 -0.013
0 0 2 22.513 22.532 22.525 0.007
0 4 1 27.808 27.827 27.841 -0.013
1 2 2 31.256 31.275 31.239 0.036
2 0 0 34.581 34.600 34.605 -0.005
SQRT(SUM(TH O-C)**2)/(NREF-NPAR))*1000 = 0.7047
FACTEUR R : 0.0020
[1] Line 60 Col 1 < I > K: 1 P: 1 C:\IA\WORK\EMINA\LIPO3\CELREF
Start
08:24

e.g. Thermal variation of cubic lattice parameter in Bi_3YO_6



Structure Refinement

The Rietveld method is a structure refinement technique for powder diffraction data which fits the whole powder pattern including peak shapes and background.

Stages in Rietveld Refinement

(1) Decide on initial structural model
(2) Refine background and overall scale
(3) Refine Unit cell dimensions
(4) Refine zero-point correction
(5) Refine peak shape
(6) Refine atomic coordinates
(7) Refine thermal parameters and/or occupancies
(8) Check model and closeness of fit

Structure Determination

For structure refinement an initial structural model is required before refinement can proceed.

In structure determination the initial model is found using an *ab-initio* approach.

There are a number of stages in structure determination

(1) Unit cell determination and indexing
(2) Space Group identification
(3) Intensity extraction
(4) Initial model determination
(5) Rietveld refinement
(6) Difference Fourier maps generated to locate remaining atoms
(7) Final Rietveld Refinement

Unit cell determination and indexing

There are a number of methods for indexing. All require accurate measurement of diffraction peaks.

Typically 20 peaks or more are used. These should include all the high *d*-spacing peaks.

The most popular programs are

Visser

ITO

TREOR

DICVOL

Typically these programs will offer a number of possible solutions.

TREOR output for bismuth zirconium vanadate

```
NUMBER OF SINGLE INDEXED LINES=    5 TOTAL NUMBER OF LINES=    8
 NUMBER OF SINGLE INDEXED LINES =    5
  TOTAL NUMBER OF LINES =    8
  A =  9.969106  0.001236 A   ALFA = 90.000000  0.000000 DEG
  B =  9.969106  0.001236 A   BETA = 90.000000  0.000000 DEG
  C = 19.823130  0.008515 A  GAMMA = 90.000000  0.000000 DEG
  UNIT CELL VOLUME =   1970.08 A**3
   H   K   L SST-OBS  SST-CALC   DELTA   2TH-OBS 2TH-CALC D-OBS   FREE PARAM.
   1   1   2 0.018007 0.018009 -0.000001  15.424  15.424  5.7448
   2   0   0 0.023954 0.023919  0.000035  17.807  17.794  4.9809
   3   0   0 0.053641 0.053818 -0.000177  26.783  26.828  3.3285
   2   2   2          0.053887                      26.846
   3   1   0          0.059798                      28.309
   3   0   2 0.060039 0.059867  0.000172  28.367  28.326  3.1462
   1   0   6          0.060424                      28.460
   3   1   3 0.073461 0.073409  0.000052  31.452  31.440  2.8443
   3   2   0          0.077737                      32.379
   3   0   4 0.078010 0.078015 -0.000006  32.437  32.438  2.7601
   2   0   6          0.078364                      32.513
   5   0   0 0.149477 0.149494 -0.000017  45.489  45.492  1.9939
   3   3   6 0.162067 0.162080 -0.000013  47.479  47.481  1.9149
NUMBER OF OBS. LINES =    8
NUMBER OF CALC. LINES =   13
M(  8)=  11  AV.EPS.= 0.0000592
F  8 =   5.(0.014699,  120)
 M   CF. J.APPL.CRYST. 1(1968)108
 F  CF. J.APPL.CRYST. 12(1979)60
    0  LINES ARE UNINDEXED
CHECK IF THERE IS ANY COMMON FACTOR IN THE QUADRATIC FORMS
CHECK CONVERGENCE IN THE REFINEMENT (EV. USE PROGRAM PIRUM OR PURUM)
END OF CALCULATIONS
USED CPU-TIME=      0. SEC.
```

Space Group Assignment

Space group assignment is carried out using systematic absences in the reflection data.

Intensity Extraction

Intensity extraction is usually carried using either the method of Pawley or Le-Bail.

Both methods use a Rietveld-like approach in that they fit the whole pattern, but with no structural model.

These methods rely on accurate high resolution data since peak overlap needs to be minimised.

The result is a set of quasi-single crystal data which can be analysed using standard single crystal packages.

Determination of Initial Model

Three methods are now commonly used.

(1) Patterson vector density methods

(2) Direct methods

(3) Probabilistic methods

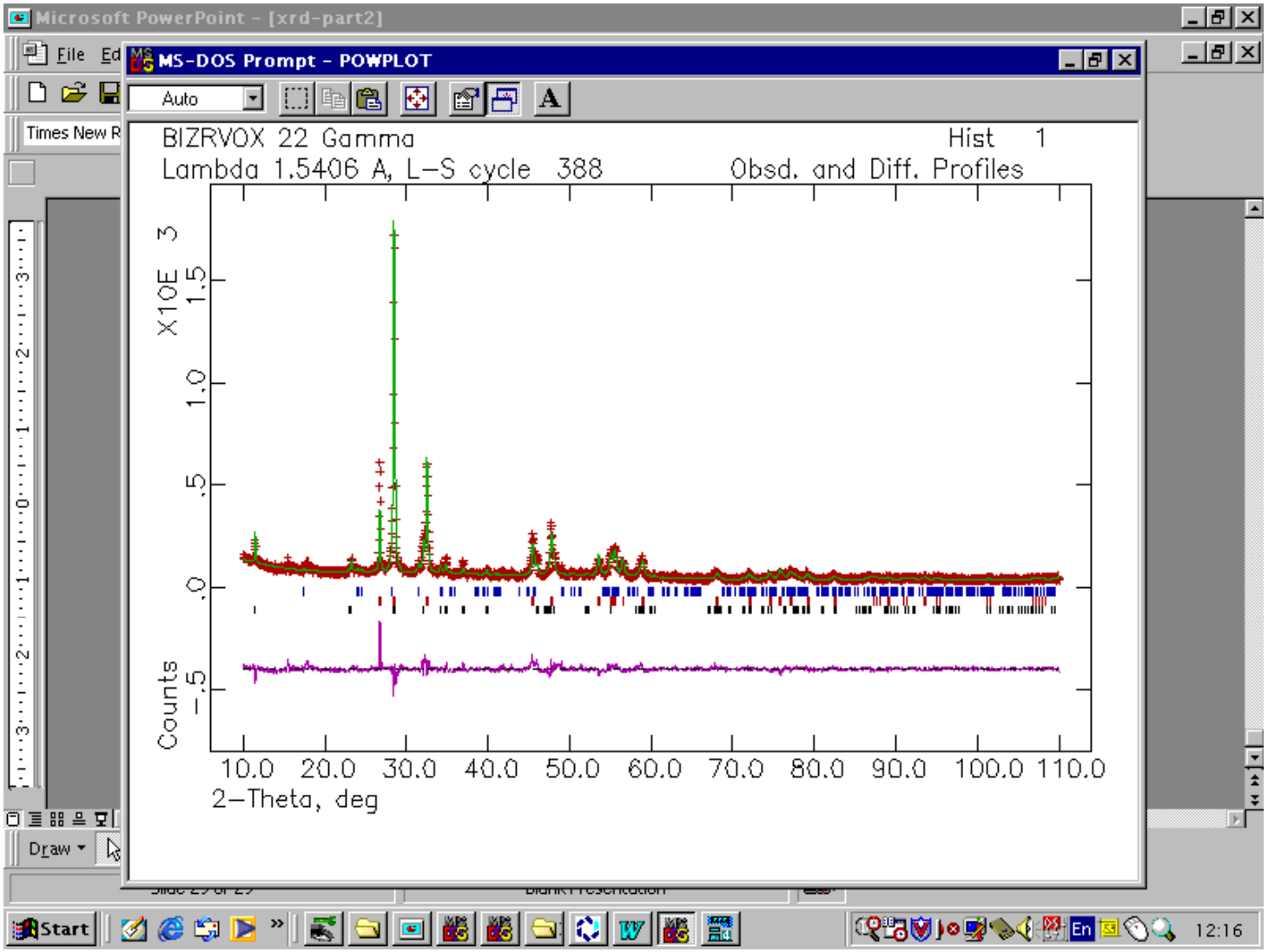
The first two are identical to the single crystal methods already discussed.

Quantitative Analysis

For mixtures of phases X-ray powder diffraction can be used to quantify the different fractions present. In some cases it may be the only method possible for example a mixture of different phases of silica.

There are a number of well established methods. However, the Rietveld method offers a quick and accurate way to determine phase fractions through multi-phase refinement.

Accuracy is a problem. Typically percentage weights have $\pm$ 5% error.


Microsoft PowerPoint - [xrd-part2]
MS-DOS Prompt - POWPLOT
Auto
BIZRVOX 22 Gamma
Hist 1
Lambda 1.5406 A, L-S cycle 388
Obsd. and Diff. Profiles
X10E 3
1.5
1.0
.5
.0
-.5
Counts
10.0 20.0 30.0 40.0 50.0 60.0 70.0 80.0 90.0 100.0 110.0
2-Theta, deg
Draw
Start
12:16

Final refinement x = 0.30

Phase 1 γ-$Bi_2Zr_{0.25}V_{0.75}O_{5.375}$, Fw = 564.97
Phase 2 $Bi_8V_2O_{17}$, Fw = 2045.71
Phase 3 ZrO_2, Fw = 123.22

Rwp = 0.1229, Rp = 0.0940, Rex = 0.1117, χ^2= 1.219, nvar = 30

Phase 1

a	b	c	alpha	beta	gamma	volume
3.94477	3.94477	15.44026	90.000	90.000	90.000	240.269
.00031	.00031	.00214	.000	.000	.000	.057

Phase 2

a	b	c	alpha	beta	gamma	volume
3.80731	3.80731	10.00677	90.000	90.000	120.000	125.621
.00029	.00029	.00092	.000	.000	.000	.022

Phase 3

a	b	c	alpha	beta	gamma	volume
5.14166	5.21076	5.31369	90.000	99.225	90.000	140.523
.00390	.00463	.00426	.000	.042	.000	.100

Phase/element fractions for phase no. 1
Wt. Frac.: .39231
Sigmas : .276381E-02

Phase/element fractions for phase no. 2
Wt. Frac.: .48831
Sigmas : .273864E-02

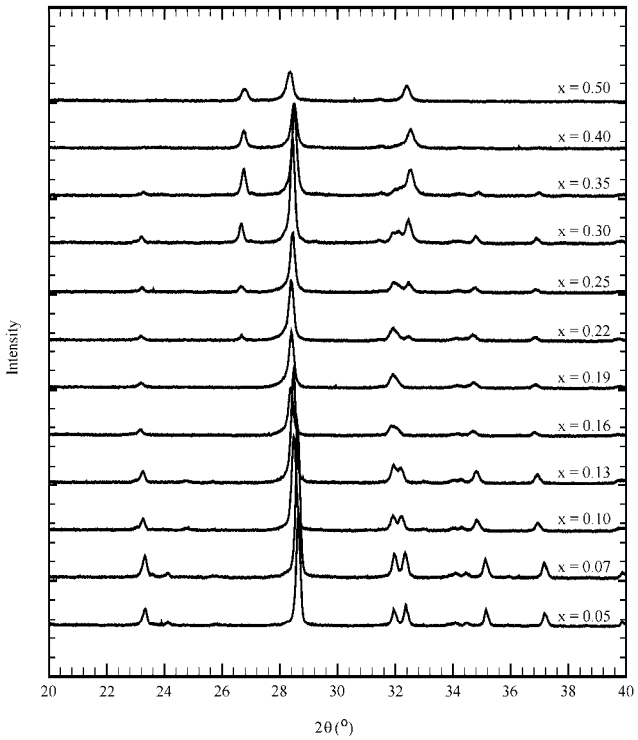
Phase/element fractions for phase no. 3
Wt. Frac.: .11938
Sigmas : .571275E-02

Mol %
Phase 1 36.5%
Phase 2 12.6%
Phase 3 50.9%

Phase Transition Studies

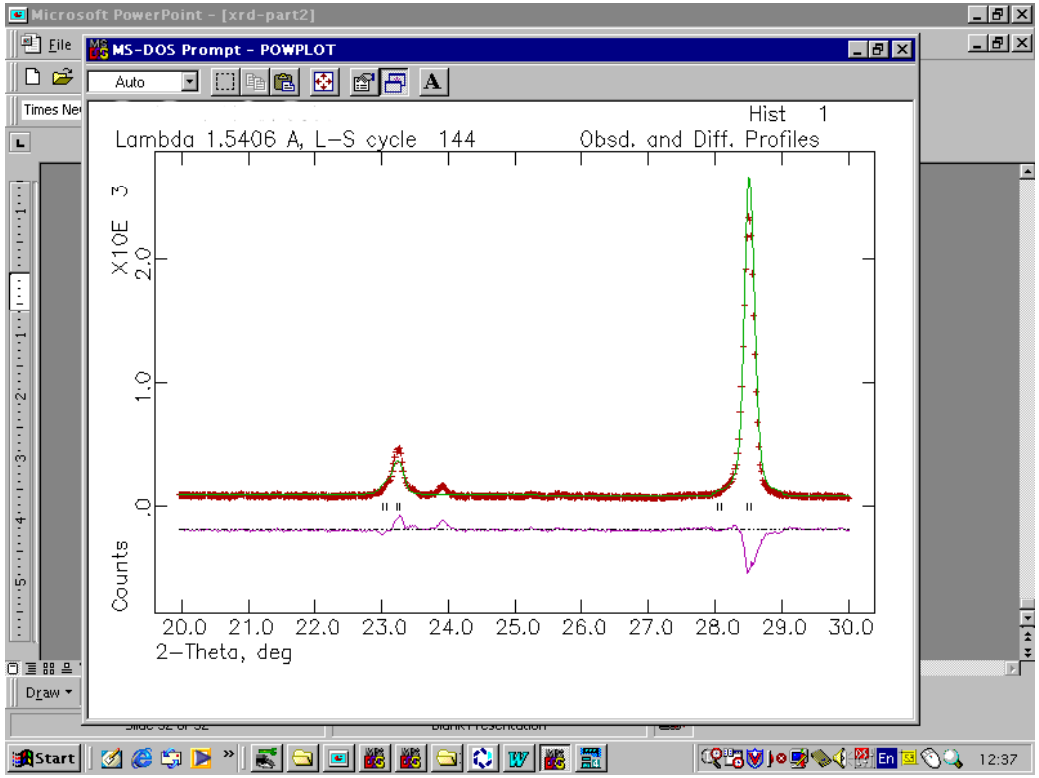
X-ray powder diffraction is ideally suited for examining crystallographic phase transitions

Both compositional and temperature dependence can be examined.



Superlattices

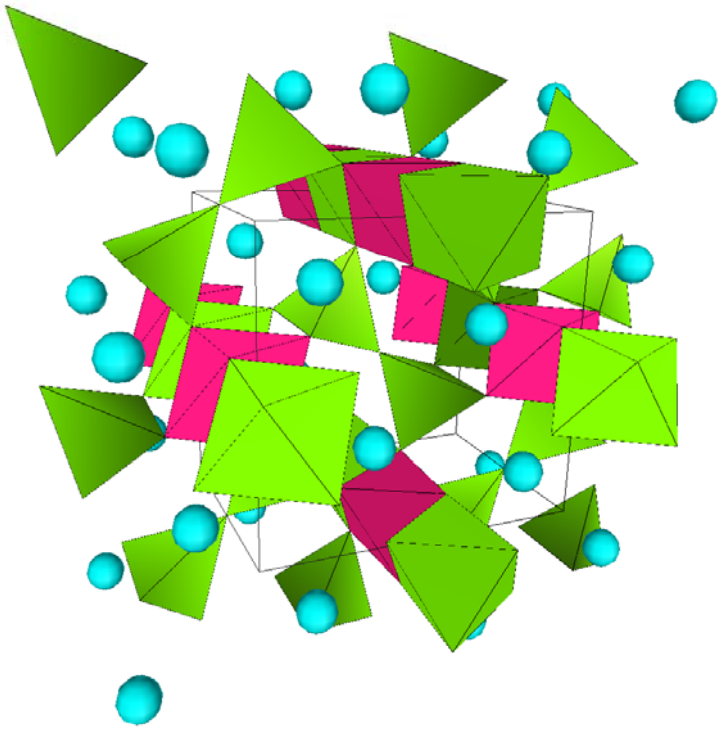
X-ray powder diffraction is superior to Single crystal diffraction in identifying superlattice reflections.



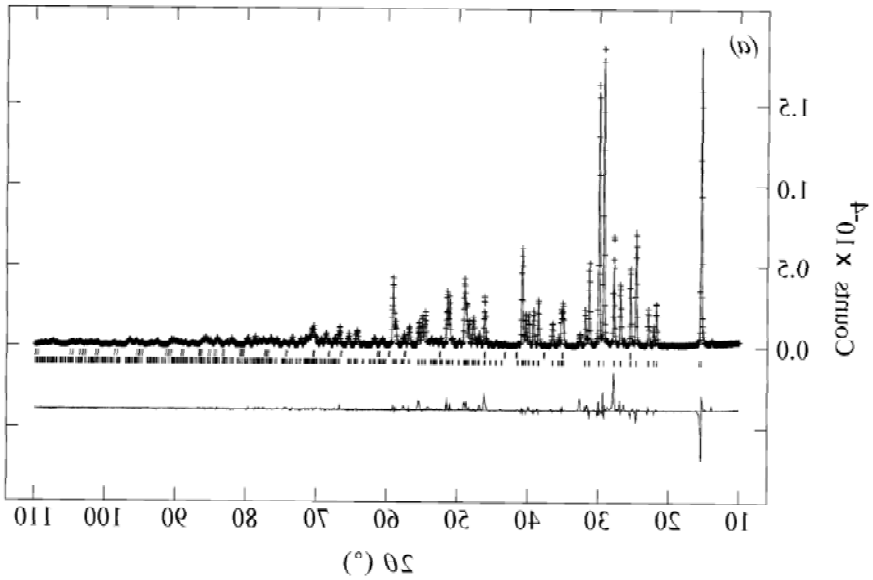
Joint X-ray and Neutron Refinements

Joint refinements combine the advantages of neutron and X-ray refinements. Neutron refinements are particularly useful for accurate refinement of light atoms, while X-ray refinements give better parameters on the heavy atoms.

e.g. $Bi_4Al_2O_9$



Fitted X-ray data



Fitted neutron data