

The XRD-Files: Identification of the crystal fingerprint

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Abstract

X-ray diffraction is a useful way of identifying crystals. By measuring the diffraction pattern, or "fingerprint", produced by subjecting a sample to X-ray radiation, one can use the peaks for analysis of the crystal. We present results of our analysis of silicon and an initially unknown material. In our results we calculate inter-planar spacings and relative intensities, and compare the calculated values to tabulated ones in order to identify the unknown sample. Lastly we discuss other aspects of X-ray diffraction in our experiments, such as grain size and the advantages of using a powder sample.

Introduction

One of the many ways of identifying a material is by X-ray diffraction (XRD). Since the wavelength of X-rays is comparable in magnitude to the lattice parameter in certain crystals, the radiation will be able to diffract when passing through such a crystal. According to Bragg's law there will be certain angles with respect to the incident X-ray beam in which diffracted rays interfere constructively. Bragg's law reads as such

$$n\lambda = 2d \sin \theta, \quad (1)$$

where n is a positive integer, λ is the wavelength of the radiation source, d is inter-planar spacing in the crystal, and θ is half the angle of the diffracted beam relative to the incident beam (see Fig. 1). It is then apparent that one can measure a diffraction pattern from X-rays diffracted through a crystal. Since this pattern will depend upon the inter-planar spacing, one can utilise this technique to identify crystals.

The inter-planar spacing, or d -spacing, of a crystal is given by

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

where a is the lattice parameter, and indices (hkl) are Miller indices of the plane in question. Using known values for d -spacing in a crystal, we can work out the material using an encyclopedia.[3]

Methods

We placed a small vial of pulverised sample in the centre of a goniometre. An X-ray source, using a molybdenum cathode and a monochromator, was used to shine a beam of 0.7093 \AA X-rays at the sample. The monochromator is used to filter out the unwanted parts of the X-ray spectrum, mainly being composed of bremsstrahlung. In this way the X-ray beam consists of photons with frequency around the characteristic $K\alpha$ frequency of the anode specified above. For our purposes the X-ray beam consists of a broader frequency range in favour of a larger photon flux.

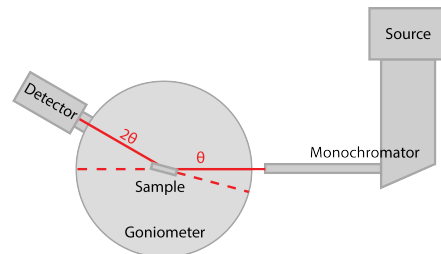


Figure 1: Diagram of setup

The sample and detector were slowly rotated relative to the incident beam using a computer controlled goniometer to account for all grain orientations. We acquired measurements of the diffraction pattern for angles of $2\theta \in [1^\circ, 40^\circ]$ through 391 steps of 0.1° . Our X-ray source accelerated electrons with a voltage and current

through the apparatus of 40 kV and 30 mA, respectively.

In the analysis of our data we have calculated d -spacings, the relative intensity, and the Miller indices (hkl) of each diffraction peak. d -spacings were calculated using measured values of 2θ and Bragg's law (Eq. 1). We only calculated the values for d -spacing for the first couple of peaks for each crystal to ensure we are only assessing peaks within the first diffraction order; $n = 1$. Relative intensities were calculated computationally by integrating over each peak using Simpson's method for sets of data, and dividing each intensity by the intensity of the first peak. Hence, the relative intensity for the first peak would always be 100%. To identify the respective Miller indices we found numbers that yielded the correct relationship between each value for the d -spacing, as defined by Eq. 2. This was done by clever trial and error.

Results

Fig. 2 shows the resulting counts as a function of 2θ for our unknown sample as well as the silicon reference sample. We used calculated values for d -spacings and relative intensities for the first three peaks in each diffraction pattern to look the crystals up in an encyclopedia. The tabulated values matched well with our known silicon sample; results summarised in Table 2. For the unknown sample, however, we did not find any adequate match, seeing that the first peak has a lower intensity than the second one which is not seen in any of the tabulated values. Therefore, we must assess the peaks in a different way. We observe that our unknown sample has peaks which seem to be coupled in pairs (most clearly around angular position of 15° and 20°), whereas the silicon peaks appear to be companion-less. With this, we theorise that our unknown powder does not consist of one distinct crystal type, as with the mono-atomic silicon powder, but rather a composition of multiple ones.

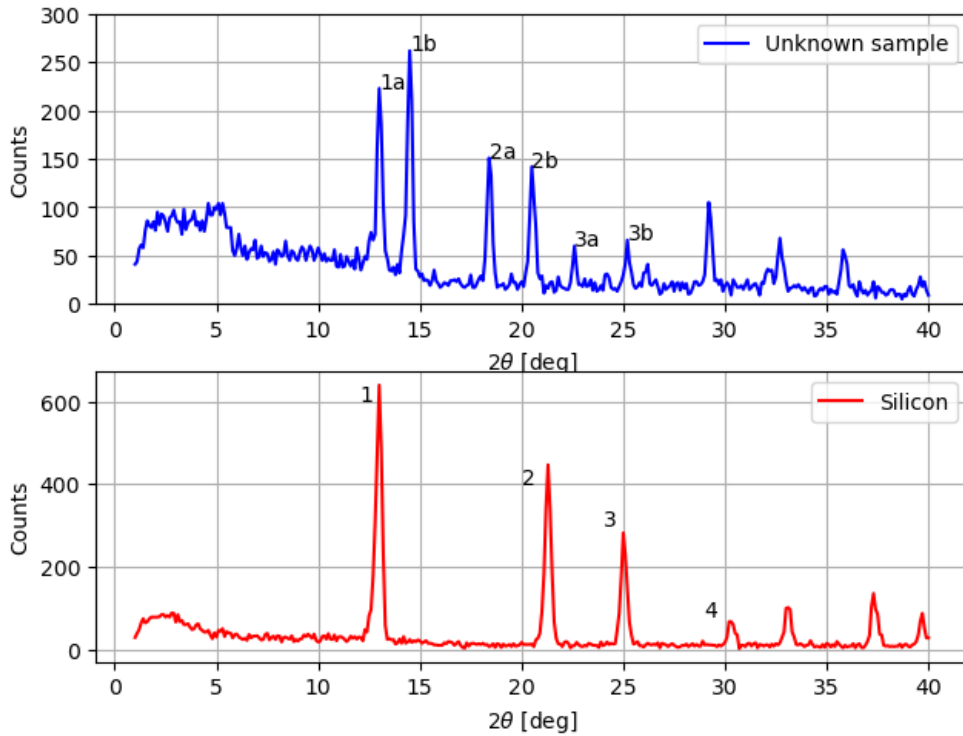


Figure 2: XRD counts as a function of angular position

This assumption would explain the intensities observed. Also, if the composite crystals are comparable in structure and contain similar elements, it would explain why the diffraction pattern of the second crystal is similar, but shifted ever so slightly relative to the first one, thereby yielding pairs of peaks. We have in Fig. 2 denoted such pairs with numbers, and the two speculated diffraction patterns with "a" and "b", respectively. Now, by treating the data-sets separately, and calculating relative intensities and searching up d -spacings for each one, the results match well with the crystals sylvite (KCl) and halite (NaCl) for the first and second set of peaks, respectively. These crystals are both cubic in structure, but have face-centered cubic Bravais lattices with di-atomic bases, and they both contain chloride and an alkaline metal. Our previous predictions are thus

supported, leading us to conclude that our unknown sample is the sedimentary rock sylvinite; composed of both sylvite and halite. The resulting d -spacings, relative intensities and Miller indices are summarised in Table 1.

Peak index	2θ [deg]	d [Å]	Relative intensity [%]	hkl
1a	13.0	3.133	100	100
2a	18.4	2.218	67.42	110
3a	22.6	1.81	16.04	111
1b	14.5	2.81	100	100
2b	20.5	1.993	48.9	110
3b	25.2	1.626	20.86	111

Table 1: d -spacing, relative intensity and Miller indices of diffraction peaks for Sylvinite

Peak index	2θ [deg]	d [Å]	Relative intensity [%]	hkl
1	13.00	3.133	100	111
2	21.30	1.919	62.42	220
3	25.00	1.639	40.42	311
4	30.25	1.359	11.59	400

Table 2: d -spacing, relative intensity and Miller indices of diffraction peaks for Silicon

Discussion

In both of samples we notice a broad region of larger intensity for small angles of 2θ . This region stands out compared to the other distinguishable peaks and the rest of the background noise in the diagram. It is likely that it corresponds to diffraction from the capillary containing the sample, which consists of an amorphous plastic material.

An amorphous material differs from a crystal because the atoms order themselves in a more random manner compared to the periodic ordering of the lattice in a crystal. One can then imagine an amorphous material subjected to XRD not obeying Bragg's law in the way that crystals do, but instead producing a broader and more continuous diffraction pattern. Such a broad and continuous peak is exactly what we observe in our X-ray diffractogram, leading us to conclude that the larger intensity measured for small angles of 2θ are indeed due to diffraction from the plastic capillary.

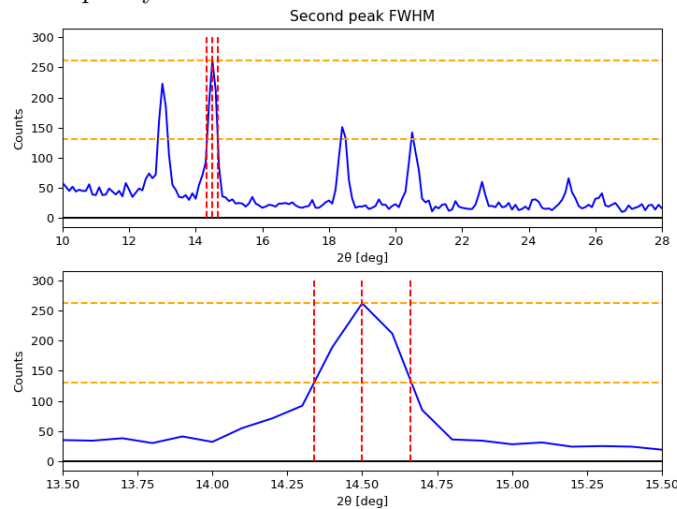


Figure 3: FWHM of the peak 1b from Sylvinite sample is 0.32 degrees

The advantage of using a sample in powder form for XRD is that producing one large coherent crystal is very hard and such crystals are bound to be imperfect. Subjecting such a crystal to XRD would not yield clear results because different parts of the crystal would diffract at different angles. However, by using a fine powder

and rotating the sample, one accounts for the multiple orientations of the lattices in each grain, and get a more accurate reading of the diffraction pattern of the material. The grains should however not be too small, as the bulk of the lattices are too close to the surface of its corresponding grain.

It is therefore compelling to calculate the grain size of the sample, and we do this by using Scherrer's equation, $\tau = \frac{K\lambda}{\beta \cos \theta}$. Here, τ is the mean size of ordered crystalline domain, which is about the same as grain size, or smaller. K is a dimensionless constant varying a bit with grain size, but has a typical value of 0.9. β is the broadening of the peak at full width at half maximum (FWHM) in units of radians, and θ the Bragg angle. With our measured values, Scherrer's equation yields $\tau = 118.61 \text{ \AA}$. [2]

Ideally, the FWHM should be measured from the baseline of our measurement, and not 0. However, our count measurements fluctuate around ground level, which makes it hard to determine where a peak starts and where it stops. Consequently, the relative intensities and FWHM may not be as exact as desired. Sharper peaks with an orderly ground level would make it easier to determine the peak limits, and thus yield more accurate intensities and values for FWHM. We have corrected for this in our calculations of relative intensities by choosing the zero level for our integrations at the bottom of a peak rather than at 0. For the FWHM however we have measured from 0, as correcting it would have little impact on β either way.

Lastly, a noteworthy difference between the two samples is that the silicon powder measures much higher counts than our unknown powder - as much as 600 at the highest peak. In comparison, the former unknown sample measures just above 250 at the most. However, integrating over each of the total data-sets separately, shows us that the total number of counts is practically the same (within 5%).

Conclusion

With the powerful tool that is X-ray diffraction, we have obtained two distinct patterns, or fingerprints, for each of our samples. By calculating inter-planar spacings and relative intensities, we used tabulated values from a mineral-encyclopedia, leading us to conclude that our unknown crystal is the mechanical mixture of halite and sylvite, namely sylvinitite. By calculating and analysing the Miller indices for each crystal, we have also concluded that the two crystals have a cubic structure (though the crystals do not have cubic Bravais lattices, but rather face-centered cubic ones). Lastly we have discussed why powder is used in XRD and why the sample is rotated when measurements are done, which is to ensure all possible grain orientations are accounted for.

References

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