chem 5390

Advanced X-ray Analysis

LECTURE 13

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Diffraction Theory

Diffraction Methods

3. Diffractometer (Powder) Method

What can we learn from the diffractometer experiments?

- **Phase Analysis**
- **Texture Analysis**
- **Lattice Parameters**
- **Crystallite Size**
- **Stress Analysis**
- **Strain Analysis**

Diffraction Theory

Diffractometer (Powder) Method

Phase Analysis

When X-rays interact with a crystalline substance, the x-ray diffraction pattern of a substance is like a fingerprint of the substance.

It can be used or identification of the various crystalline compounds, known as 'phases', present in solid materials and powders.

The powder diffraction method is thus ideally suited for characterization and identification of polycrystalline phases.

The main use of powder diffraction is to identify components in a sample by a search/match procedure.

Diffraction Theory

Diffractometer (Powder) Method

Phase Analysis

When thousands of crystallites are sampled, for every set of planes, there will be a small percentage of crystallites that are properly oriented to diffract

All possible diffraction peaks should be exhibited

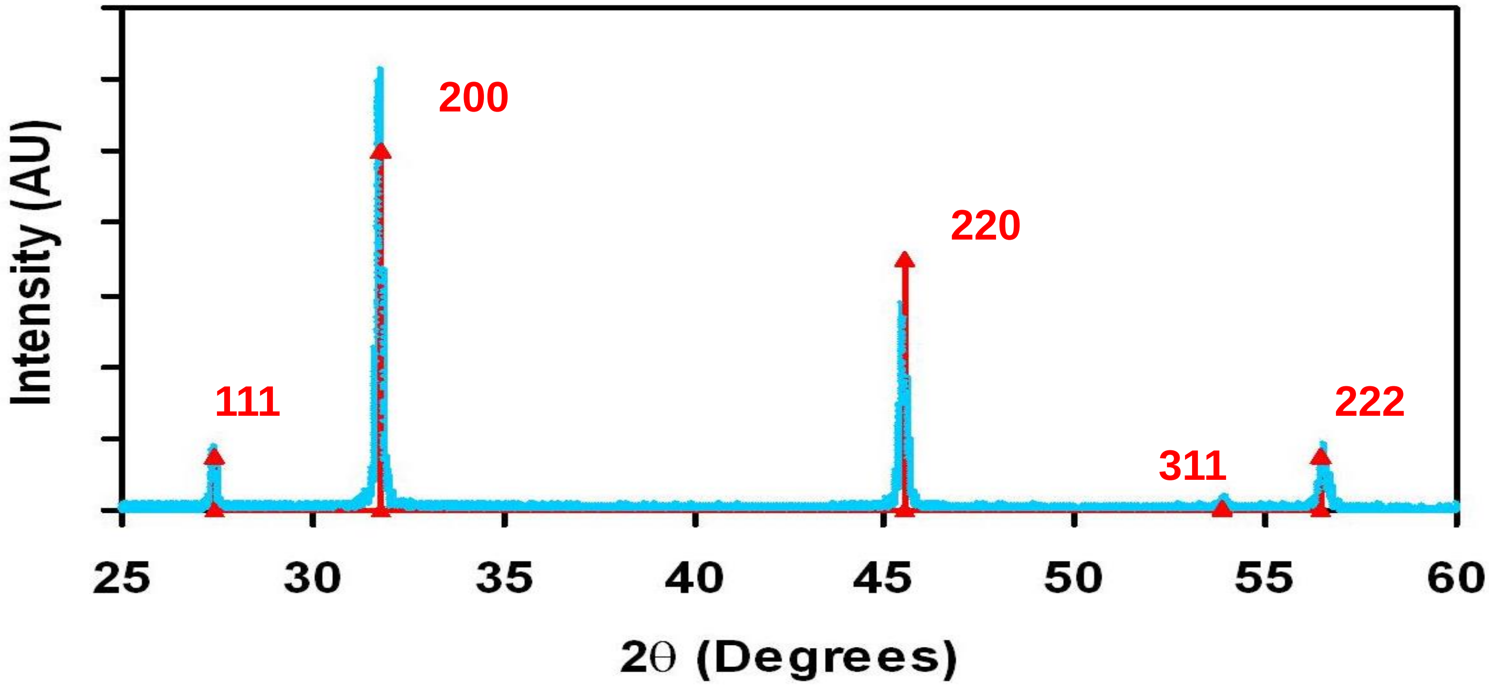
Their intensities should match the powder diffraction file.

Diffraction Theory

Diffractometer (Powder) Method

Phase Analysis

For phase identification you want a random powder (polycrystalline) sample.

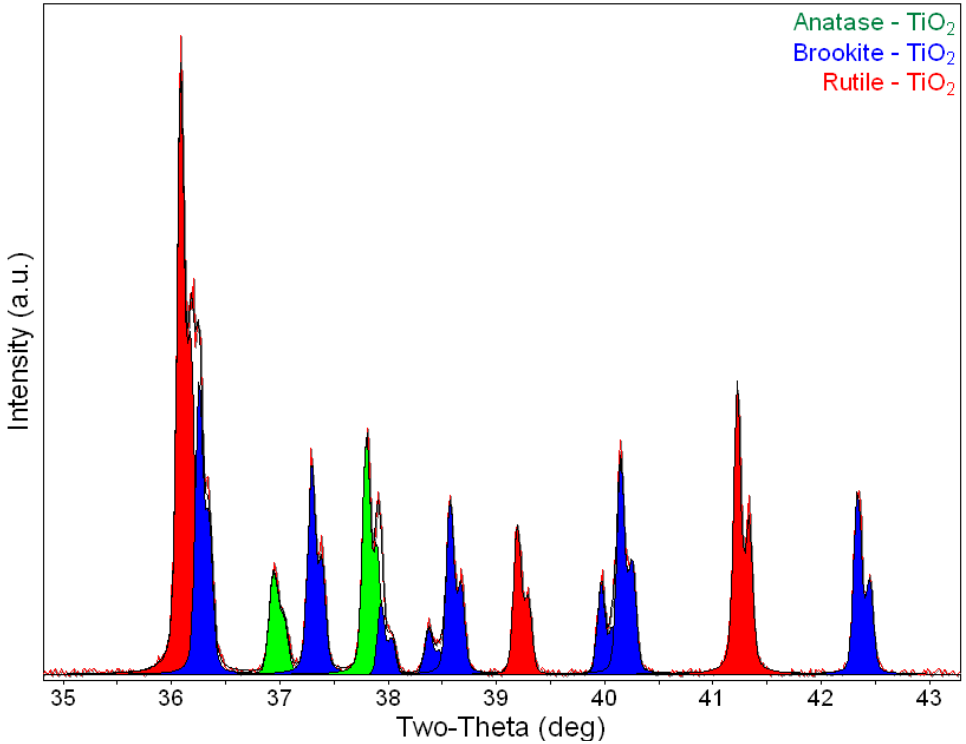


Diffraction Theory

Diffractometer (Powder) Method

Phase Analysis

Phases with the same chemical composition can have drastically different diffraction patterns.

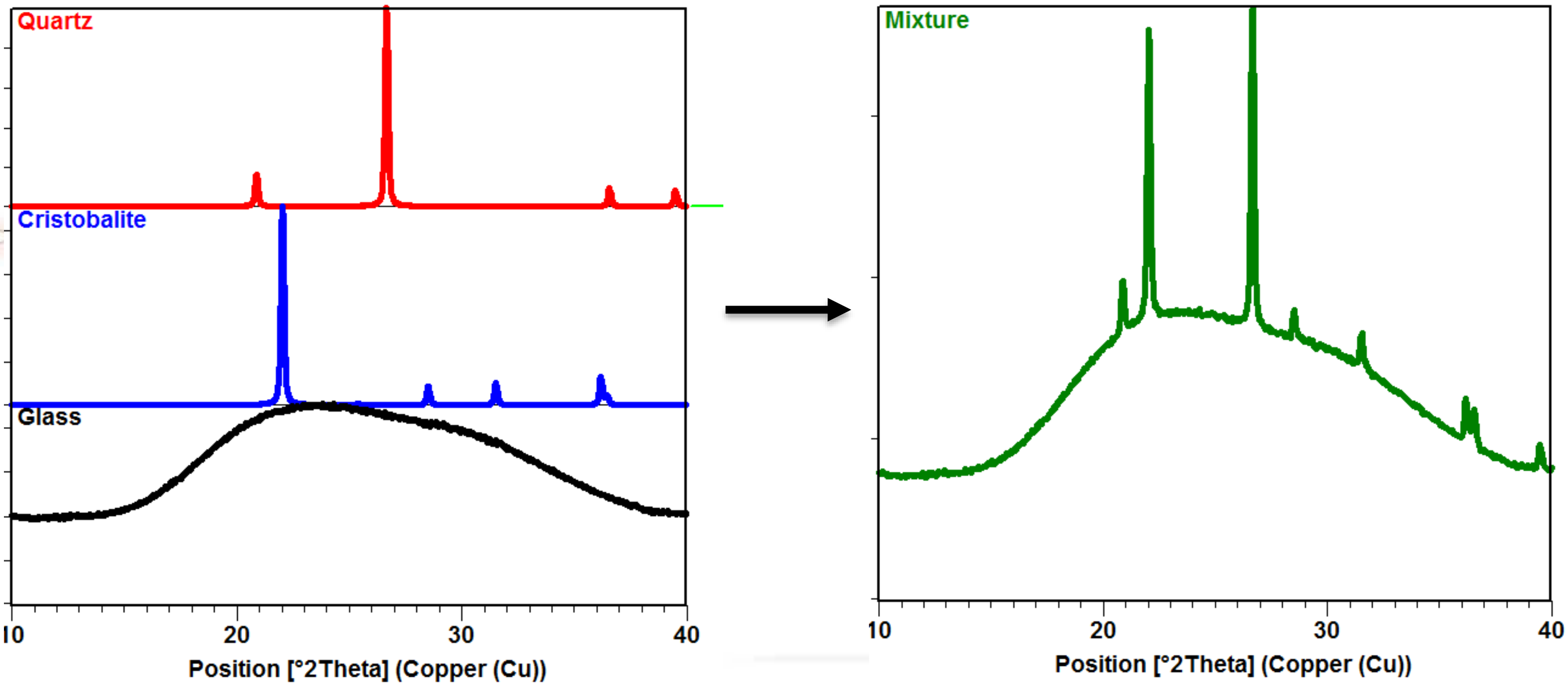


Diffraction Theory

Diffractometer (Powder) Method

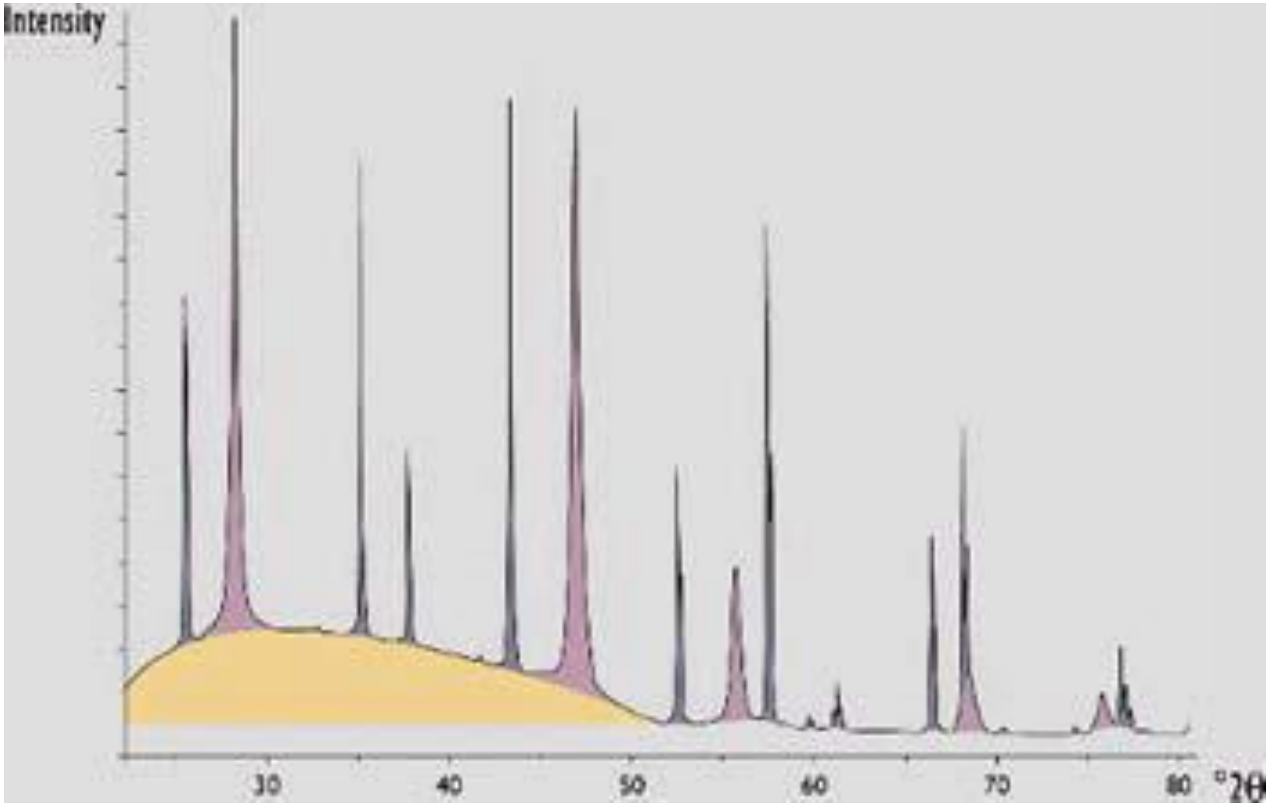
Phase Analysis

The diffraction pattern of a mixture is a simple sum of the scattering from each component phase.



Diffraction Theory

Diffractometer (Powder) Method



Diffraction Theory

Diffraction Methods

What determines the possible directions, i.e. angles or 2θ in which a crystal will diffract a beam of x-rays?

Can combine Bragg's law with the plane - spacing equation (see handout).

Diffraction Theory

Diffraction Methods

Example. For a cubic crystal:

$n\lambda = 2d\sin\theta$ **Bragg's law**

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

$$\sin^2\theta = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2)$$

Diffraction Theory

Diffraction Methods

Example. For a cubic crystal:

For the 110 plane:

$$\sin^2\theta = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2)$$

$$\sin^2\theta_{110} = \frac{\lambda^2}{4a^2}(1^2 + 1^2 + 0^2) = \frac{\lambda^2}{4a^2}(2) = \frac{\lambda^2}{2a^2}$$

Diffraction Theory

Diffraction Methods

For the 110 plane:

$$\sin^2\theta_{110} = \frac{\lambda^2}{4a^2}(1^2 + 1^2 + 0^2) = \frac{\lambda^2}{4a^2}(2) = \frac{\lambda^2}{2a^2}$$

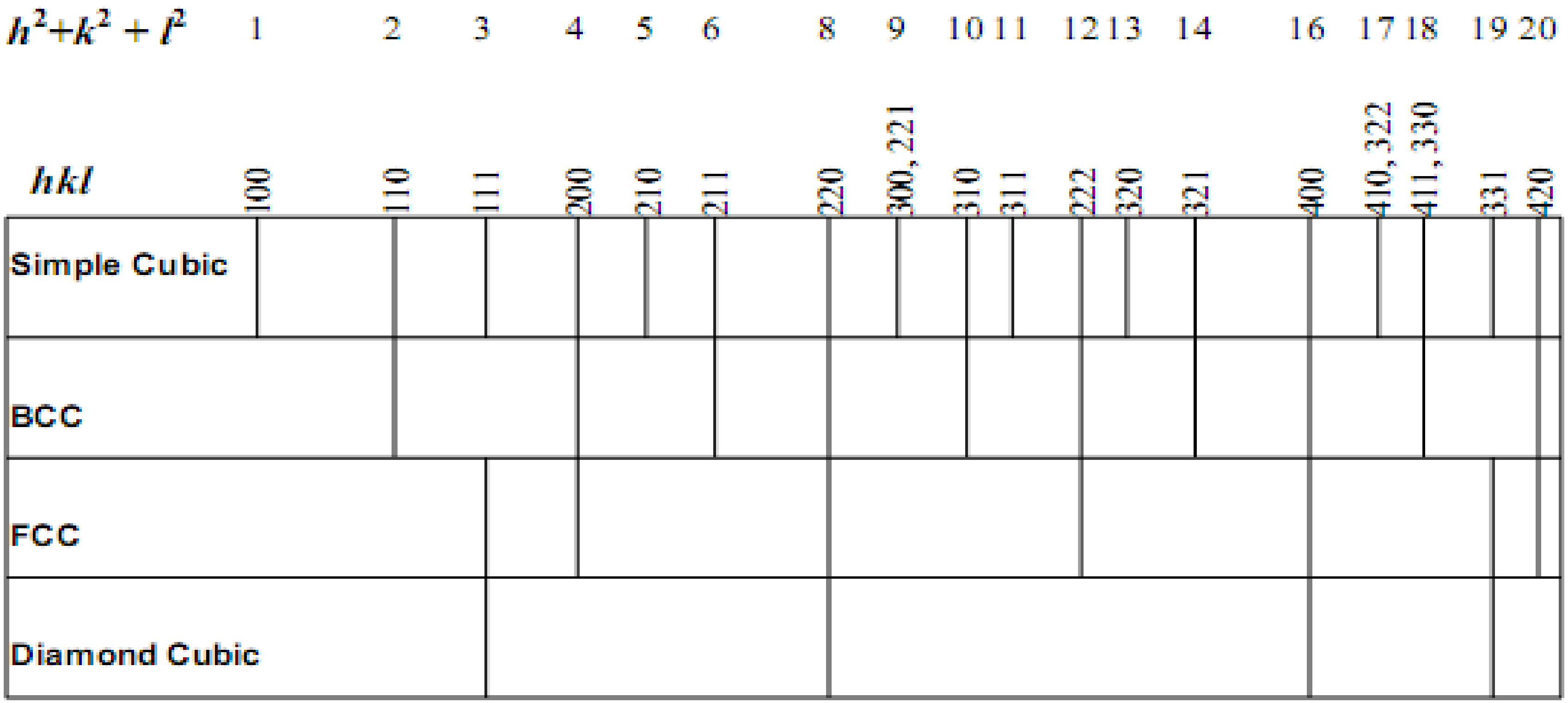
λ = 1.54056Å

$$\sin^2\theta_{110} = \frac{(0.154056nm)^2}{2a^2}$$

Diffraction Theory

Diffractometer (Powder) Method

For cubic structures it is often possible to distinguish crystal structures by considering the periodicity of the observed reflections.



Schematic comparison of XRD results from materials with differing CUBIC crystal structures

Diffraction Theory

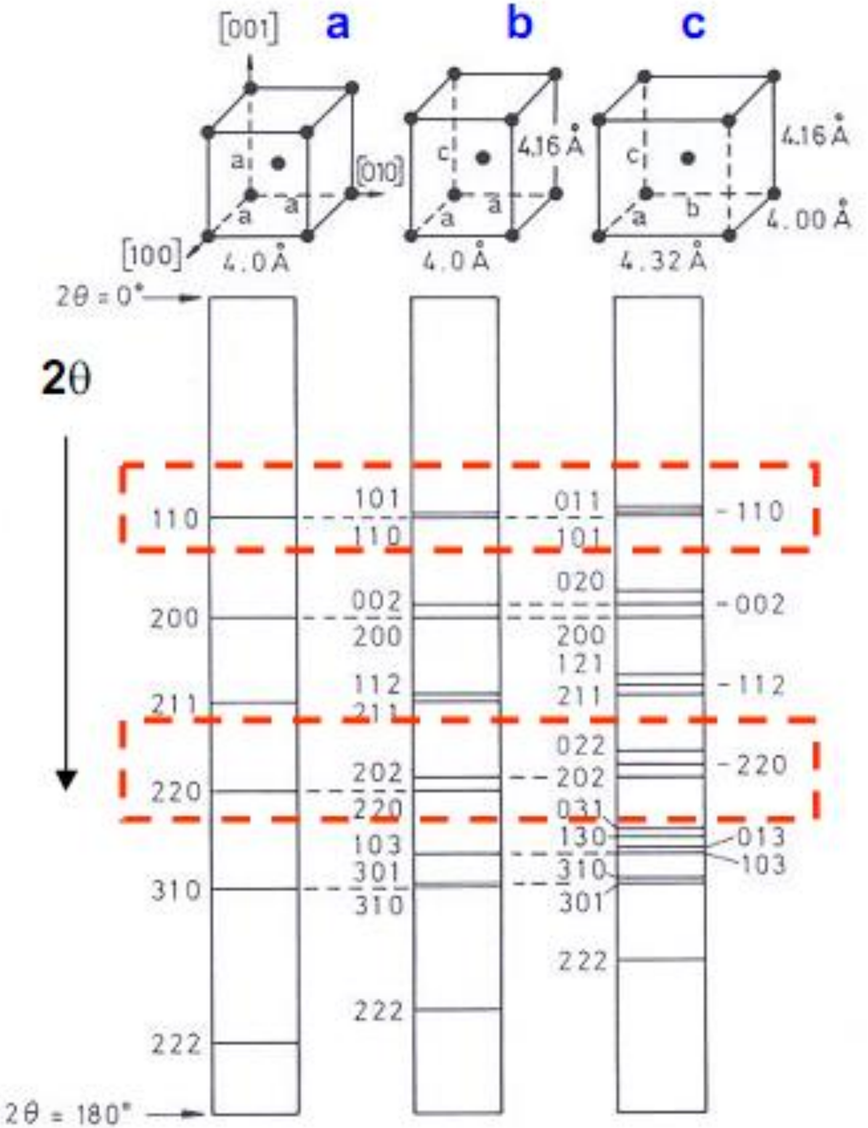
Diffractometer (Powder) Method

For a cubic structure

$$d_{hkl} = \sqrt{\frac{a^2}{h^2 + k^2 + l^2}}$$

Diffraction Theory

Identifying Non-Cubic Phases



- Effect of Symmetry on XRD Pattern

a. Cubic
a=b=c, (a)

b. Tetragonal
a=b≠c (a and c)

c. Orthorhombic
a≠b≠c (a, b and c)

- **Number of reflections**
- **Peak position**
- **Peak splitting**

Diffraction Theory

Diffraction Methods

3. Diffractometer (Powder) Method

What can we learn from the diffractometer experiments?

Phase Analysis

Lab Assignment: **Lab 2: Solving a Cubic system**

Group 1	Cr and Si
Group 2	Cu and Si
Group 3	Fe and Si
Group 4	Ni and TiN and Si

Diffraction Theory

Diffraction Methods

From your Lab 2 we know that for Chromium a = 0.2883 nm

So,

$$\sin^2\theta_{110} = \frac{(0.154056nm)^2}{2(0.2883nm)^2} = 0.14277$$

$\sin\theta_{110}$ = 0.377849 **θ_{110} = 22.20** **$2\theta_{110}$ = 44.40**

Diffraction Theory

Diffraction Methods

Lab 2: Solving a Cubic system

Bravais Lattice	**Allowed Reflections**
SC	All
BCC	(h + k + l) even
FCC	h, k and l unmixed
DC	h, k and l are all odd *Or* all are even *(h + k + l) divisible by 4*

Diffraction Theory

Diffraction Methods

Lab 2: Solving a Cubic system

The ratio of $(h^2 + k^2 + l^2)$ derived from extinction rules

SC	1	2	3	4	5	6	8	…
BCC	1	2	3	4	5	6	7	…
FCC	3	4	8	11	12	…		
DC	3	8	11	16	…			

Diffraction Theory

Diffraction Methods

Lab 2: Solving a Cubic system

Crystal Structure Determination

Al	fcc	0.4049
Cr	bcc	0.2883
Cu	fcc	0.3615
Fe	bcc	0.2866
Ni	fcc	0.3523
Si	diamond	0.5430
TiN	fcc	0.4241

Diffraction Theory

Diffraction Methods

Qualitative

ID phases by comparison with standard patterns. Estimate of proportions of phases by comparing peak intensities attributed to the identified phases with standard intensity ratios.

Quantitative

Determination of amounts of different phases in multi-phase samples based on precise determination of diffraction intensity and/or determination of the fit of the pattern of each phase to the characteristics of that phase (i.e., amount, crystal structure, crystallite size and shape).

Diffraction Theory

Diffraction Methods

Quantitative Phase Analysis

Can be difficult – need to do a complete calibration of instrument, careful prepping of standards, and repetitive measurements.

For quantitative analysis, must equate a concentration of a given phase or phases with line intensities.

Line intensities are affected by a variety of factors.

Diffraction Theory

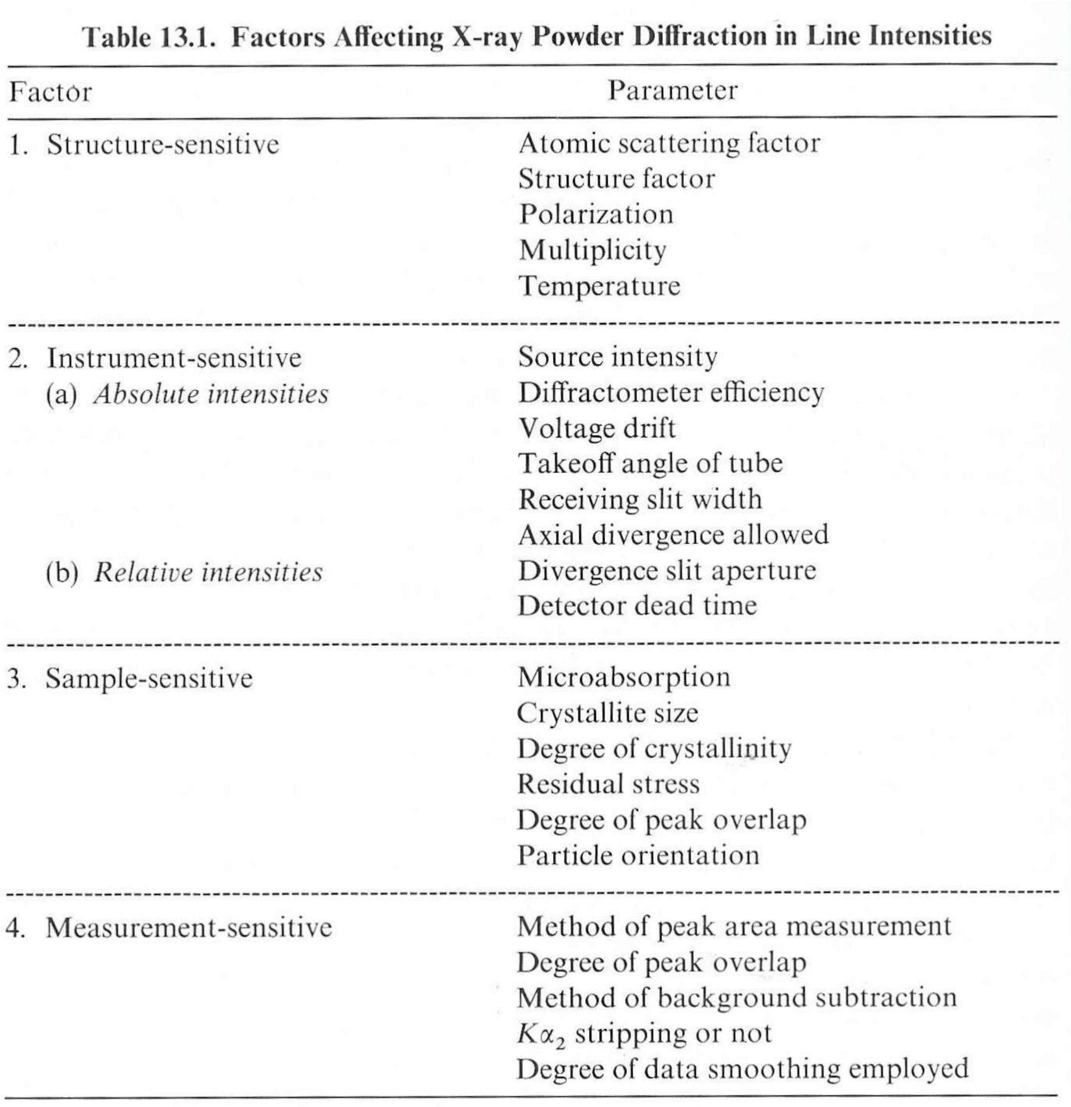


Table 13.1. Factors Affecting X-ray Powder Diffraction in Line Intensities

Factor	Parameter
1. Structure-sensitive	Atomic scattering factor
	Structure factor
	Polarization
	Multiplicity
	Temperature
2. Instrument-sensitive	Source intensity
(a) *Absolute intensities*	Diffractometer efficiency
	Voltage drift
	Takeoff angle of tube
	Receiving slit width
	Axial divergence allowed
(b) *Relative intensities*	Divergence slit aperture
	Detector dead time
3. Sample-sensitive	Microabsorption
	Crystallite size
	Degree of crystallinity
	Residual stress
	Degree of peak overlap
	Particle orientation
4. Measurement-sensitive	Method of peak area measurement
	Degree of peak overlap
	Method of background subtraction
	$K\alpha_2$ stripping or not
	Degree of data smoothing employed

Diffraction Theory

Diffraction Methods

The intensity equation (from lecture 7, ex: structure factor, multiplicity, Lorenz-polarization factor, temperature factor, absorption factor) describes the dependence of intensity of the diffraction line for a phase α. The entire equation shown here can be reduced, since the 1st and 2nd terms in brackets are constant for the particular setup.

$$I_{(hkl)\alpha} = \left[\frac{I_o\lambda^3}{64\pi r}\left(\frac{e^2}{m_e c^2}\right)^2\right]\left[\frac{M_{hkl}}{V_\alpha^2}\left|F_{(hkl)\alpha}\right|^2\left(\frac{1+\cos^2 2\theta\cos^2 2\theta_m}{\sin^2\theta\cos\theta}\right)\right]\left[\frac{X_\alpha}{\rho_\alpha\left(\mu/\rho\right)_s}\right]$$

I(hkl)α = Intensity of reflection of (hkl) in phase α
r = distance from specimen to detector
2ndterm = square of classical electron radius

I_0= incident beam intensity
λ = X-ray wavelength
M_{hkl} = multiplicity of reflection hkl of phaseα

Next to last term on right = Lorentz-polarization (and monochromator) correction for (hkl)
In that term, 2θm = diffraction angle of the monochromator
Vα = volume of the unit cell of phase α
F(hkl)α = structure factor for reflection hkl of phase α

Diffraction Theory

Diffraction Methods

The intensity equation (from lecture 7, ex: structure factor, multiplicity, Lorenz-polarization factor, temperature factor, absorption factor) describes the dependence of intensity of the diffraction line for a phase α. The entire equation shown here can be reduced, since the 1st and 2nd terms in brackets are constant for the particular setup.

$$I_{(hkl)\alpha} = \left[\frac{I_o \lambda^3}{64\pi r} \left(\frac{e^2}{m_e c^2} \right)^2 \right] \left[\frac{M_{hkl}}{V_\alpha^2} \left| F_{(hkl)\alpha} \right|^2 \left(\frac{1 + \cos^2 2\theta \cos^2 2\theta_m}{\sin^2 \theta \cos \theta} \right) \right] \left[\frac{X_\alpha}{\rho_\alpha (\mu / \rho)_s} \right]$$

X_α – weight fraction of α
ρ_α – density of phase α
$(\mu/\rho)_s$ – mass attenuation coefficient of sample.

Diffraction Theory

Quantitative Phase Analysis

Therefore the total adsorption of the sample is a sum of the products of the individual attenuation coefficients and weight factions (two unknowns)

So need to use various methods to solve equation.

Methods

- absorption-diffraction
- standard additions
- internal standards

Diffraction Theory

Quantitative Phase Analysis

Absorption-Diffraction Method

$$\frac{I_{(hkl)\alpha}}{I^{o}_{(hkl)\alpha}} = \frac{(\mu/\rho)_{\alpha}}{(\mu/\rho)_{s}} X_{\alpha}$$

where

$I_{(hkl)\alpha}$ – intensity of phase α of unknown
$I^{o}_{(hkl)\alpha}$ – intensity of pure sample of phase α

Diffraction Theory

Quantitative Phase Analysis

For a binary mixture:

$$\frac{I_{(hkl)\alpha}}{I^{o}_{(hkl)\alpha}} = \frac{X_{\alpha}(\mu/\rho)_{\alpha}}{X_{\alpha}(\mu/\rho)_{\alpha} + X_{\beta}(\mu/\rho)_{\beta}}$$

Since Xα + Xβ = 1, can simplify equation to the <u>Klug equation</u>:

$$X_{\alpha} = \frac{(I_{(hkl)\alpha}/I^{o}_{(hkl)\alpha})(\mu/\rho)_{\beta}}{(\mu/\rho)_{\alpha} - (I_{(hkl)\alpha}/I^{o}_{(hkl)\alpha})\left[(\mu/\rho)_{\alpha} - (\mu/\rho)_{\beta}\right]}$$

Diffraction Theory

Quantitative Phase Analysis

$$X_\alpha = \frac{(I_{(hkl)\alpha} / I^o_{(hkl)\alpha})(\mu/\rho)_\beta}{(\mu/\rho)_\alpha - (I_{(hkl)\alpha} / I^o_{(hkl)\alpha})\left[(\mu/\rho)_\alpha - (\mu/\rho)_\beta\right]}$$

Example: SiO_2 in $SiO_2/CaSiO_3$

$(\mu/\rho)_\alpha$ for SiO_2 is 35.9 and $(\mu/\rho)_\beta$ for $CaSiO_3$ is 74.1

I for SiO_2 phase is 4270 counts and I for pure SiO_2 is 10,000 counts

then $$X_\alpha = \frac{0.427 \times 74.1}{35.9 - (0.427 \times (35.9 - 74.1))} = 60.6\%$$

Diffraction Theory

Quantitative Phase Analysis

Standard Addition Method or “spiking” method

Method used to determine α phase in a mixture, as long as one other phase, β, has a diffraction line that does not overlap with any α line.

β does not even have to be identified.

Diffraction Theory

Quantitative Phase Analysis

With this method, some of the pure α phase is added to the mixture containing the unknown concentration of α.

$$\frac{I_{(hkl)\alpha}}{I_{(hkl)'\beta}} = K(X_{\alpha} + Y_{\alpha})$$

where

X_α is the initial weight fraction of phase α

X_β is the initial weight fraction of phase β

Y_α is the number of grams of pure phase α added per gram of the original sample.

Diffraction Theory

Quantitative Phase Analysis

After several additions of $Y\alpha$ grams of the α phase, a plot of I_α/I_β versus $Y\alpha$ can be constructed.

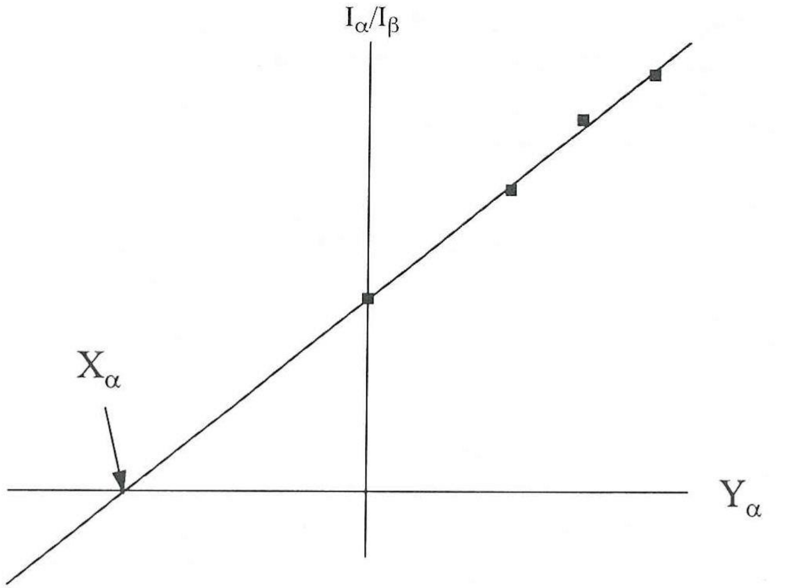


Figure 13.8. Spiking method analysis: plot of the ratio of I_α to the intensity of a reference line as a function of Y_α, the number of grams of α added per gram of sample.

Diffraction Theory

Quantitative Phase Analysis

Internal Standard Method

Most common

Plot a calibration curve of $I_{(hkl)\alpha}/I_{(hkl)'\beta}$ versus X_α/X_β with k as the slope.

$$\frac{I_{(hkl)\alpha}}{I_{(hkl)'\beta}} = k\,\frac{X_\alpha}{X_\beta}$$

Diffraction Theory

Quantitative Phase Analysis

In this method, a known amount, X_β, of an internal standard is added to a mixture of phases.

The addition of this new phase increases the complexity of the pattern, so must be careful in choosing the standard.

Usually, F-centered cubic materials with small unit cells are used because of their simple patterns.

Diffraction Theory

Quantitative Phase Analysis

Rietveld Method

Quantitative method based on the use of the total pattern.

Involves fitting the entire diffraction pattern with a synthetic diffraction pattern, which is either a produced or calculated standard pattern.

Rietveld refinement is conducted by minimizing the sum of the weighted, squared differences between observed and calculated intensities at each step.

Diffraction Theory

Quantitative Phase Analysis

The full-pattern approach pioneered by Dr. Hugo M. Rietveld attempts to account for all of the contributions to the diffraction pattern to discern all of the component parts by means of a least-squares fit of the diffraction pattern.

The method is made possible by the power of digital data processing and very complicated software.

Input data needed includes space group symmetry, atomic positions, site occupancies, lattice parameters for each phase, profile shape, a background function, and a scale factor.

Can set certain data and let others vary, i.e. scale factor, profile, background, and lattice parameter.

Diffraction Theory

Quantitative Phase Analysis

Rietveld Method

Quantitative method based on the use of the total pattern.

The method is made possible by the power of digital data processing and very complicated software

Originally conceived only for use with extremely clean neutron diffraction data, the method has evolved to deal with the relatively poor-quality of data from conventionally-sourced diffractometers.

Rietveld refinement is conducted by minimizing the sum of the weighted, squared differences between observed and calculated intensities at each step.

Quantitative Methods

Rietveld Method

The method is capable of much greater accuracy in quantifying XRD data than any peak-intensity-based method because of the systemic “whole-pattern” approach

The initial primary use of the method was (and still is) to make precise refinements of crystal structures based on fitting the experimental diffraction pattern to precise structure

Though it generally has a fairly steep learning curve, very sophisticated software is available at no cost to do the refinements: Major packages include GSAS and FullPROF

Reitveld’s 1969 paper is recommended for further reading

http://crystal.tau.ac.il/xtal/paper2/paper2.html

Quantitative Methods

FULLPAT: A Full Pattern Quant System

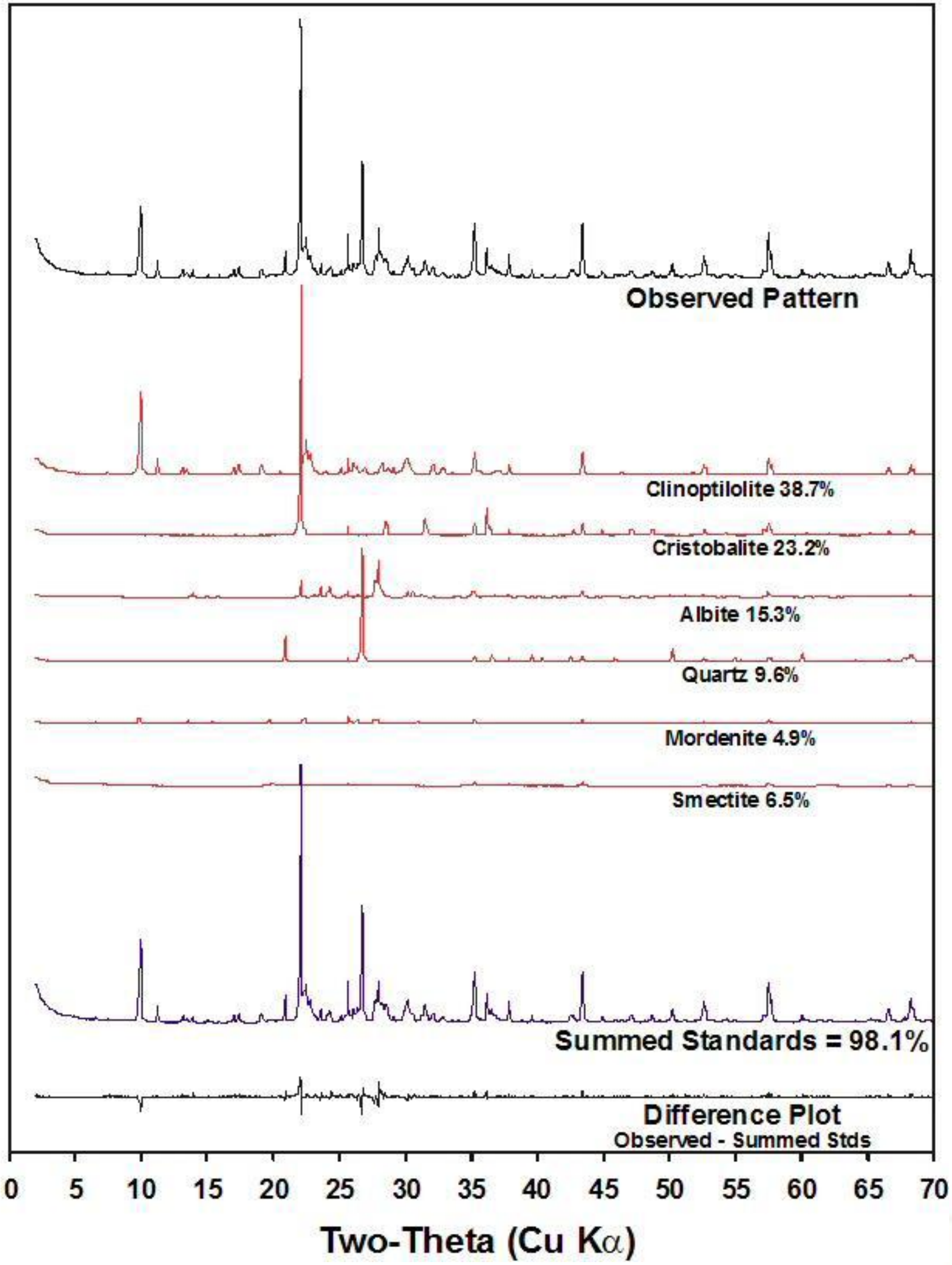
Developed by Steve Chiperaand Dave Bishat LANL (primarily for use in analysis of Yucca Mountain Tuff samples).

Is a full pattern fitting system but (unlike Reitveld) does not do detailed structure determination.

Uses the built-in Solver functions of Microsoft Excel. Will work on virtually any computer that has MS Excel on it (as long as the correct extensions are installed).

Software is free and in the public domain (your tax dollars at work); available on ftp://eps.unm.edu/pub/xrd

Basically, the program makes use of the fact that the total diffraction pattern is the sum of the diffraction patterns of the constituent phases, and does a least-squares fit on the observed (sample) pattern to the appropriate standard patterns.


Observed Pattern
Clinoptilolite 38.7%
Cristobalite 23.2%
Albite 15.3%
Quartz 9.6%
Mordenite 4.9%
Smectite 6.5%
Summed Standards = 98.1%
Difference Plot
Observed - Summed Stds
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
Two-Theta (Cu Kα)

Diffraction Theory

Diffraction Methods

3. Diffractometer (Powder) Method

What can we learn from the diffractometer experiments?

Phase Analysis

Lab Assignment:

Lab 3: Solving a Hexagonal system

Group 1	Mg
Group 2	Ti
Group 3	Mg
Group 4	AlN

Reading Assignment:

Read Chapter 8 from:

- -X-ray Diffraction Procedures by Klug and Alexander

Read Chapter 13 from:

- -Elements of X-ray Diffraction, 3rd edition, by Cullity and Stock