

LAB 02

POWDER DIFFRACTION

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ABSTRACT

The goal of this experiment was to analyze and identify unknown powder diffraction samples.

In this report, three different unknown powder samples (of eleven unknowns) were characterized and compared to known diffraction peak curves in order to identify each particular sample. It was found that the samples labeled 3, 6, and 7 were copper, magnesium oxide (Periclase) and calcium carbonate (Calcite) respectively.

INTRODUCTION

The x-ray powder diffraction method is used to characterize specific crystals using specific characteristic diffraction peak patterns. In this method, monochromatic x-ray radiation (usually copper K α radiation) strikes a powdered crystal sample and the resulting intensity peak vs. diffraction angle data can be used to identify the sample specimen.

A powder sample represents almost every possible orientation of a particular crystal sample. There are many grains in a single sample, each of which are randomly oriented. As a result, the incident x-ray beam can now possibly be diffracted for any of the crystal orientation spacings as if the beam itself were striking at the ideal angle for that particular diffraction. Essentially, by introducing a sample that incorporates almost all possible orientations, almost all possible d-spacings of lattice plane families in the crystal specimen are sampled in the powder diffraction experiment.

The traditional x-ray powder diffraction method developed by Hull/Debye-Scherrer uses a fixed incident angle and captures the resultant diffraction on a cylindrical film surrounding the powder sample. In this lab, we use a diffractometer which serially samples the powder diffraction. Serial quantification is more time intensive than the traditional method, but is still well documented. For specimen identification, the International Center for Diffraction Data (ICDD) has online powder diffraction files (PDFs) to which it is possible to compare unknown samples for identification. Most often, the highest intensity peaks are compared first to narrow down the list,

EXPERIMENTAL PROCEDURES

For this experiment, our materials were an x-ray diffractometer with a copper target, three unknown powdered specimen samples (Samples 3, 6, and 7) and a glass powdered sample holder.

Before beginning both sections of the lab, we initialized the Rigaku Miniflex II X-Ray Diffractometer. This included turning on the cooling water, initializing the data collection software, and checking for background radiation. The voltage for this diffractometer is preset at 30kV and 15 mA.

POWDER DIFFRACTION DATA COLLECTION

Each unknown sample was packed and loaded into the diffractometer. The powder was packed into the holder then pressed down and flattened in order to present a smooth diffraction surface. Then, the diffractometer was run over a 2θ range of 3° to 90° .

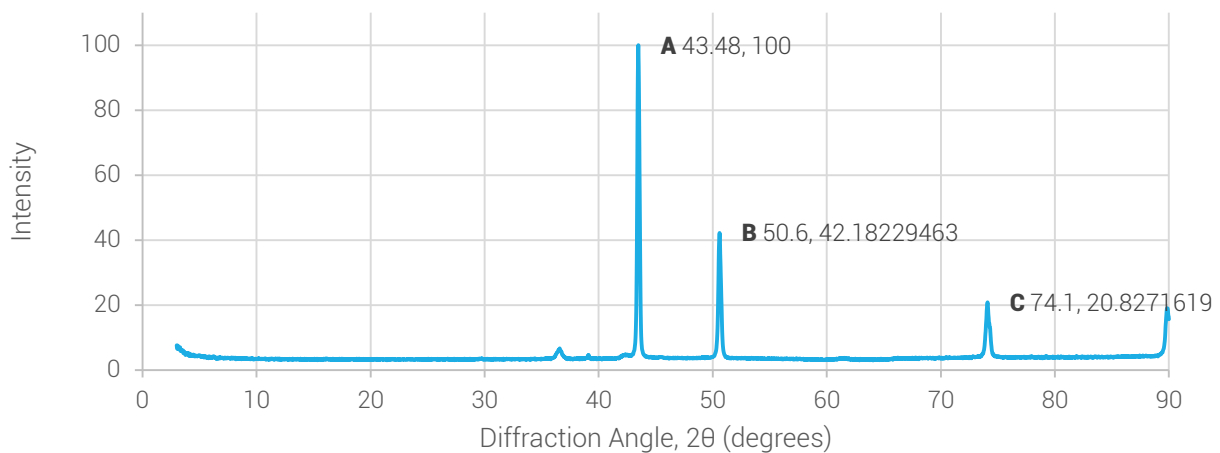
EXPERIMENTAL RESULTS

In all x-ray experiments, the background radiation was found to be 0.02 mR/hr using a Geiger counter during x-ray emission and before emission.

SAMPLE 3

Figure 1: Intensity vs. Wavelength for X-Ray Diffraction using Unknown Sample 3. The incident wavelengths were produced by a copper tube target. The physical appearance of this sample was a loose reddish powder. The three highest peaks occur at **A** 43.5°, **B** 50.8°, and **C** 74.2°.

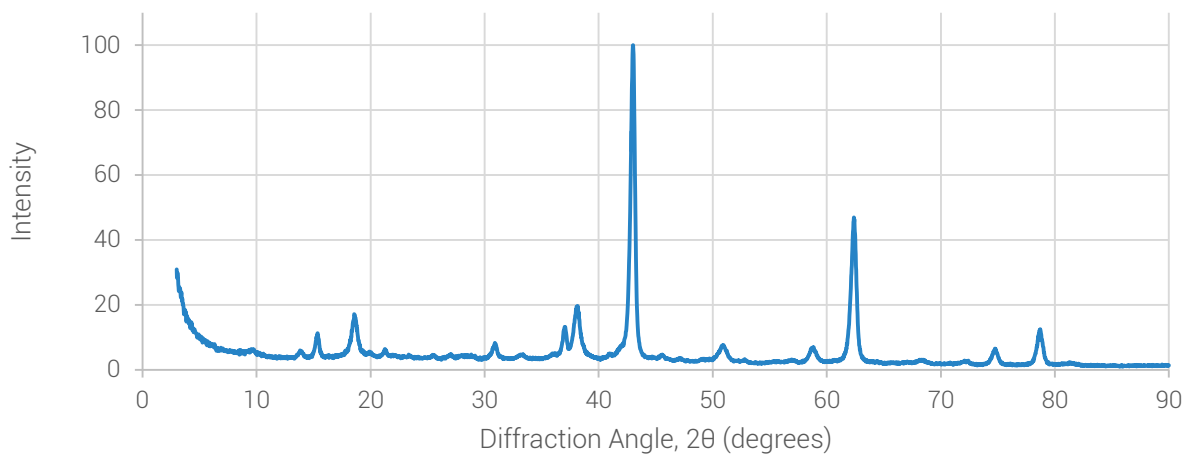
Intensity vs. Diffraction Angle: Unknown Sample 3



SAMPLE 6

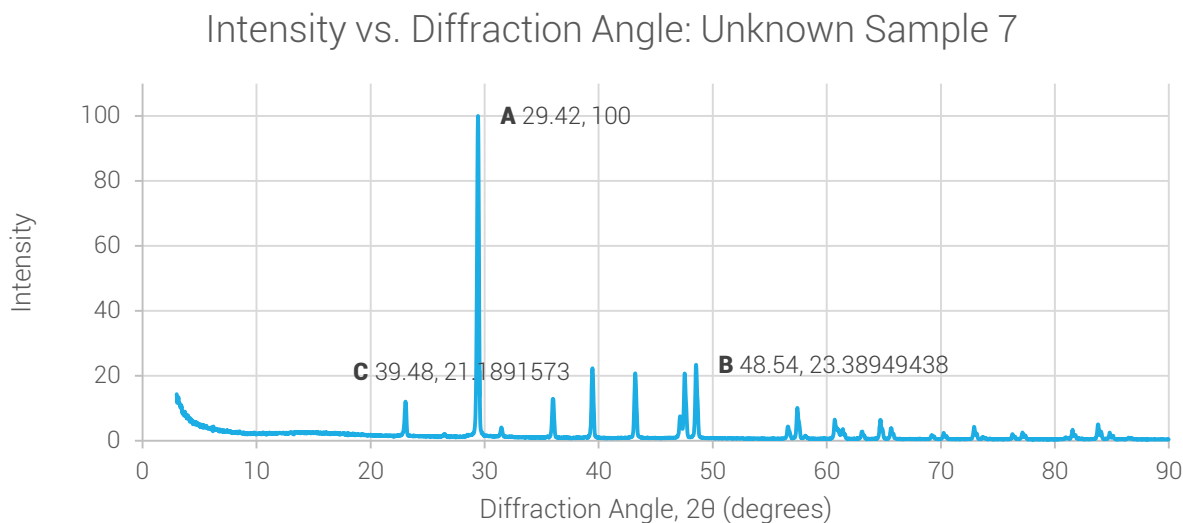
Figure 2: Intensity vs. Wavelength for X-Ray Diffraction using Unknown Sample 6. The incident wavelengths were produced by a copper tube target. Sample 6 was a stiff, white powder that packed easily into the holder. The three highest diffraction peaks were 43.06°, 62.5°, and 38.2°.

Intensity vs. Diffraction Angle: Unknown Sample 6



SAMPLE 7

Figure 3: Intensity vs. Wavelength for X-Ray Diffraction using Unknown Sample 7. The incident wavelengths were produced by a copper tube target. This sample was white and packed well into the sample holder. The three highest peaks were **A** 29.4°, **B** 48.6°, and **C** 39.4°.



DISCUSSION

Our results displayed significant peaks which we were able to use to determine the identities of the samples which we worked with. Further, we were able to determine a likely lattice structure and parameter for each of the powder samples.

DATA REDUCTION

OBSERVATIONS

My primary method for sample characterization was the three highest peaks in each sample. All the peaks in each sample were tabulated in **Table 1**, then compared by Bragg angle and Relative Intensity to the eleven PDFs provided by Ronald Gronsky in MSE 104 Lab 02: Powder Diffraction Lab Manual. After determining the corresponding PDF sample, I listed d spacings for each peak location. Below the table is more analysis regarding sample identity.

Table 1: Measured $2\theta_B$ Values and Corresponding d Spacings. These values were first observed from the plots in the data section, then compared to the PDFs provided in MSE 104 Lab 02: Powder Diffraction Lab Manual. There, each peak was compared to a known peak and the expected angles and intensities were written under those respective columns. Tabulated d spacings were found based on the best fitting PDF peak for the Sample Peak. It was clear to see from the comparisons that a correspondence of more than four peaks and a corresponding reference peak was enough to identify each sample.

Sample	Peak (2θ)	Intensity	PDF	PDF (2θ)	PDF Intensity	h k l	dÅ
3	36.8	5.47	ZnO (Hex)	36.25	"100"	1 0 1	2.4759
3	43.48	100	Copper	43.29	100	1 1 1	2.088
3	50.6	42.1	Copper	50.433	46	2 0 0	1.808
3	74.1	20.82	Copper	74.13	20	2 2 0	1.278
6	15.44	9.53	Nahcolite	14.98	"16"	1 1 0	5.91
6	18.7	15.4	Nahcolite	18.3	"25"	0 2 0	4.84
6	31.04	6.85	Nahcolite	30.42	"100"	2 1 0	3.482
6	37.76	11.3	Periclase	36.94	10	1 1 1	2.431
6	38.32	18.47	Nahcolite	39.04	"30"	2 2 1	2.305
6	43.1	100	Periclase	42.9	100	2 0 0	2.106
6	62.38	46.97	Periclase	62.3	52	2 2 0	1.489
6	74.96	4.9	Periclase	74.66	4	3 1 1	1.270
6	78.82	10.37	Periclase	78.61	12	2 2 2	1.216
7	23.02	10.3	Calcite	23.02	12	0 1 2	3.86
7	29.42	100	Calcite	29.4	100	1 0 4	3.035
7	36.04	11.82	Calcite	35.96	14	1 1 0	2.495
7	39.42	30.81	Calcite	39.401	18	1 1 3	2.285
7	43.2	20.7	Calcite	43.15	18	2 0 2	2.095
7	47.62	28.64	Calcite	47.48	17	0 1 8	1.913
7	48.54	23.38	Calcite	48.51	17	1 1 6	1.875
7	56.58	3.267	Calcite	56.55	4	2 1 1	1.62
7	57.48	8.41	Calcite	57.4	8	1 2 2	1.6094
7	61.4	3.48	Calcite	61.34	3	1 1 9	1.510
7	64.76	4.915	Calcite	64.67	5	3 0 0	1.440

Sample 3 had distinctive peaks at 43.5° , 50.8° , and 74.2° . These peaks line up only with the PDF for Copper, which has peaks at the same loci. A possible contaminant was Zinc Oxide (Hexagonal).

Similarly, Sample 6 had highest peaks at 43.06° , 62.5° , and 38.2° , which are the first three spacings listed in the PDF for Magnesium Oxide, and are unique to Periclase. Based on the unique highest peak pattern, this sample must be Periclase, but there is significant sample contamination. Additional peaks at 14° and 18° can only be caused by the other unknown Nahcolite. Other characteristic peaks of Nahcolite such as those at 30° and 34° also appear at low intensities in the Periclase sample, making Nahcolite a likely culprit.

Sample 7 had characteristic peaks at 29.4° , 48.6° , and 39.4° , the first of which is very much characteristic of Calcite, as this is the highest peak only for calcite. In total, all eleven of the sample peaks corresponded to calcite, indicating very little sample contamination. This is most likely because this was the first sample we tested.

The d-spacings listed were found from the PDFs for each sample.

In addition to the highest peaks which were already noted in the Data section, another identification method for our crystals is the spacing between peaks. Of the three samples, the two which most resembled cubic systems were Sample 3 and Sample 6. The FCC structure is generally indicated in a powder diffraction experiment by the pattern of peaks in a pair, then single, then in a pair, single again and so on.

Sample 3 had few peaks, but the peaks at 43.5° and 50.8° formed a pair and 74.2° was a separate single peak. This fits the pattern, but does not satisfy the BCC requirement of uniform evenly spaced peaks or the simple cubic regularly spaced peaks.

Sample 6 had many more peaks, but which followed a similar pattern. Because there was contamination, the contaminant peaks are italicized in the table and not taken into account for this analysis. Periclase is a FCC oxide structure, and my data gave results which look very much like FCC. Peak sets were the 37.76° and the 43.1° pair, the 62.38° single, and then the $74.96, 78.82^\circ$ pair. These peaks are consistent with the PDF, so this structure is likely correct.

Sample 7 had a rhombohedral structure instead. The peaks did not seem to be particularly correlated except for the very small peaks (which I omitted in tabulation because I had enough data with the larger peaks). These peaks seems to have a nearly triplet structure to them, with one triplet that is a large peak and two small ones on either side, then a triplet with three decreasing intensity values in succession. However, a specific pattern was difficult to determine.

Finally, the calcite peaks at 39.42° , 47.62° and 48.54° were much higher than the tabulated value, which means there may have been peak overlap here.

DATA ANALYSIS

SAMPLE IDENTIFICATION

As determined in the data reduction section, the samples were most likely Copper, Periclase, and Calcite for samples 3, 6, and 7 respectively. The d – spacings for these samples were listed in **Table 1** above, and can be justified using h k l plane descriptions resolved with the expected crystal structure.

Copper forms an FCC structure, meaning the lattice planes associated with copper powder diffraction should fit 1 1 1, 2 0 0, and 2 2 0 based off the FCC structure. This is because face centered cubic has planes across the cube diagonal, at half spacings within the cube, and at the diagonal half cube line respectively. The d spacings that we found correlate to these values with no error. This is also the case for the other samples.

By comparing the angles associated with each peak, we can confirm that Samples 3 and 6 (Copper and Periclase) are FCC and that the planes in Calcite agree with rhombohedral structure.

SAMPLE LATTICE PARAMETERS

Table 2 below is an extension of **Table 1**, indicating the probable lattice parameters of each of the samples based on the relationship between interplanar spacing and hkl for each of the specific structural systems.

In a cubic system, the structure of the relationship d_{hkl} and h, k and l is written as:

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

Where a is the lattice parameter. If we rearrange, we can find an equation for lattice spacing in terms of our known values.

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

However, in a rhombohedral system we need to use a different relationship². Calcite has an α value of 46° , which I used to calculate a.

$$\frac{1}{d_{hkl}^2} = \frac{(h^2 + k^2 + l^2) \sin^2 \alpha + 2(hk + kl + hl) \cos^2 \alpha - \cos \alpha}{a^2(1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha)}$$

Which can be re-written as

$$a^2 = d_{hkl}^2 \frac{(h^2 + k^2 + l^2) \sin^2 \alpha + 2(hk + kl + hl) \cos^2 \alpha - \cos \alpha}{(1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha)}$$

Table 2: Measured $2\theta_B$ Values and Corresponding Lattice Parameters. In this table, the values for the contaminants were omitted because the peak constructions were not close enough to confirm the contaminant species. Namely, for Nacholite, many peaks were missing which would have had higher intensities compared to those that were found as contaminants. The contaminant was likely a species which was not in one of the PDFs.

Sample	Peak (2θ)	A	PDF	PDF (2θ)	PDF a, c	h k l	dA
3	43.48	3.616522	Copper	43.29	3.6150	1 1 1	2.088
3	50.6	3.616	Copper	50.433	3.6150	2 0 0	1.808
3	74.1	3.61473	Copper	74.13	3.6150	2 2 0	1.278
6	37.76	4.210616	Periclase	36.94	4.213	1 1 1	2.431
6	43.1	4.212	Periclase	42.9	4.213	2 0 0	2.106
6	62.38	4.211528	Periclase	62.3	4.213	2 2 0	1.489
6	74.96	4.212113	Periclase	74.66	4.213	3 1 1	1.270
6	78.82	4.212348	Periclase	78.61	4.213	2 2 2	1.216
7	23.02	4.989, 17.06	Calcite	23.02	4.989, 17.062	0 1 2	3.86
7	29.42	15.99023	Calcite	29.4	4.989, 17.062	1 0 4	3.035
7	36.04	22.24051	Calcite	35.96	4.989, 17.062	1 1 0	2.495
7	39.42	6.039622	Calcite	39.401	4.989, 17.062	1 1 3	2.285
7	43.2	16.5973	Calcite	43.15	4.989, 17.062	2 0 2	2.095

7	47.62	11.99724	Calcite	47.48	4.989, 17.062	0 1 8	1.913
7	48.54	25.84508	Calcite	48.51	4.989, 17.062	1 1 6	1.875
7	56.58	22.30156	Calcite	56.55	4.989, 17.062	2 1 1	1.62
7	57.48	9.232678	Calcite	57.4	4.989, 17.062	1 2 2	1.6094
7	61.4	11.65526	Calcite	61.34	4.989, 17.062	1 1 9	1.510
7	64.76	24.90328	Calcite	64.67	4.989, 17.062	3 0 0	1.440

LATTICE PARAMETER ERRORS

Interestingly, the lattice parameter error for the cubic system is relatively small, but the error decreases with increasing 2θ . This may be because the increased diffraction angle will absorb more of the error when computing values, due to the squared relationship between diffraction angle and lattice parameter. My values for the rhombohedral crystal oscillated, likely because the system would fit better under the hexagonal structure. However, the PDF sheet claimed rhombohedral, so I showed data using a rhombohedral calculation. The formula for a hexagonal system would be²:

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

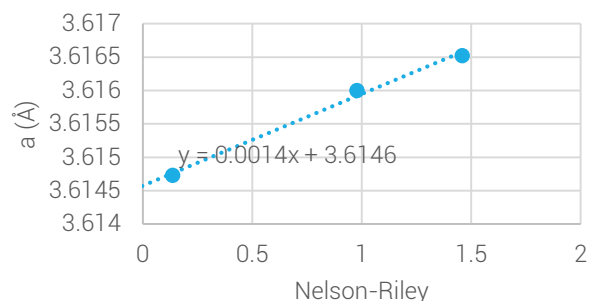
From which it is possible to solve for a/c . This ratio will end up being 3.9190 on average, from which we can plug in the 3 0 0 value to get $9/a^2$, solve for a^2 , from which we get 4.32. Then, we multiply this value by our ratio and get 16.930. The actual value is closer to 17, but this is one way to try to solve for the value.

NELSON–RILEY FUNCTION AND CUBIC CRYSTALS

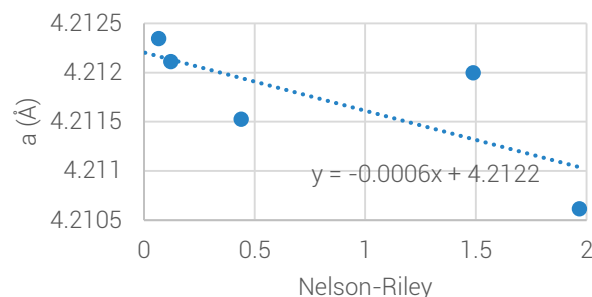
It is possible to determine a more exact value of a using the Nelson–Riley function to find the cubic lattice constant a_0 . Here, I have plotted a in the Nelson–Riley function for my two cubic systems (Sample 3 and 6).

Figure 3: Nelson – Riley function vs. lattice parameter in cubic samples. **A** Sample 3 **B** Sample 6. The a_0 value determined by plotting these points gives us the most accurate value of a . These values were 3.6146 Å for sample 3 and 4.2122 Å for Sample 6, which agree strongly with the values on the PDFs. In each case, reducing the error of the closest value by 0.008%.

A Sample 3



B Sample 6



POSSIBLE CONTAMINANTS

I was not able to satisfactorily determine the contaminants in my sample because the highest peaks did not significantly match up. However, I have hypothesized that Sample 3 may have been contaminated with Zinc Oxide (Hexagonal) or a Copper Oxide (for which we do not have a PDF). Sample 6 may have been contaminated with Nahcolite, however the 100% intensity peak for Nahcolite was not seen, indicating the actual contaminant may have been a species not in the provided PDF files.

Sample 7 did not appear to have any contamination.

ERROR SOURCES

In this lab, sources for error were primarily in the cleaning of the sample holder. When the sample holder was cleaned, possible contamination could have occurred.

The other error had to do with the sample packing. Sample 3, determined to be copper, packed loosely despite careful packing and smoothing, and ultimately fell out of the holder somewhere near the end of that particular experiment. Because it is hard to tell the angle at which the sample fell out, it is unclear how many of the peaks presented were a result of the sample holder diffraction or unusual packing/ motion. This may explain the unexpected peak at the higher degrees for sample 3.

CONCLUSIONS

From this lab we can conclude that our three samples, 3, 6, and 7, were Copper, Magnesium Oxide, and Calcium Carbonate respectively.

Further, we have shown that the structures of these samples were Cubic, Cubic and Rhombohedral respectively based on the diffraction peak spacing for each sample, with lattice parameters of roughly 3.61 Å and 4.21 Å for samples 3 and 6, and about $c = 17$ Å and $a = 4.6$ Å for sample 7.

REFERENCES

¹ R. Gronsky. Lab 02 Manual: Powder Diffraction. *MSE 104*. University of California Berkeley, Berkeley, CA.

² B.D. Cullity and S.R. Stock, Elements of X-Ray Diffraction, 3rd Edition, Prentice-Hall, New York, (2001), Appendix 3, p. 619.

APPENDIX

Overflow materials should appear here. Examples include extra data runs, problematic data (such as interrupted data runs), copies of pertinent literature or other documentation, computer source code listings, or derivations of equations.

No additional Information was required.