Characterization:

Depending on the type of material you make there are a variety of different, general characterization techniques that one can use to determine the chemical and physical properties of solid materials. However, there are some basic types of characterization that are used for most solid materials.

The principle methods used to characterize crystalline solids are typically

1). Elemental analysis allows one to determine composition
ICP-OES, ICP-MS, EDX, Prompt Gamma Neutron Activation Analysis, PGAA and combustion analysis (C, O, and N)
2). Thermal analysis to look at stability, reactivity, and phase changes. (DSC, TGA, and DTA)
3). Microscopy to look at morphology of crystallites, particularly in polycrystalline materials (SEM and TEM)
4). Spectroscopic techniques can give valuable insight into the structure of molecular materials and also the optical properties of materials, for instance the size of the band gap and give insight into the origin of color of materials. NMR is particularly good to look at organic structures. There is also solid state NMR that is used to understand the structures of inorganic materials. IR is used for instance to look at certain vibrational modes and UV/Vis is often used to assess optical properties of materials.
5). X-ray and neutron spectroscopies
XAS (includes both XANES and EXAFS metal oxidation states and local coordination environmnents) and INS and QENS are techniques used for neutrons probes vibrational modes and other dynamic properties of materials, like rotations or molecule jumping etc.
6). Single crystal and powder x-ray diffraction allow one to study the structure of crystalline materials.

While spectroscopy can be used to determine the structure of organic molecules, for inorganic materials in particular the structures as you have seen are much more diverse with regard to coordination numbers and geometries. As such, diffraction is required. Further, spectroscopy doesn't give you any clue about how molecules are arranged in 3-D space in solid form, so even for organic molecules diffraction is the technique you use to see precise interatomic distances and angles as well as how the molecules are arranged in space.

X-ray Diffraction

The general things that we obtain form diffraction:

a). Identify structure of unknown materials

-Crystal System (triclinic, monoclinic, etc….)
-Lattice Type (P, I, F, or C)
-Symmetry and hence the space group
-Unit Cell dimensions (parameters) and volume
- Offers a precise determination of atomic positions in solid materials and the types of atoms.
- Particularly of importance is being able to determine the distances between atoms and angles which give insight into oxidation states

The structure solutions for a number of different materials are placed in what are called crystallographic information files .cif and these are reported to structural databases like, Cambridge Structural Database and then the data can be downloaded by any researcher if you simply have the deposition number that is reported inside a manuscript for instance.

b). Allow you to simply determine if what you have made already exists or if you made what you wanted to make.

Most x-ray diffractometers come with software that can use an x-ray powder pattern to look for specific phases already reported in a database. So, using this software you can often rapidly determine whether the material you have made is new or existing.

c). Determine phase purity (from powder diffraction) as long as the secondary crystalline phase is above approximately 3% on average.

If it is below 3% it might be drowned in the background noise. You can simulate the powder pattern of an existing structure and compare it with the powder pattern you have obtained from your sample and by overlaying them you can see if there are any extra peaks from impurity crystalline phases. You can use refinement software in order to determine how much of each crystalline impurity is present.

d). Determine how much of each impurity you have.

Exercise: What other problems can you think of for impurities, what else might we not be able to see?

Answer: -impurity is amorphous
-impurity has light elements

e). Size distribution of crystallites in polycrystalline powders

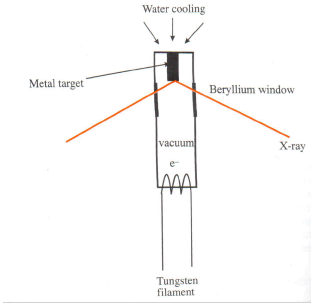
f). Can provide us with valuable insight into the structure-derived function of materials. How materials behave as a function of temperature, pressure, and under various atmospheres. See phase changes and whether materials expand or contract during operation and we can understand the structural origins for this. We can also see how materials potentially interact with other species.

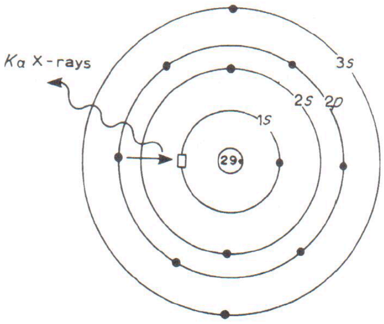
X-ray generation – used because their wavelengths are similar to interatomic spacings.

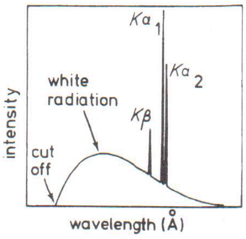
X-rays are produced when high energy charged particles like electrons are accelerated (via an accelerating voltage, typically 30kV) and then collide with a target. The resulting x-ray spectrum will be in one of two forms:

(1) A broad spectrum of x-rays that means of many different wavelengths referred to as white radiation
(2) Or monochromatic, a single wavelength

While there are a broad spectrum of ways x-rays are produced I will describe the most common, which is done for lab based x-ray source that results in monochromatic wavelength that is usually 1.5418 Å for Cu. For this a tungsten filament is heated and the resulting electron beam is accelerated via an accelerating voltage of 30 kV which are then allowed to strike a metal target fixed to the anode. It is this metal target that dictates what the resulting wavelength is. For lab-based powder x-ray sources this is usually copper while for single crystal this is usually Molybdenum (but also at times can also be copper). Wavelengths used in diffraction experiments range from 0.6 to 2.3 Å.







The anode is cooled continuously during x-ray production because not all of the energy is converted into x-rays, much of it is converted into heat and the anode would melt otherwise.

They typical source is Cu. You see the structure of the Cu atom in the middle above. The ionizing electrons strike the Cu, ejecting an electron from the 1s core orbital and then an electron from the 2p orbital falls down into the spot giving off an x-ray that is characteristic of the energy difference between the two states. You can see the emission spectrum in the right. The most intense wavelength is known as the K alpha radiation.

For transitions the orbital angular moment quantum number l must change by + or – 1 in order for a transition to be allowed. For s, p, d, and f orbitals l = 1, 2, 3, and 4, respectively. So, you can have transitions between s and p for instance.

The characteristic lines in an atom's emission spectra are called *K, L, M,* and correspond to the n = 1, 2, 3, energy states, respectively, of the electron hole being filled.

K refers to a loss of an electron in the n=1 energy level
L refers to a loss of and electron in the n=2 energy level
M refers to a loss in the n=3 energy level…Etc…

When the two atomic energy levels differ by only one quantum level then the transitions are described as α lines (n = 2 to n = 1, or n = 3 to n = 2). For instance, the $K\alpha$ is 2p to the 1s

When the two levels are separated by one or more quantum levels, the transitions are known as β lines (n = 3 to n = 1 or n = 4 to n = 2). So for $K\beta$ it refers to the 3p to 1s

You can filter out the $k\beta$ (1.3922 Å) radiation by adding a filter. This is done by using an element with a slightly lower atomic number, like Ni. The $k\beta$ wavelength is enough to ionize the 1s electron of Ni (requires a wavelength of 1.488Å for ionization of the 1s e- of Ni) and it permits the lower energy wavelength $k\alpha$ to go through. At the same time, Ni can also absorb most of the white radiation as well.

The wavelengths of some common sources are shown below:

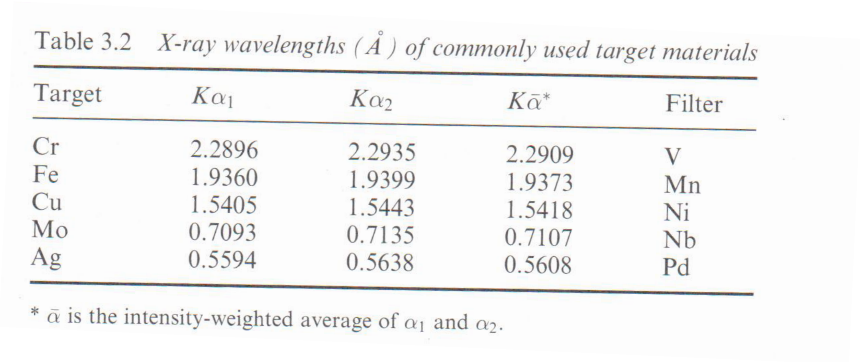


Table 3.2 *X-ray wavelengths (Å) of commonly used target materials*

Target	$K\alpha_1$	$K\alpha_2$	$K\bar{\alpha}$*	Filter
Cr	2.2896	2.2935	2.2909	V
Fe	1.9360	1.9399	1.9373	Mn
Cu	1.5405	1.5443	1.5418	Ni
Mo	0.7093	0.7135	0.7107	Nb
Ag	0.5594	0.5638	0.5608	Pd

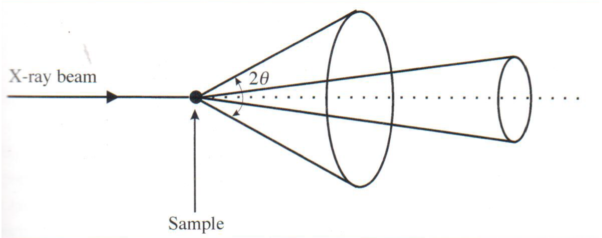
* $\bar{\alpha}$ is the intensity-weighted average of α_1 and α_2.

In some experiments the kα_2 is filtered out but in most the two peaks are not well resolved due to the similarities in wavelength as so the average in the 4th column is instead used.

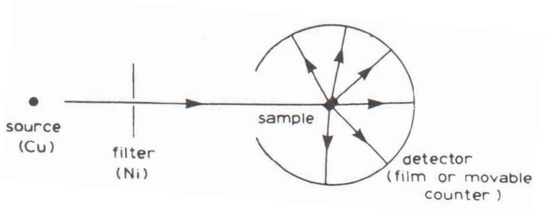
Sample types

For powder samples they must be finely ground so that you get a sample of all orientations in the material. If you do not have this then some hkls will have higher intensity than expected while others will have lower intensity than expected. The diffraction pattern is detected by a detector that moves along 2theta, or it is detected by an area detector that is immobile.

Since the powder is finely ground you have all possible orientations there and so the diffracted beam is diffracted in all possible orientations and what this translates into is a cone. See below:



The inner cone has a smaller 2theta value than the outer cone and hence the inner cone represents a larger d-spacing. If you have an area detector you can see the circles associated with the diffraction cones.



In standard laboratory-based powder diffraction, the data is usually collected by a detector with a slit that is moved along the above circle and it collects data as a function of increasing angle.

In contrast for single crystals you have a single orientation and so you will see a single round spot on the cone. For most lab-based sources you do not have an area detector that detects the entire ring, instead you have a detector with a slit that scans along a portion of the diffraction cone. In either case the intensity is integrated and then the output are intensity plotted as a function of 2θ.

Exercise: What do you think is the most accurate representation of the unit cell, one from a single crystal or one from a powder?

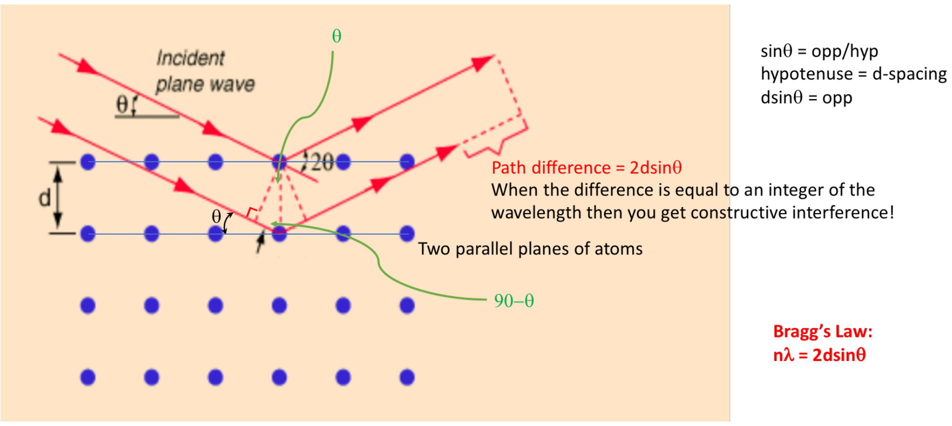
Answer: The most accurate representation is definitely powder. You can imagine if you determine a unit cell from powder it is representative of every crystallite in the beam, while single crystal is a single unit and hence you might miss non-stoichiometries or disorder that are representative of the bulk material.

Braggs Law

In 1913 a father son duo realized if they took a crystal and put it in an x-ray beam that at certain angles they would get very intense reflections. And so what they have derived from this is Bragg's law. It is the condition under which you get this intense reflection. If you have a beam incident on a crystal surface you get strong constructive intereference when the path distance is an integer of the wavelength. The intensity is reflected from parallel planes of atoms.

The team won the 1915 Nobel Prize in Physics for their discovery, Bragg's law shows the connection between the wavelength of the X-rays, the distance between the planes and the angle at which the X-rays are reflected. At the same time, William Henry Bragg designed the X-ray spectrometer, a device that could examine the reflections of X-rays from crystals. Together the two scientists used the spectrometer to analyse the structure of several salts and small molecules, establishing fundamental mathematical relationships between an X-ray diffraction pattern and the dimensional arrangement of atoms in a crystal that produced the pattern.

The below picture shows the derivation of Bragg's Law:



sinθ = opp/hyp
hypotenuse = d-spacing
dsinθ = opp

Path difference = 2dsinθ
When the difference is equal to an integer of the wavelength then you get constructive interference!

Two parallel planes of atoms

Bragg's Law:
$n\lambda = 2d\sin\theta$

So if you know the angle and you know the wavelength, you can calculate the distance between those planes, which is d in the Bragg equation.

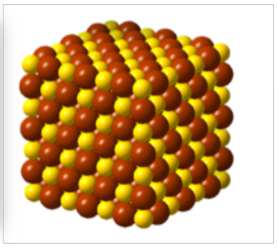
Usually materials with few numbers of distinct atoms and high symmetries have simple patterns and then you can have complex powder patterns as in the case of MOFs where we have large unit cells with large numbers of distinct atoms. And so, because of the complexity analysis form powder can in some occasions be quite difficult. And this is why it is hugely beneficial to have large high-quality single crystals. It makes our lives a lot easier. Below is the slide from the course. It shows you the different things that can influence the intensities and peak positions. It also shows you a simple powder pattern obtained for a material like NaCl compared to that of a metal-organic framework, which have very large unit cells and large numbers of crystallographically distinct atoms.

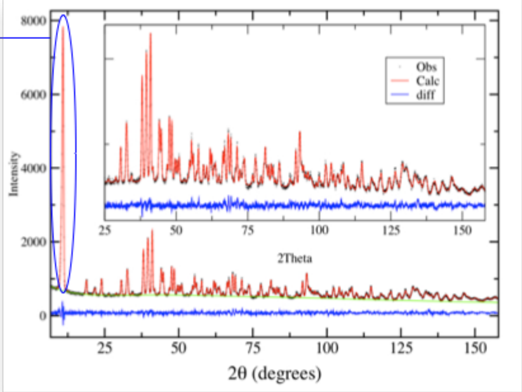
Representing a parallel set of planes

hkl

Things that effect Intensities and Peak positions

- Crystal System (triclinic, monoclinic, etc….)
- Lattice Type (P, I, F, or C)
- Symmetry
- Unit Cell Parameters
- Atom distributions and types
- Preferred orientation
- Crystal size





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

Each powder pattern is like a fingerprint for compounds.

Exercise: Using Bragg's law calculate the 2theta value for a d-spacing of 20 Å and also for 1 Å both Cu and Mo radiation with wavelengths of 1.5408 Å and 0.71Å, respectively.

Answer:

$n\lambda = 2d\sin(\theta)$

For Cu:
$1.54 = 2d\sin(\theta)$
$1.54/(2*20) = \sin(\theta)$, $\theta = 2.2$ so 2θ is 4.4°
$1.54/(2*1) = \sin(\theta)$, $\theta = 50.35$ σο 2θ is 100.71°

For Mo:
$0.71 = 2d\sin(\theta)$
$0.71/(2*20) = \sin(\theta)$, $\theta = 1.01$ so 2θ is 2.03°
$0.71/(2*1) = \sin(\theta)$, $\theta = 20.79$ σο 2θ is 40.58

Points:

1. For Cu (longer lamda) a much wider range of 2□ is needed to get the same resolution. This can limit the resolution for low d-spacing which is where you determine structural detail.
2. For Cu (longer lamda), you do not need to go to such a low angle to see the large unit cell as you do with Mo.
3. For Mo (shorter lamda) also you get a larger amount of data within a very small 2□□range, which might mean that a lot of peaks overlap because there is smaller spacing between the peaks.
4. Longer wavelengths like Cu give you a larger spacing between peaks and this can be good if we need to deconvolute overlapping peaks.
5. While Cu is great for indexing and determining the cell dimensions. It is often not always good to give you the atomic resolution you need unless you can go to very high angles. Usually for lab sources you do not go much above 60°□(which gives you about 1.54 Å resolution which is still quite good for most materials).

-So a summary to spread peaks apart and to look at unit cells with very large dimensions, go to longer wavelengths

-If you want more data over a short 2θ range then you go with Mo.

-It should be noted that there are also differences in intensity with different sources. As such this can play a big role in what source you choose. Molybdenum is usually more intense of a source and so if you have a material that does not diffract so well then sometimes I might choose to go with that even if my unit cell is large. However, more often than not you will not have the luxury of choosing if you are using a lab source as most facilities only offer one source per instrument. Varying wavelength is more prevalent at synchrotron x-ray sources and also neutron scattering sources.

Determining unit cell dimensions

The calculated d-spacing obtained from the Bragg equation can be used to directly estimate the unit cell parameters.

For instance, using the following equation you can calculate the unit cell dimension for a cubic system.

$$1/d^2 = (h^2 + k^2 + l^2)/ a^2$$

now if we make a substitution with the Bragg equation

$$\lambda = 2d\sin(\theta)$$

then $1/d^2 = 4\sin^2(\theta)/\lambda^2$

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

Then $\sin^2(\theta) = \lambda^2 (h^2 + k^2 + l^2) / 4a^2$

Using the above equation, we can now calculate the unit cell parameters from the diffraction pattern. It should be noted that the above equation is for a cubic unit cell. You can imagine that this relationship is very different for other crystal systems. Indeed, there are ways to relate them all to the diffraction angle θ. From this point forward, we will only work with the cubic system as it is the least complicated given that all unit cell axes (a, b, and c) are equivalent.

Powder x-ray diffraction is the most common method to use for structure determination because growing single crystals can be quite difficult.

Indexing and Identify the structure of unknown materials

For the following equation we saw earlier, $\lambda^2 (h^2 + k^2 + l^2) / 4a^2 = \sin^2(\theta)$, the wavelength and unit cell dimension is constant so we can rewrite the equation as…

$$C(h^2 + k^2 + l^2) = \sin^2(\theta)$$

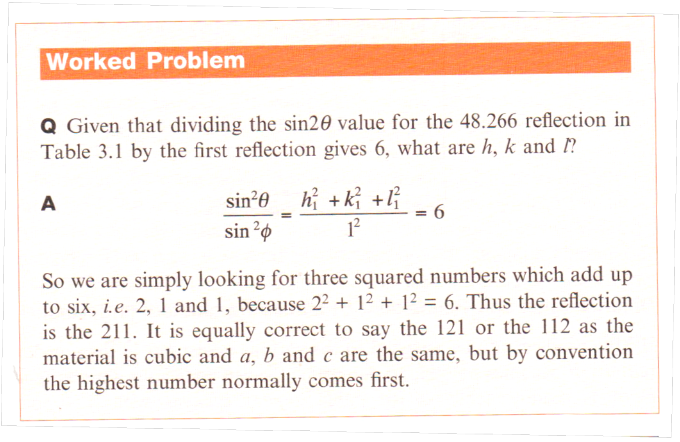
If we divide this by the values obtained from the very first reflection then we can get rid of C.

$$\sin^2\theta / \sin^2\phi = (h_1^2 + k_1^2 + l_1^2) / (h_2^2 + k_2^2 + l_2^2)$$

For a primitive lattice the first reflection is the (100). As such, the equation is now simplified.

$$\sin^2\theta / \sin^2\phi = (h_1^2 + k_1^2 + l_1^2) / 1^2$$

So, you can now calculate the value for the h, k, and l.



Worked Problem

Q Given that dividing the sin2θ value for the 48.266 reflection in Table 3.1 by the first reflection gives 6, what are *h*, *k* and *l*?

A

$$\frac{\sin^2\theta}{\sin^2\phi} = \frac{h_1^2 + k_1^2 + l_1^2}{1^2} = 6$$

So we are simply looking for three squared numbers which add up to six, *i.e.* 2, 1 and 1, because $2^2 + 1^2 + 1^2 = 6$. Thus the reflection is the 211. It is equally correct to say the 121 or the 112 as the material is cubic and *a*, *b* and *c* are the same, but by convention the highest number normally comes first.

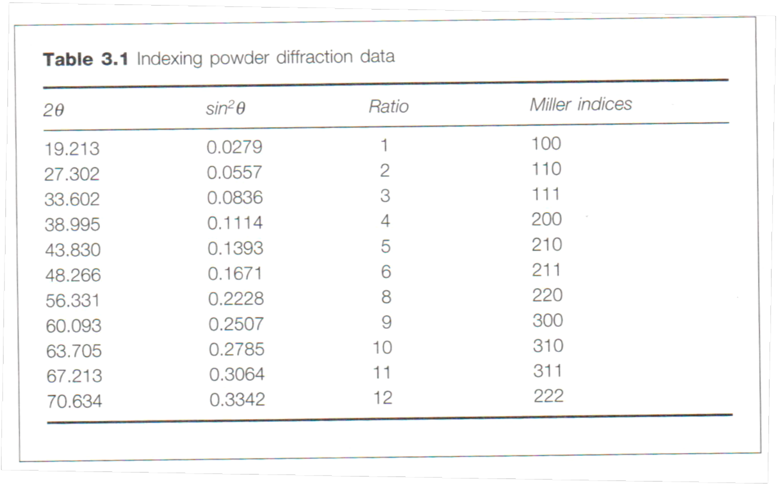


Table 3.1 Indexing powder diffraction data

2θ	$\sin^2\theta$	Ratio	Miller indices
19.213	0.0279	1	100
27.302	0.0557	2	110
33.602	0.0836	3	111
38.995	0.1114	4	200
43.830	0.1393	5	210
48.266	0.1671	6	211
56.331	0.2228	8	220
60.093	0.2507	9	300
63.705	0.2785	10	310
67.213	0.3064	11	311
70.634	0.3342	12	222

So if you extend this problem that we just did for all reflections and you obtain the ratio of the first peak, the 100, to the other peaks then you can determine the hkl values, Miller indices, for all reflections. This process is referred to as indexing.

I would like for you to note that ratio of 7 is missing. Also, we would have found if we had higher angle reflections that 15 would also be missing. The reason is because there is no combination of squares of three whole numbers that add up to 7 or 15.

So once we obtain the hkl values, then we can calculate what? The unit cell dimensions, *a*

Usually the last reflection indexed is used for this because if there is an error associated with measuring the 2q, it is the error is the smallest percentage if the highest angle is used.

Exercise: Given that the source is copper, use the 222 reflection to calculate the unit cell dimensions.

Answer: $\sin^2\theta = \lambda^2 (h^2 + k^2 + l^2) / 4a^2$
So $a^2 = (1.54)^2(12)/0.3342(4)$
So $a = 4.614$ Å