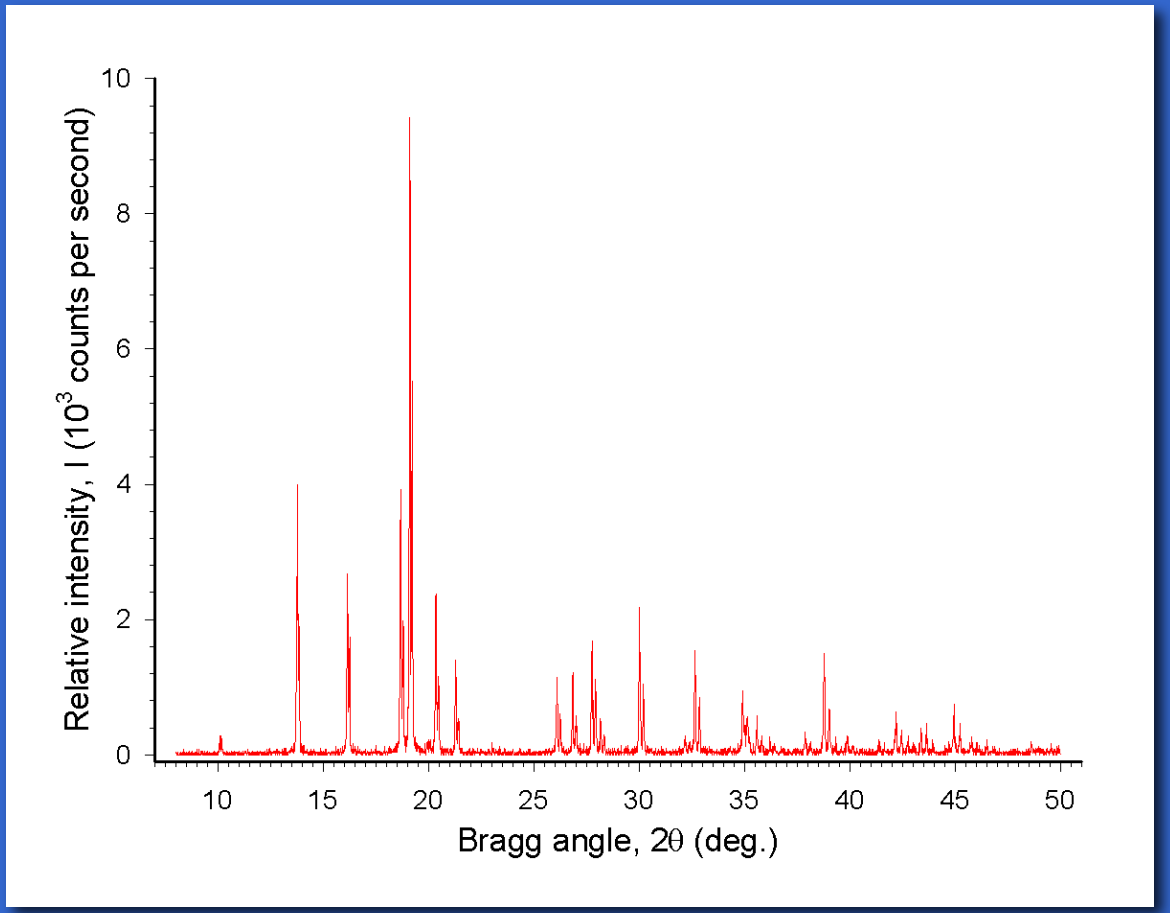
What do X-ray powder diffraction patterns look like?



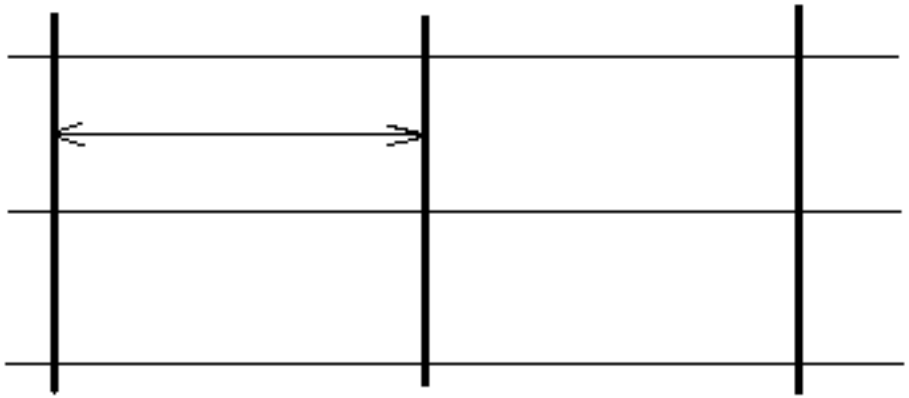
What do X-ray powder diffraction patterns look like?

$$\lambda = 2d_{hkl}\sin\theta_{hkl}$$

So what does x-ray diffraction pattern look like?

Ideally, λ is fixed at a single value
Measure positions of reflections as θ is changed

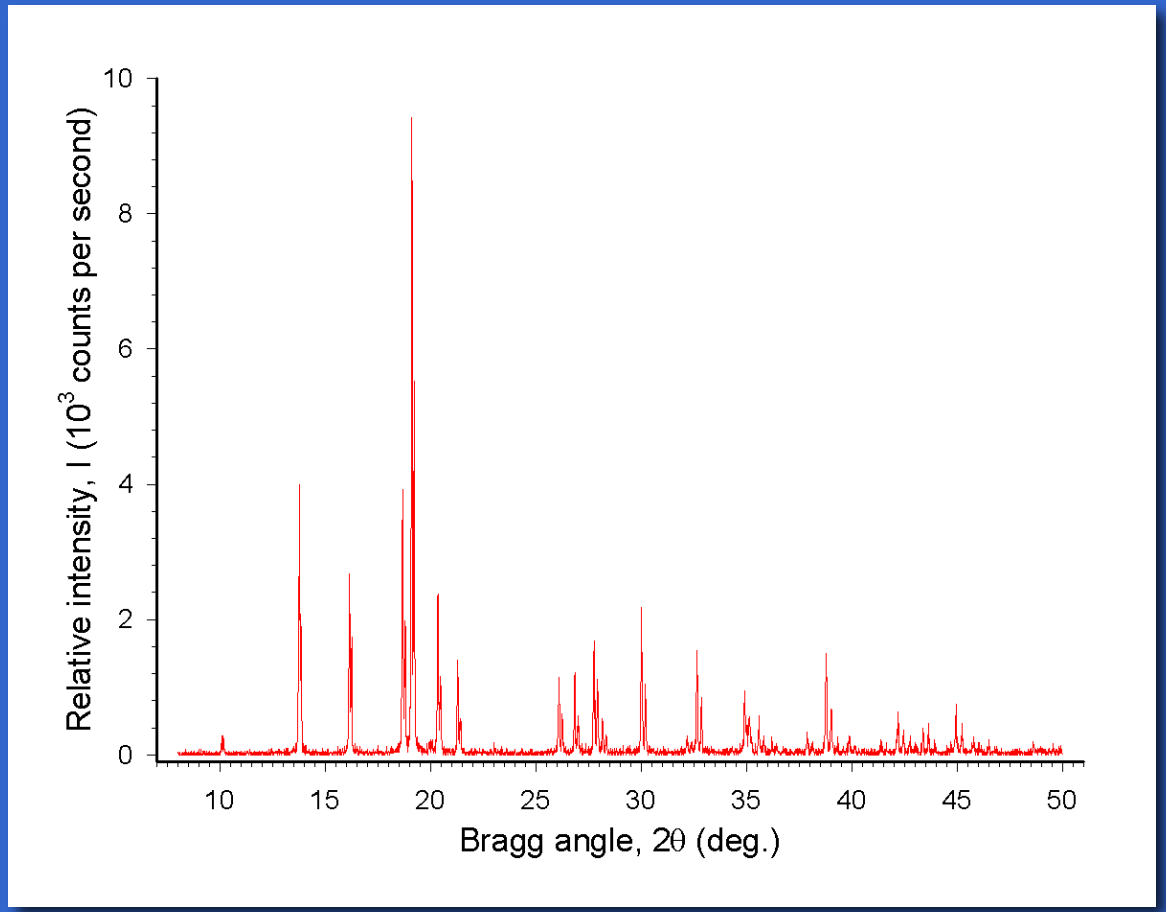
What values of d_{hkl} are possible?



What do X-ray powder diffraction patterns look like?

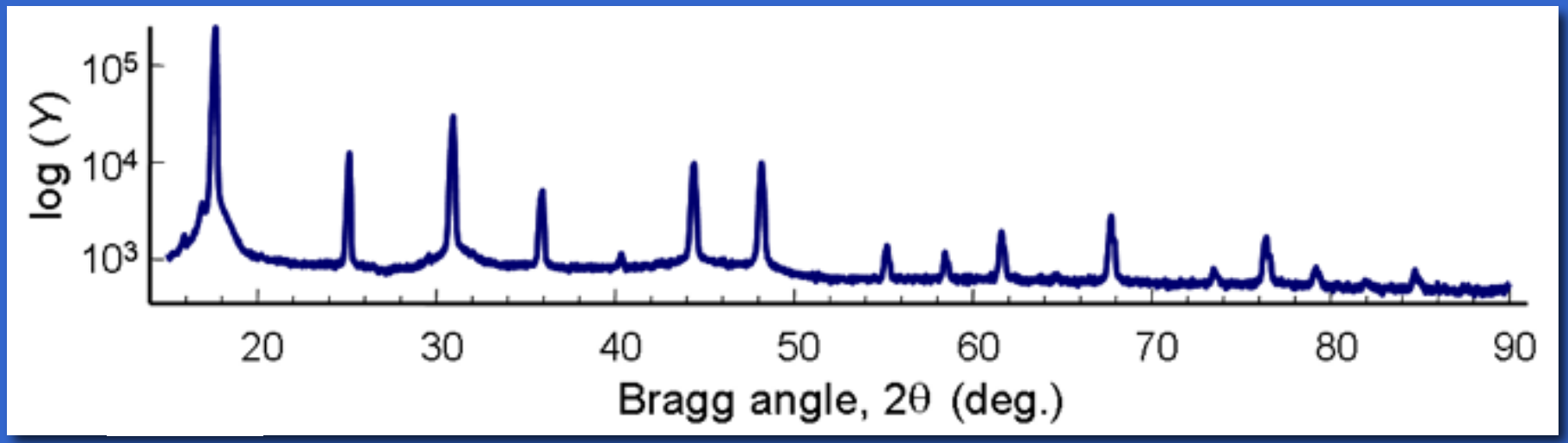
Each peak in pattern is a reflection from a different set of planes

By determining 2θ for a peak, can use Braggs' law to get d for that set of planes



Powder patterns -
what information available in pattern?

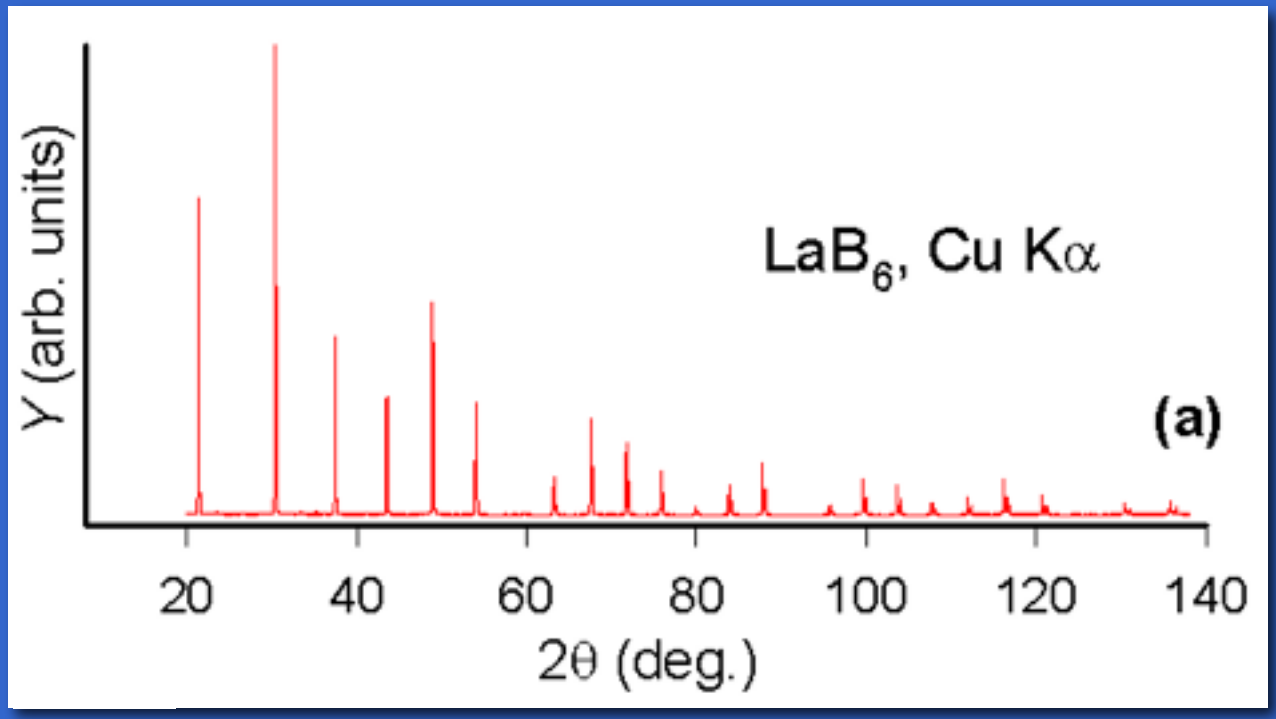
1. peak positions
2. peak intensities
3. peak shape
4. background structure



Powder patterns - what information available in pattern?

1. peak positions - give unit cell shape, size, and symmetry

Simple example - P cubic:



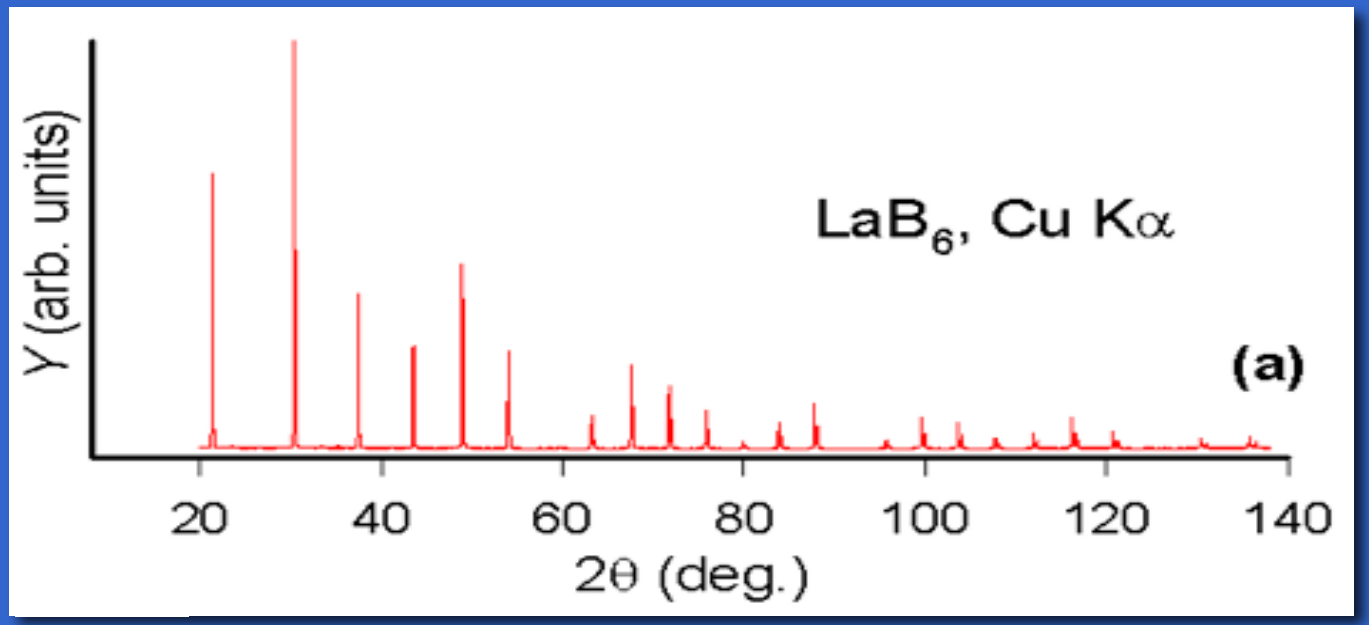
Naming each peak with Miller indices is called " indexing the pattern"

Indexing

Message: indexing cubic patterns is usually pretty easy
especially, if done visually

Why:

usually, relatively few reflections
reflections evenly spaced
only one lattice parameter to guess



Indexing

In cubic:

$$d_{hkl} = a/(h^2 + k^2 + l^2)^{1/2} = a/s^{1/2}$$

$$a = s^{1/2}\, d_{hkl}$$

s is an integer …… 1, 2, 3, 4….

Since $\lambda = 2d_{hkl} \sin \theta_{hkl}$, smallest θ means largest d_{hkl}

Since $a = s^{1/2}\, d_{hkl}$, largest d_{hkl} means smallest s value

Thus, lowest 2θ reflections in pattern are those with small s values

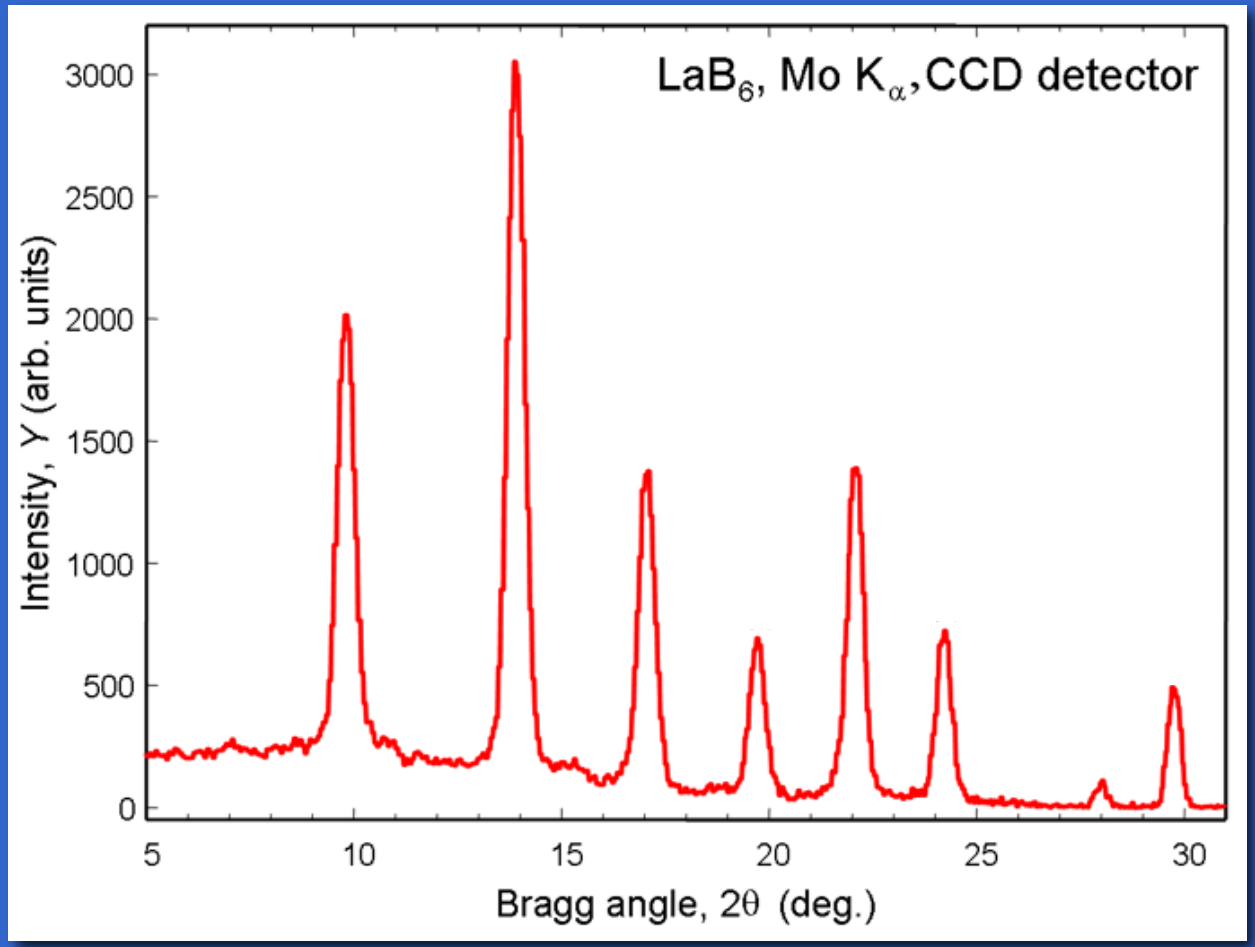
Indexing

Fill in the (hkl)s for these s values

$h^2 + k^2 + l^2$	P
1	(100)
2	
3	
4	
5	
6	
7	
8	
9	
10	
11	
12	

Indexing

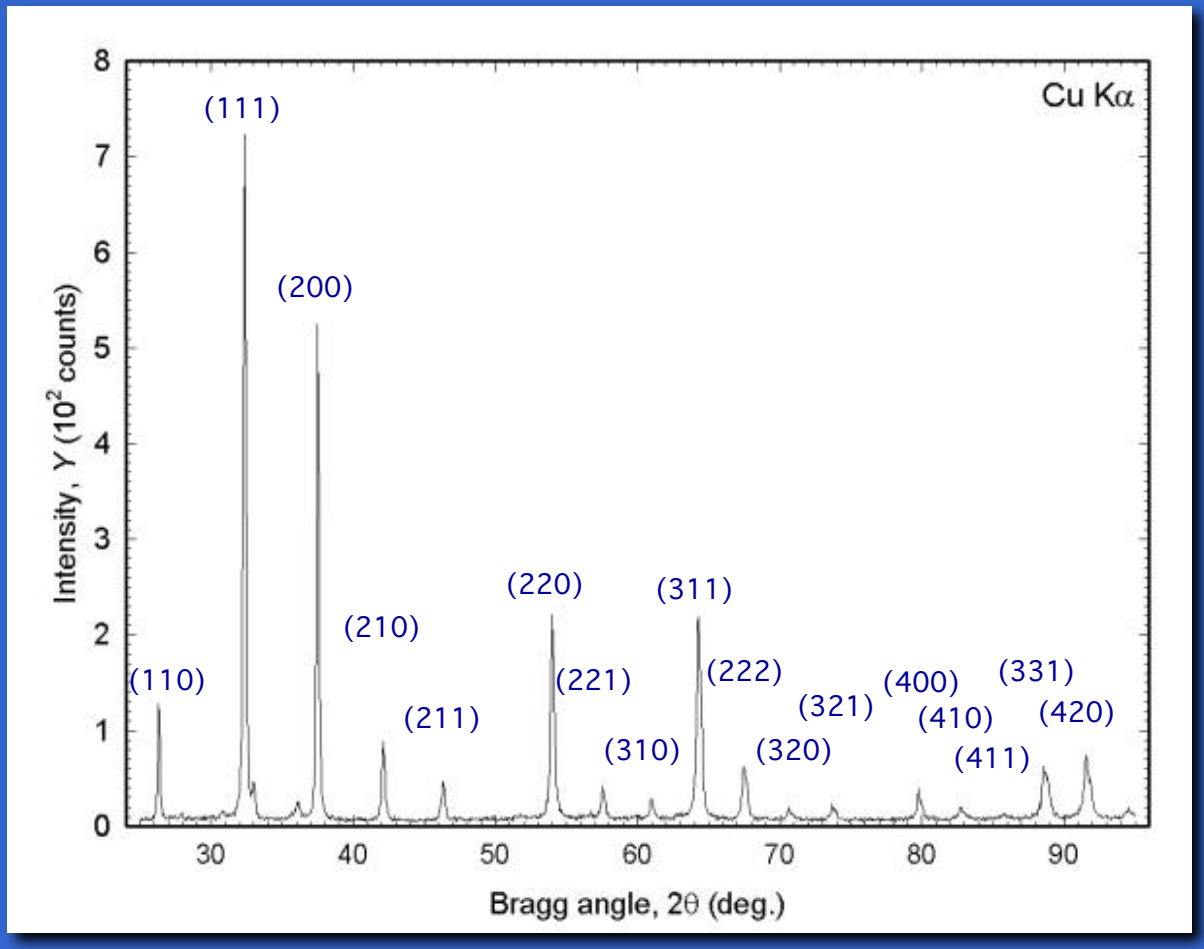
	Index
1	(100)
2	(110)
3	(111)
4	(200)
5	(210)
6	(211)
7	
8	(220)
9	(300)
10	(310)
11	(311)
12	(222)



Indexing

1	(100)
2	(110)
3	(111)
4	(200)
5	(210)
6	(211)
7	
8	(220)
9	(300)
10	(310)
11	(311)
12	(222)

Index



Indexing

Slight complication: 3 different Bravais lattices in cubic

P cubic	All planes, reflections possible
I cubic	(hkl) present only if h + k + l = even
F cubic	(hkl) present only if h,k,l all even or all odd

Translational symmetry gives missing planes -
thus missing reflections

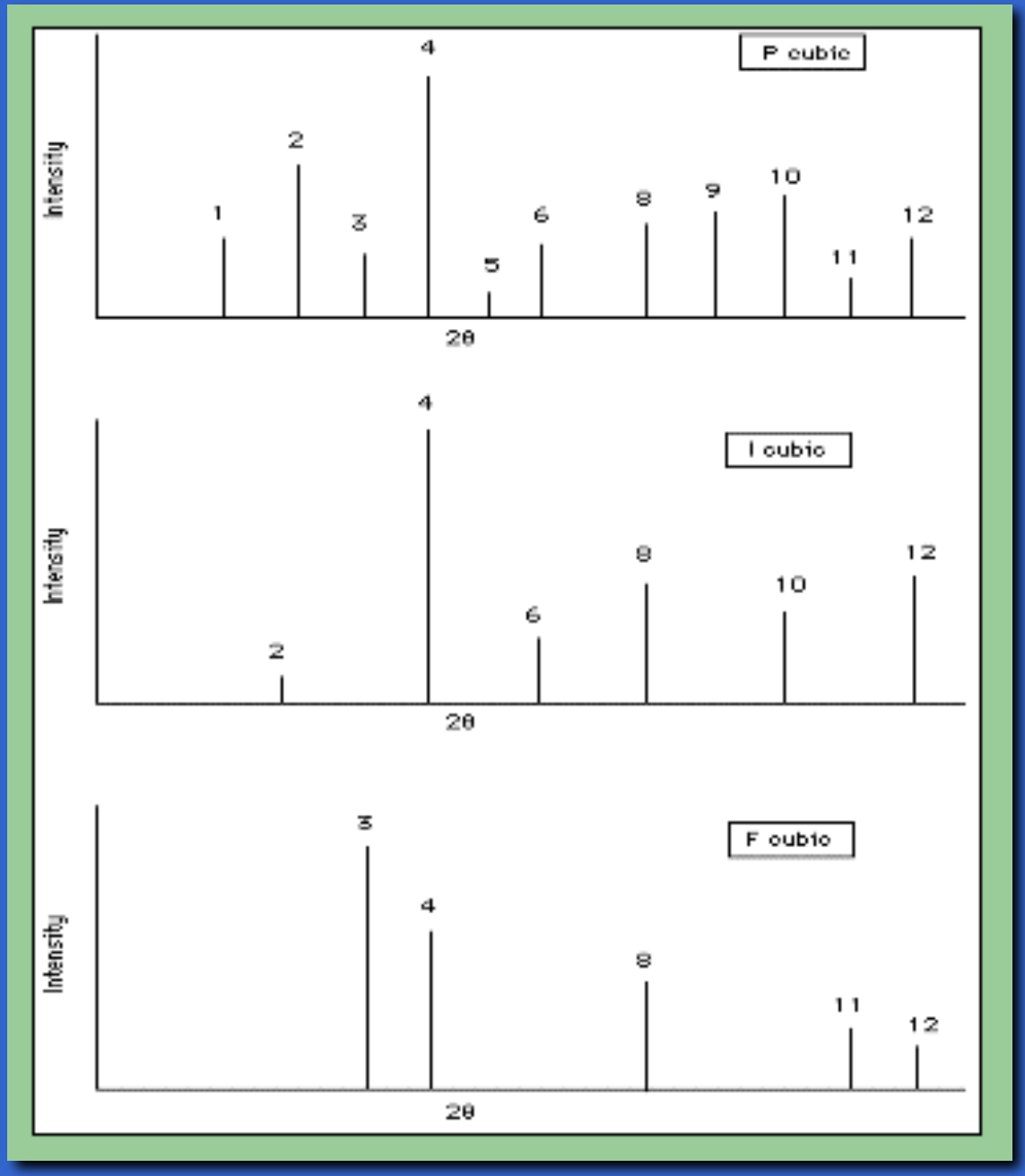
These are "extinction rules"

Indexing

Fill in the (hkl)s for these I cubic (h + k + l = even) & F cubic (h,k,l all even or all odd)

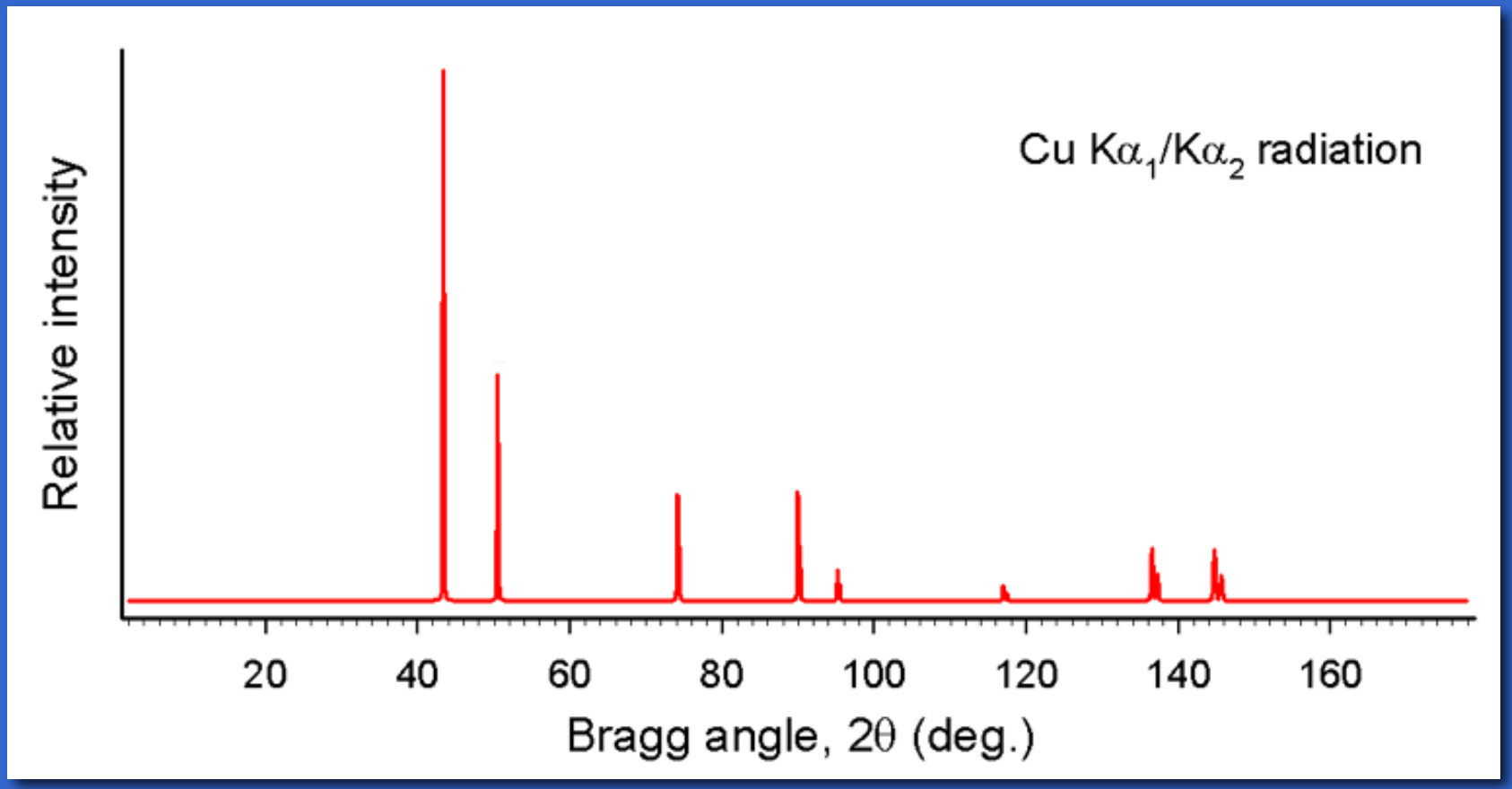
$h^2 + k^2 + l^2$	P	I	F
1	(100)		
2	(110)		
3	(111)		
4	(200)		
5	(210)		
6	(211)		
7			
8	(220)		
9	(300)		
10	(310)		
11	(311)		
12	(222)		

Indexing


P cubic
Intensity
1
2
3
4
5
6
8
9
10
11
12
2θ
I cubic
Intensity
2
4
6
8
10
12
2θ
F cubic
Intensity
3
4
8
11
12
2θ

Indexing

Index



Indexing

How to know indexing is correct?

Correct indices give consistent set of lattice parameters

Example for cubic:

d(Å)	(hkl)	a(Å)	(hkl)	a(Å)
3.157			(111)	5.468
1.931			(220)	5.462
1.647			(311)	5.462
1.366			(400)	5.464

Indexing

Other types of translational symmetry also give missing planes

glide planes and screw axes

Ex: F $4_1/d$ $\bar{3}$ 2/m

(0kl) present if k + l = 4n

(hhl) present if h + l = even

(hkl) if h + k + l = odd or 4n
(for some structures w/ this space group)

Indexing

What if it's not cubic?

Manual indexing methods usually very tedious - use computer indexing programs such as "Ito", "Treor", "Crysfire", "Dicvol", others

Computer indexing frequently not easy - sometimes have to use several, or all, indexing programs to figure out right answer

Why index?

It can be fun! Like solving a puzzle

Indices needed to calculate lattice parameters
need (hkl) and d_{hkl} for all reflections

use all reflections to get high precision

cubic: $d_{hkl}^2 = a^2/(h^2 + k^2 + l^2)$

tetragonal: $1/d_{hkl}^2 = (h^2 + k^2)/a^2 + l^2/c^2$

hexagonal: $1/d_{hkl}^2 = (4/3)(h^2 + k^2 + hk)/a^2 + l^2/c^2$

orthorhombic: $1/d_{hkl}^2 = h^2/a^2 + k^2/b^2 + l^2/c^2$

etcetera

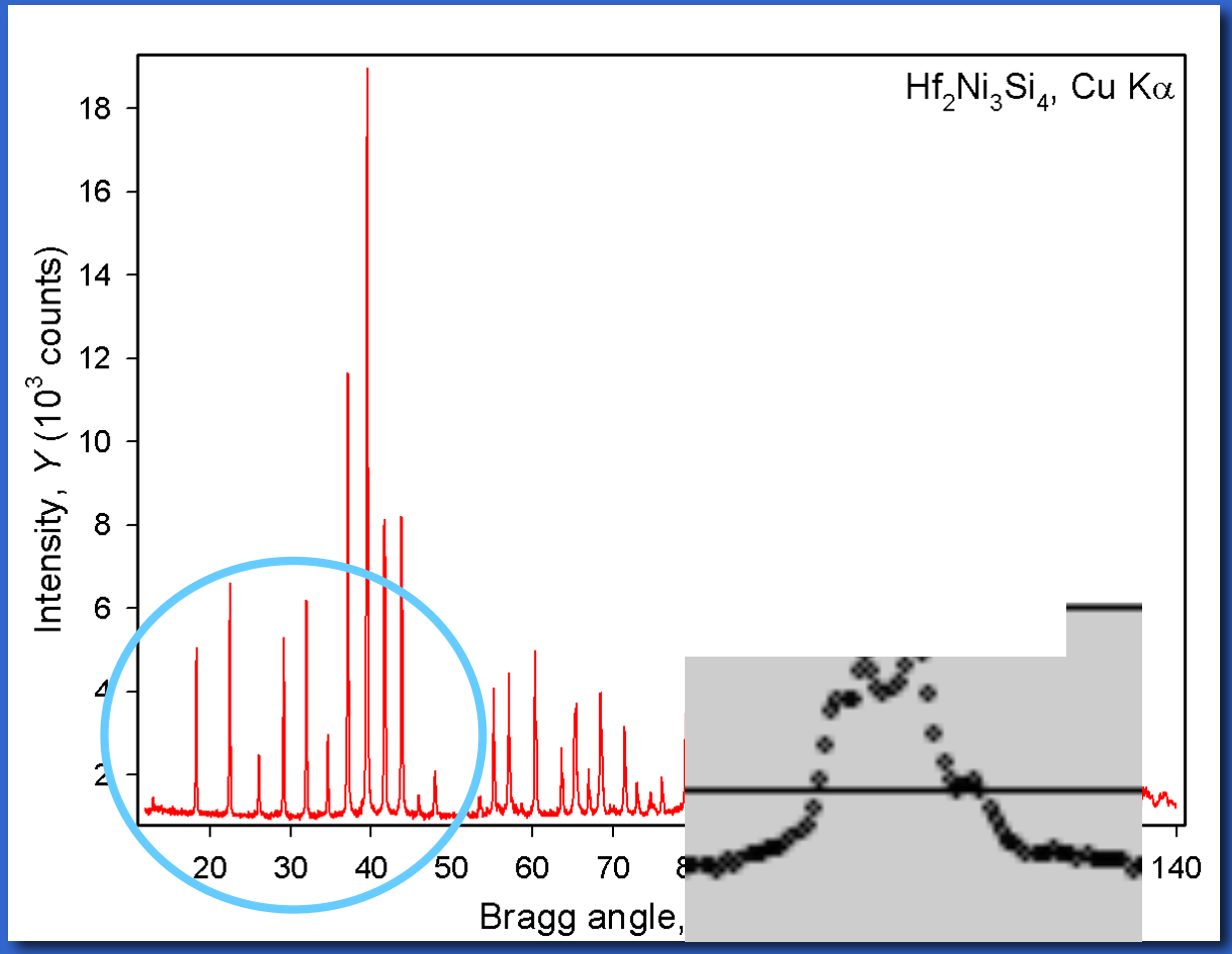
Indexing

ATCF!!!

But……小心

Looks cubic

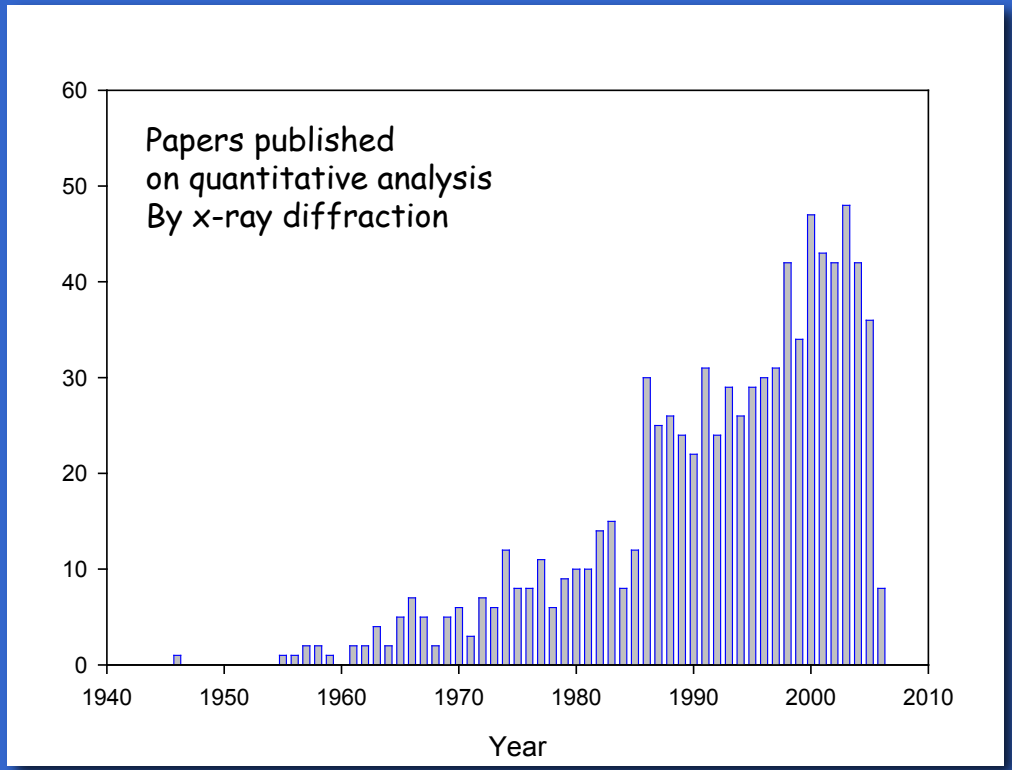
But it is not!
(C orthorhombic)



Powder patterns - what information available in pattern?

1. peak positions
2. peak intensities - how much?
3. peak shape
4. background structure

Relatively recent increase in use of X-ray diffraction for quantitative analysis



Powder patterns - what information available in pattern?

1. peak positions
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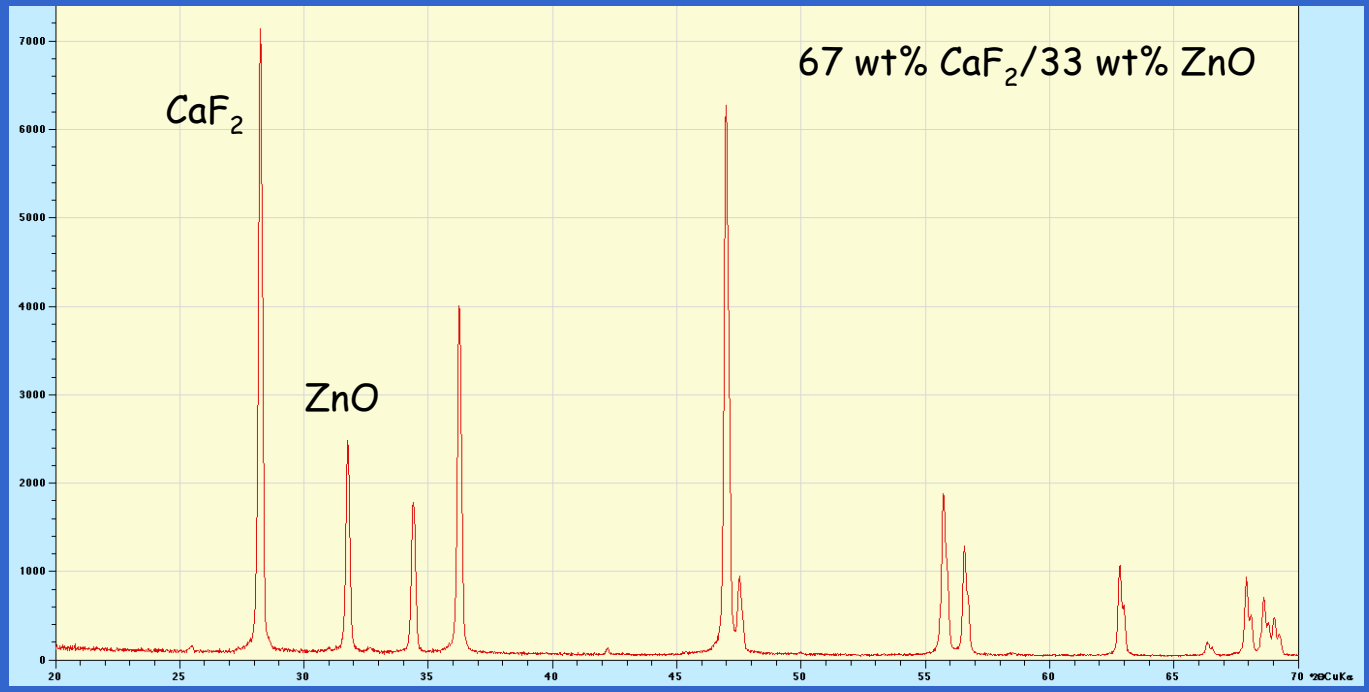
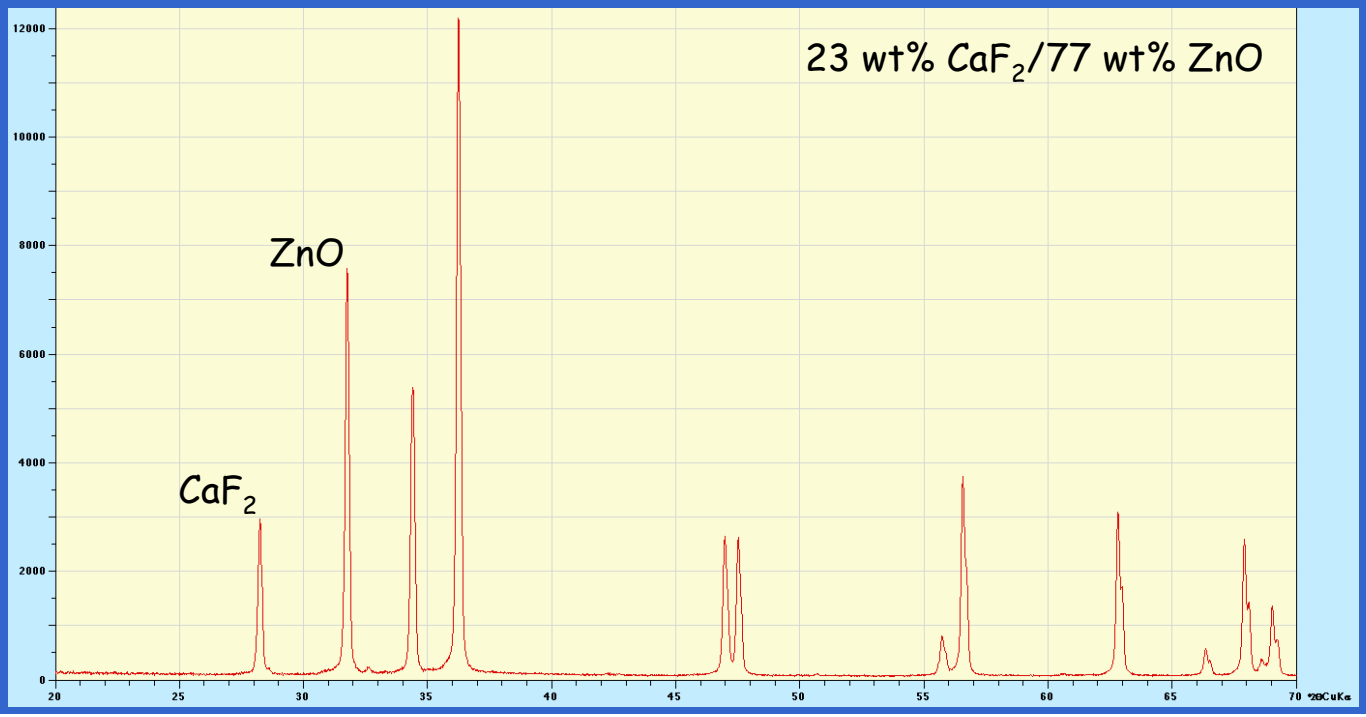
Quantitative analysis

Example: 2-phase mixtures of CaF_2 & ZnO


67 wt% CaF_2/33 wt% ZnO
CaF_2
ZnO
7000
6000
5000
4000
3000
2000
1000
0
20
25
30
35
40
45
50
55
60
65
70
°2θCuKα


23 wt% CaF_2/77 wt% ZnO
ZnO
CaF_2
12000
10000
8000
6000
4000
2000
0
20
25
30
35
40
45
50
55
60
65
70
°2θCuKα

Quantitative Analysis

Use measured intensities ….. but not simple

Main equation for quantitative analysis

$$I_{ia} = \frac{K_{ia} X_a}{\rho_a \mu}$$

Quantitative Analysis

Use measured intensities ….. but not simple

Main equation for quantitative analysis

I_{ia} = intensity of reflection i of phase a

$$I_{ia} = \frac{K_{ia} X_a}{\rho_a \mu}$$

Quantitative Analysis

Use measured intensities ….. but not simple

Main equation for quantitative analysis

$$I_{ia} = \frac{K_{ia} X_a}{\rho_a \mu}$$

ρ_a is density of phase a

Quantitative Analysis

Use measured intensities ….. but not simple

Main equation for quantitative analysis

$$I_{ia} = \frac{K_{ia} X_a}{\rho_a \mu}$$

K_{ia} contains structure factor, multiplicity, Lorentz-polarization factor, temperature factor + scale factor for reflection i of phase a

Quantitative Analysis

Use measured intensities ….. but not simple

Main equation for quantitative analysis

$$I_{ia} = \frac{K_{ia} X_a}{\rho_a \mu}$$

X_a = wt fraction of phase a (want this!!)

Quantitative Analysis

Use measured intensities ….. but not simple

Main equation for quantitative analysis

measure this!!

$$I_{ia} = \frac{K_{ia} X_a}{\rho_a \mu}$$

X_a = wt fraction of phase a (want this!!)

But what do we do with μ?

Quantitative Analysis

Use measured intensities ….. but not simple

Main equation for quantitative analysis

Measure this!!

$$I_{ia} = \frac{K_{ia} X_a}{\rho_a \mu}$$

X_a = wt fraction of phase a (Want this!!)

But what do we do with μ?

μ is mass attenuation coefficient for mixture …. unknown, unless we know

Quantitative Analysis

Use measured intensities ….. but not simple

$$I_{ia} = \frac{K_{ia} X_a}{\rho_a \mu}$$

If sample contains > one phase, then μ unknown if wt fractions unknown

$$\mu_{mix} = X_1\mu_{phase\ 1} + X_2\mu_{phase\ 2} + X_3\mu_{phase\ 3} + \text{.....}$$

μ for each phase may be calculated from the chemical composition of each phase

$$\mu_{compd} = X_1\mu_1 + X_2\mu_2 + X_3\mu_3 + \text{.....}$$

Quantitative Analysis

Use measured intensities ….. but not simple

Main equation for quantitative analysis

$$I_{ia} = \frac{K_{ia} X_a}{\rho_a \mu}$$

would also be nice not to calc K_{ia} or get ρ_a

Quantitative Analysis

Use measured intensities ….. but not simple

Simple example: rutile/anatase polymorphs
since polymorphs have same composition:

$$\mu_{mix} = \mu_{rutile} = \mu_{anatase}$$

Suppose we measure $I^{\circ}_{irutile}$ of pure rutile
can eliminate μ_{mix} (& other stuff)

$$\frac{I_{irutile} = \dfrac{K_{irutile} X_{rutile}}{\rho_{rutile} \mu}}{I^{\circ}_{irutile} = \dfrac{K_{irutile}}{\rho_{rutile} \mu_{rutile}}} = X_{rutile}$$

Quantitative Analysis

Use measured intensities ….. but not simple

$$I_{ia} = \frac{K_{ia} X_a}{\rho_a \mu}$$

For mixtures that are not polymorphs, many single & multiple peak procedures have been developed that use known amounts of

internal standards - mixed with unknown

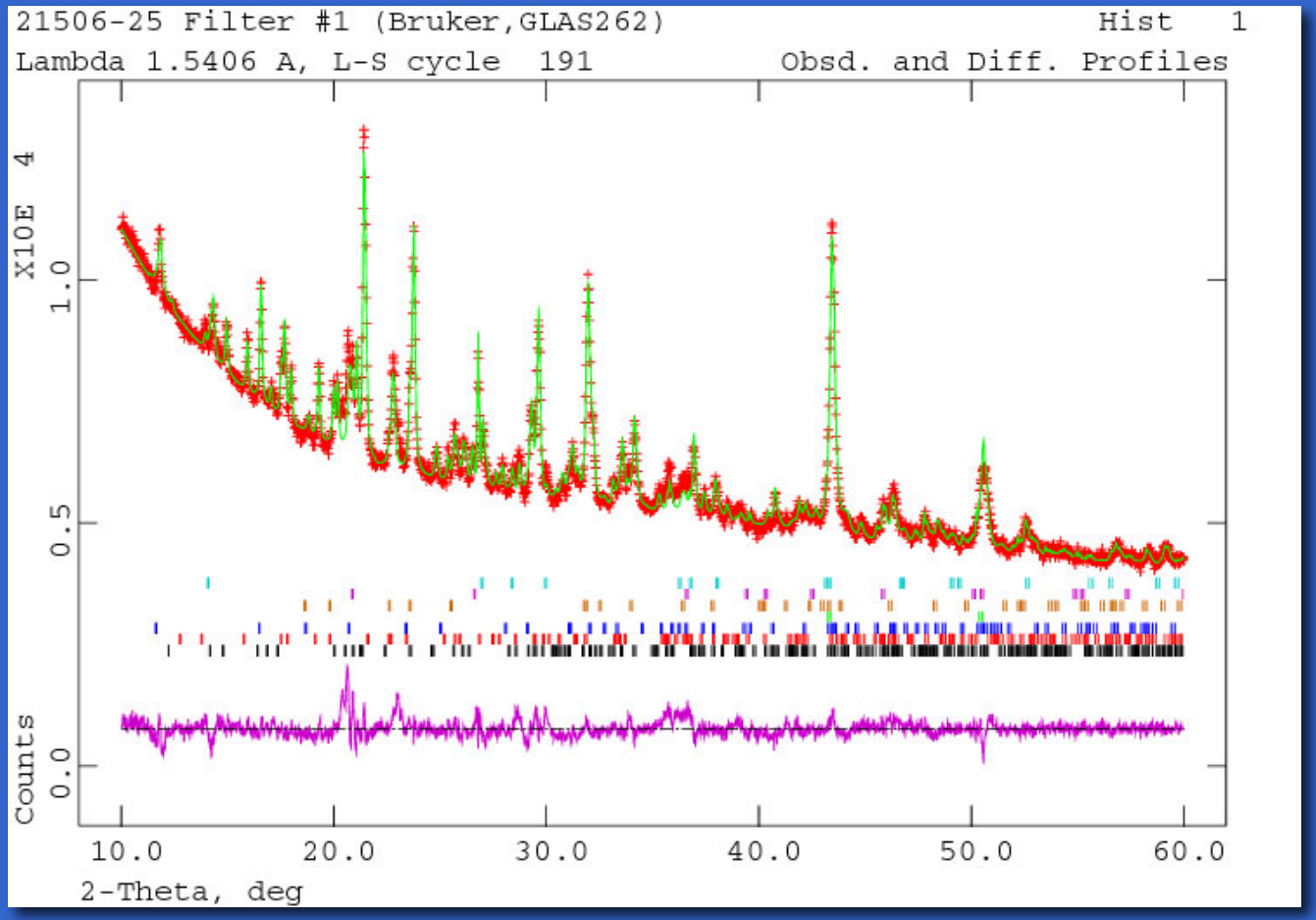
external standards - run separate x-ray pattern of standard material

Most analysis techniques tell only what elements are present & how much. X-ray diffraction tells how much of what PHASES are present

Quantitative Analysis

Recently, whole pattern analysis methods for quantitative analysis have become popular. Example: Rietveld analysis

Rietveld analysis of fuel deposit



Quantitative Analysis

Rietveld analysis of fuel deposit

mohrite, $(NH_4)_2Cu(SO_4)_2(H_2O)_6$, wt%	29.2(1)
Na_2SO_4-III, wt%	21.1(2)
lecontite, $(NH_4)NaSO_4(H_2O)_2$, wt%	18.9(2)
mascagnite, $(NH_4)_2SO_4$, wt%	8.1(2)
gypsum, $CaSO_4(H_2O)_2$, wt%	6.0(1)
copper, Cu, wt%	11.9(1)
lepidocrocite, γ-FeOOH, wt%	2.3(1)
quartz, SiO_2, wt%	2.5(1)