Name :	SID :	Course : CHEM 481
E-mail :	Cell :	Instructor : Dr. Upali
Title: POWDER X-RAY DIFFRACTION (PXRD)		

Purpose

The primary aim of this laboratory assignment is to gain further background in the theory and applications of x-ray crystallography by performing powder x-ray diffraction on rock salt NaCl.

Introduction

X-ray crystallography is a technique based on the diffraction of x-rays passing through crystal structures. X-rays, which have a proper wavelength in the Angstrom range ($\sim 10^{-10}$ m), are scattered into a diffraction pattern by the electron cloud of molecules or atoms within the crystal sample under analysis. Once a diffraction pattern is obtained from the scattering of x-rays off a crystal, one can extrapolate the electron density and atomic geometry of the sample. A model is constructed using the data and experimental electron density and then refined to obtain an accurate molecular structure.

Miller indices are often used in x-ray crystallography to indicate the location of planes along crystallographic axes and within unit cell dimensions. A generic Miller index is denoted by (*hkl*). Miller indices are found by determining the intercepts of the face along the crystallographic axes in unit cell dimensions, taking their reciprocals, clearing fractions, and reducing the final result to lowest terms to obtain the (*hkl*) values. The *h* value is the reciprocal of the x-intercept, *k* value is the reciprocal of the y-intercept, and the *l* value is the reciprocal of the z-intercept. When a plane is parallel to an axis, its intercept is at infinity and its Miller index is zero. Some planes have negative intercepts in which the negative number is denoted by a bar above the number. If a Miller index is zero, the plane is parallel to that axis. Furthermore, a smaller Miller index indicates that the plane is parallel to the axis. On the other hand, a larger Miller index is the result of a nearly perpendicular plane to the axis.

Diffraction is the interference between waves that occurs as a result of an object in their path (Shriver, 169). In x-ray crystallography, the diffraction of x-rays through the closely spaced lattice of atoms or ions in a crystalline sample is based on Bragg's law. The equation of Bragg's Law is the following: $n\lambda = 2d\sin\theta$, where d is the distance between atomic layers in a crystal, □ is the wavelength of the incident x-ray beam source (□ Cu ~ 1.5 A), and *n* is an integer with a value that is often 1. Bragg's law is often used to describe the interference pattern of x-rays scattered by crystals and can indicate the angle at which constructive interference occurs between waves of wavelength □. The intensity of x-ray diffraction depends on the details of the crystal structure and the identities of the atoms present in the closely spaced lattice. Heavier atoms in the sample tend to diffract incident x-rays at higher intensities. Therefore, the

measurements of diffraction angles and intensities enable one to ultimately derive the structure of the sample.

In X-ray crystallography, the two principal x-ray techniques are single-crystal diffraction and powder diffraction. In single-crystal diffraction, the compounds are studied in the form of a single crystal with dimensions of several micrometers or larger. Many complicated inorganic and organometallic compounds such as fullerenes and metalloporphyrins have been analyzed using the single-crystal method. In single-crystal diffraction, the diffraction data is collected using a laboratory-based four-circle or area detector diffractometer. The four-circle diffractometer uses a scintillation detector, which measures the diffracted X-ray beam intensity as a function of four angles (Shriver, 172). Since the diffraction pattern is simply the Fourier transform of the electron density in the crystal, the experimental diffraction data is then transformed back to the three-dimensional array of atoms for structure determination. Although single-crystal diffraction has been once thought to be a formally complex process involving the analysis of thousands of reflections and corresponding intensities, the advancement of technology and computational software has enable x-ray crystallographers to obtain structure determination of small inorganic molecules with ease.

In the powder diffraction method, a crystalline material is analyzed for phase identification and determination of lattice parameters and lattice type. When an X-ray beam strikes a polycrystalline sample, the x-rays are scattered in all possible directions. Then, each plane of atoms separated by different lattice spacing in the crystal resulting in a cone of diffraction intensity. In each cone, there is a set of closely spaced dots, which represents diffraction from a single crystallite within the powder sample. A diffraction cone may be formed with very large number of crystallites by joining all the dots. Powder X-ray diffraction data is not entirely useful for analysis unless there is a way to determine the positions of the various diffraction cones. Fortunately, a photographic film (Debye-Scherrer method) or a detector sensitive to x-ray radiation can be used to make sense of the diffraction cones using the data. In either case, the diffraction angle, □, of the various diffraction cones is determined. A powder diffractometer uses an x-ray detector to measure the positions of the diffracted beams. The detector scans around the sample along the circumference of a circle cutting through the diffraction cones at varying diffraction maxima while the intensity of the x-rays detected is recorded as a function of the detector angle. The effectiveness of powder X-ray diffraction has made it the major technique for the characterization of polycrystalline, solid inorganic materials (Shriver, 170). Furthermore, sample preparation for powder X-ray diffraction is relatively easy and the test itself is often rapid and non-destructive. A plethora of powder diffraction data sets collected from inorganic, organometallic, and organic compounds over the past decades have been compiled into a database

by the Joint Committee on Powder Diffraction Standards (JCPDS). This database contains several thousand unique powder X-ray diffraction patterns and serves as a fingerprint library to identify an unknown materials based solely on its powder pattern. Some applications of powder X-ray diffraction include the following: identification of unknown materials, determination of sample purity, determination of lattice parameters, determination of crystallite size, determination of phase changes, and determination of structure refinement (Shriver, 171). The emphasis of this lab activity will be on powder X-ray diffraction.

Procedure

Rock salt or NaCl was grinded to a fine powdered sample for analysis using powder X-ray diffraction. The diffraction pattern was obtained using a well-defined procedure on how to operate the instrument (Appendix A). The sample was scanned by the diffractometer at a set range of angles from 2-79 degrees. Once the diffraction pattern of NaCl was obtained, the experimental diffraction pattern was compared with similar compounds using the search/match program (Appendix A). The last step was to determine the unit cell of the compound by using treor auto indexing to select at least five peaks from the experimental spectrum. The list of operations for auto indexing is also found in Appendix A.

Results

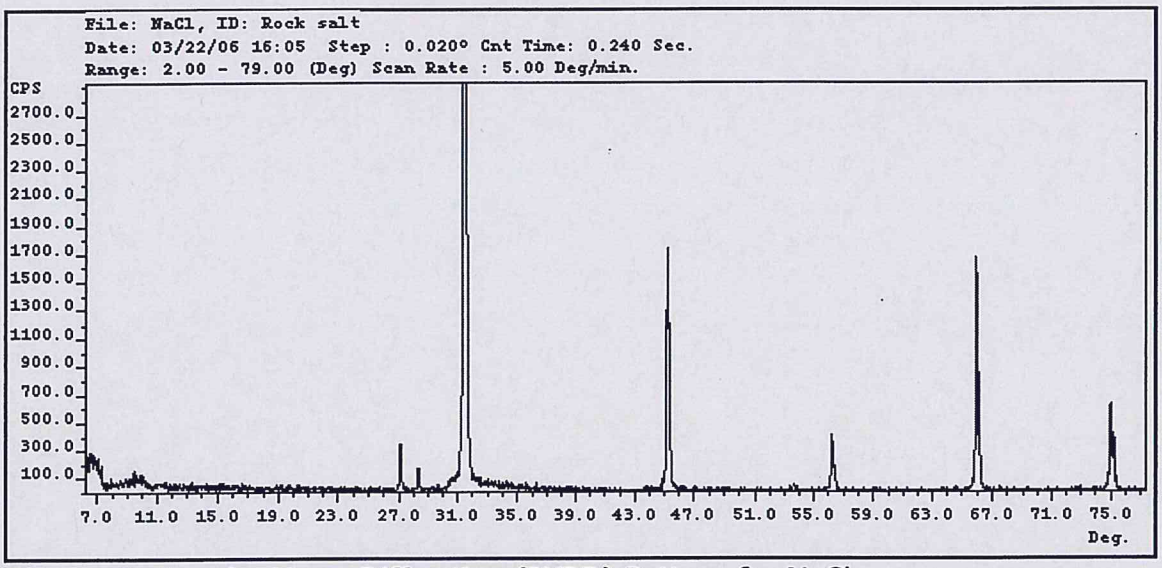

Figure 1: Powder X-ray Diffraction (PXRD) Pattern for NaCl

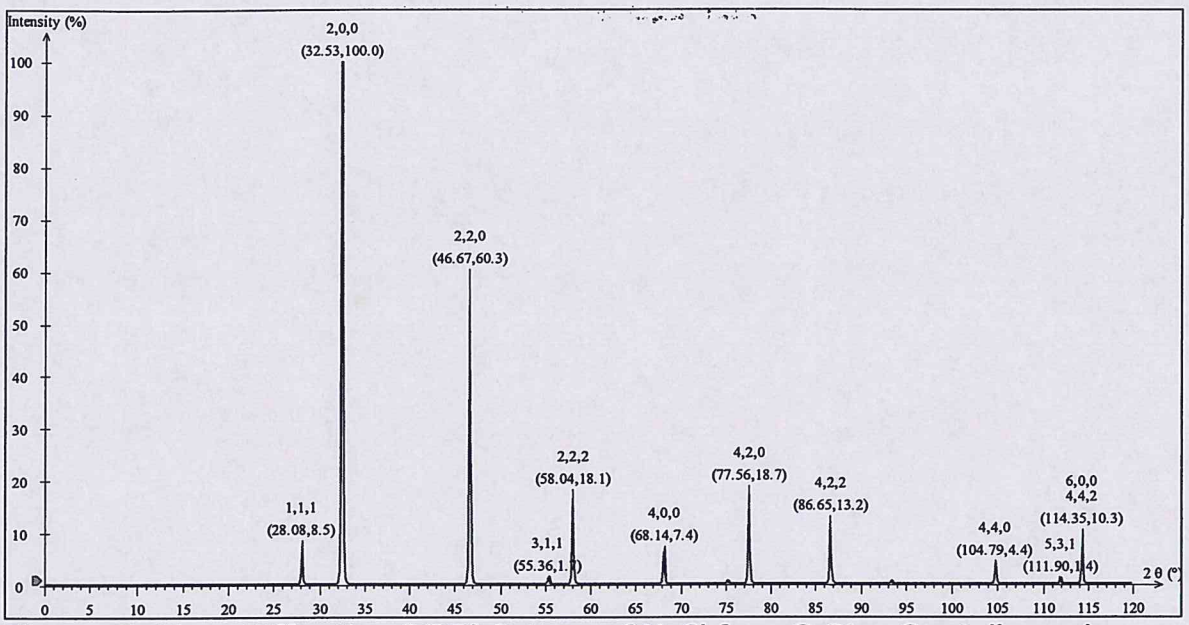

Figure 2: X-ray Diffraction (XRD) Pattern of NaCl from CaRine Crystallography Software

\colortbl\red0\green0\blue0;\red255\green0\blue0;}
\deflang1033\pard\plain\f3\fs20
\par P-E WERNER'S TREOR90\plain\f3\fs20\cf0
\par FOR PC SYSTEMS
\par 27.135630 146
\par 31.489370 154
\par 31.700000 1589
\par 45.223750 1617
\par 66.009380 580
\par STOP LIMITS
\par FIGURE OF MERIT REQUIRED= 100
\par MAX NUMBER OF UNINDEXED LINES IN FIGURE OF MERIT TEST= 1
\par THE 7 FIRST LINES ADJUSTED BY THEIR HIGHER ORDERS
\par CUBIC,TETRAGONAL,HEXAGONAL AND ORTHOROMBIC SYMMETRY
\par MAX CELL EDGE= 10.0 MAX CELL VOLUME= 300.0
\par D1= .000200 SSQTL= .050000 D2= .000400 WAVE= 1.540598
\par NUMBER OF TEST LINES= 5 IQ REQUIRED= 2
\par

\par \plain\f3\fs20\cf1 ** CUBIC TEST
**********\plain\f3\fs20\cf0
\par MAX. VOLUME= 300.
\par SELECTED BASE LINES (1) (2)
\par BASE LINE ONE.(HKL)-MAX= 4 4 4 MAX H+K+L= 6
\par
\par
\par CYCLE RESULTS
\par
\par .018385 .000000 .000000 .000000 .000000 .000000
\par .018385 .000000 .000000 .000000 .000000 .000000
\par .018385 .000000 .000000 .000000 .000000 .000000
\par NUMBER OF SINGLE INDEXED LINES = 2
\par TOTAL NUMBER OF LINES = 5
\par A = 5.680994 .004655 A ALFA = 90.000000 .000000 DEG
\par B = 5.680994 .004655 A BETA = 90.000000 .000000 DEG
\par C = 5.680994 .004655 A GAMMA = 90.000000 .000000 DEG
\par UNIT CELL VOLUME = 183.35 A**3
\par H K L SST-OBS SST-CALC DELTA 2TH-OBS 2TH-CALC D-OBS
INT(CPS)
\par 1 1 1 .055035 .055156 -.000121 27.136 27.166 3.2835 146
\par 2 0 0 .073631 .073541 .000090 31.489 31.470 2.8388 154
\par .074594 31.489 2.8204 1589
\par .147830 31.700 2.0034 1617
\par .296706 45.224 1.4142 580
\par NUMBER OF OBS. LINES = 5
\par NUMBER OF CALC. LINES = 2
\par M(5)= 94 AV.EPS.= .0001054
\par F 5 = 14.(.025048, 15)
\par M CF. J.APPL.CRYST. 1(1968)108
\par F CF. J.APPL.CRYST. 12(1979)60
\par 3 LINES ARE UNINDEXED
\par M-TEST= 94 UNINDEXED IN THE TEST= 3
\par NUMBER OF SINGLE INDEXED LINES = 2
\par TOTAL NUMBER OF LINES = 5
\par A = 5.680994 .004655 A ALFA = 90.000000 .000000 DEG
\par B = 5.680994 .004655 A BETA = 90.000000 .000000 DEG
\par C = 5.680994 .004655 A GAMMA = 90.000000 .000000 DEG
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\par H K L SST-OBS SST-CALC DELTA 2TH-OBS 2TH-CALC D-OBS
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\par F CF. J.APPL.CRYST. 12(1979)60
\par 3 LINES ARE UNINDEXED
\par M-TEST= 94 UNINDEXED IN THE TEST= 3
\par
\par

Figure 3: Auto Indexing of Sample to Determine Unit Cell Parameters

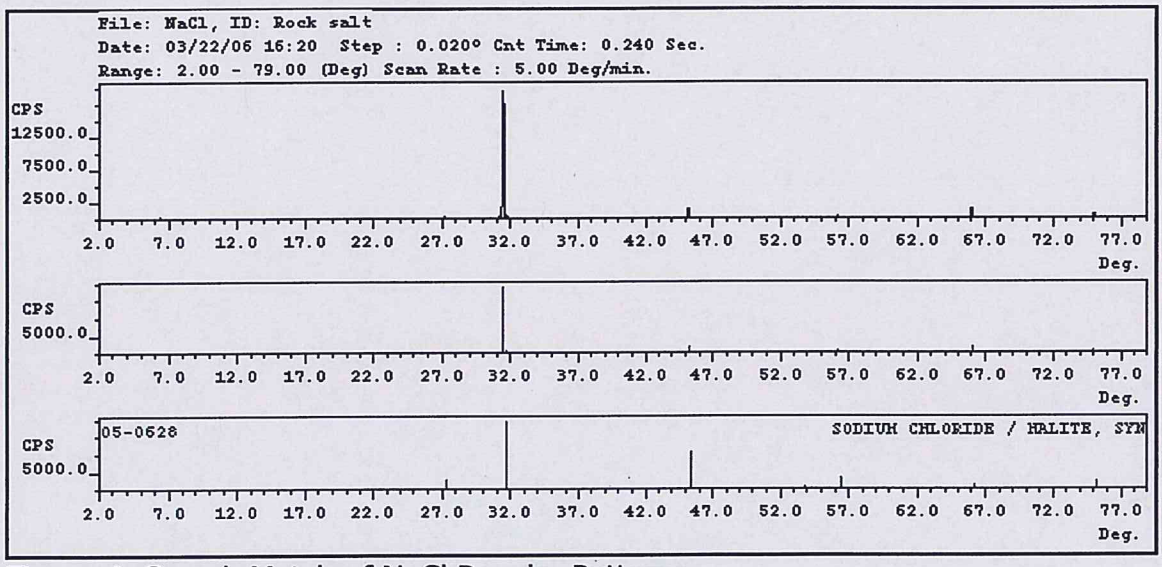


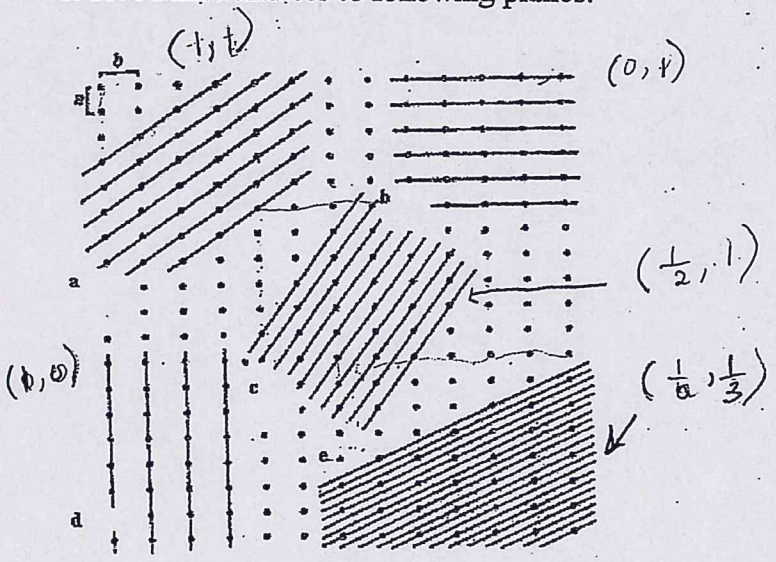
Figure 4: Search Match of NaCl Powder Patterns

Conclusion

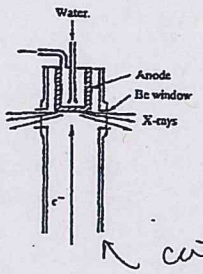
A majority of the peaks in the diffraction pattern of NaCl taken by powder X-ray diffraction did match with the previous diffraction pattern obtained from the CaRine Crystallography software. Furthermore, the auto indexing of the experimental data confirmed that NaCl has a cubic lattice system based on the calculated unit cell parameters.

The following figures show experimental x-ray diffraction patterns of cubic SiC using X-ray synchrotron radiation.

1. Give Miller indices to following planes:



2. How is X-ray produced?

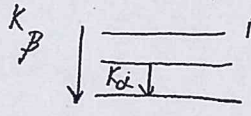


↖ cathode rays are bombarded on surface causing emission of X-rays.

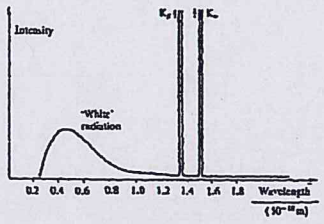
3. What are K_α and K_β lines how are they separated to get monochromated radiation?

K_α : L → K

K_β : M → K



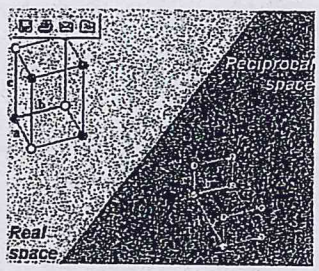
valence shells



* must separate to get monochromatic radiation a filter is applied by taking the atom with one less atomic number.

4. What's real space and reciprocal space in X-ray crystallography? How is it different from each other?

Real space is the the unit cell parameters. Reciprocal space, on the other hand, is the reciprocal dimensions of the unit cell dimensions to yield miller indices.



5. How you get the cubic cell dimensions from its reciprocal cell dimensions?

The real space cubic cell dimensions are obtained by taking the inverse of the reciprocal cell dimensions.

6. Obtain a powder diffraction pattern for NaCl and compare it with the one you calculated in the previous lab.

The powder diffraction pattern for NaCl have several peak intensities which closely match with those obtained from the x-ray diffraction pattern of the

7. Index the powder diffraction pattern for NaCl and compare it with the indexing you calculated last week.

Calme soft

PXRD: $a = b = c = 5.68$ Å

$\alpha = \beta = \gamma = 90.0°$

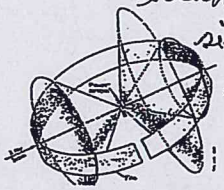
XRD from software:

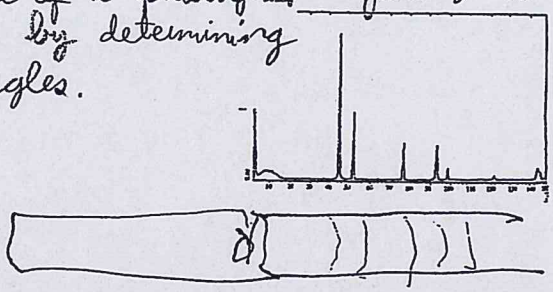
$a = b = c = 5.5$

$\alpha = \beta = \gamma = 90.$

8. Discribe how Debye-Scherrer powder diffraction is related to modern CPS vs. 2θ plots.

although the Debye-Scherrer powder diffraction technique involves the use of a photographic film, it works similarly to a detector by determining the diffraction angles.





9. A Debye-Scherrer powder diffraction experiment using incident copper Kα raditation (λ, of 1.5418 Å) gave the following set of reflections expressed as 2θ: 38.40°; 44.50°; 64.85°; 77.90°; 81.85°; 98.40°; 111.20°.

2(θ)	(θ)	sin(θ)	$\sin^2(\theta)$	$K\sin^2(\theta)$	$h^2+k^2+l^2$	hkl	a
38.4	19.2	0.3288666	0.10815324	2.952583468	3	111	3.24
44.5	22.25	0.3786486	0.14337476	3.91413101	4	200	3.32
64.85	32.425	0.5361952	0.28750529	7.848894485	8	220	3.26
77.9	38.95	0.628642	0.39519076	10.78870786	11	311	3.25
81.85	40.925	0.6550706	0.42911749	11.7149075	12	222	3.28
98.4	49.2	0.7569951	0.57304158	15.64403517	16	400	3.29
111.2	55.6	0.8251135	0.68081229	18.58617546	19	331	3.28

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

2θ

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

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

$$a = \sqrt{\frac{1.54(3)}{4(0.11)}}$$

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

λ = 1.54 Angstroms W = 180mm (Now assign whole numbers)

S_1 (mm)	θ	$\sin^2\theta$	$A\sin^2\theta$	$h^2+k^2+l^2$	hkl	a(Å)
38	19.0	0.11	3.0	3	111	4.05
45	22.5	0.15	4.1	4	200	4.02
66	33.0	0.30	8.2	8	220	4.02
78	39.0	0.40	10.9	11	311	4.04
83	41.5	0.45	12.3	12	222	4.02
97	49.5	0.58	15.8	16	400	4.04
113	56.5	0.70	19.1	19	331	4.03
118	59.0	0.73	19.9	20	420	4.04
139	69.5	0.88	24.0	24	422	4.01
168	84.0	0.99	27.0	27	511	4.03

Multiply by 27.3 in this case

θ	$\sin^2\theta$	$K\sin^2\theta$	$h^2+k^2+l^2$	hkl
2.46				
1				
1.4				

a) calculate the indices for each reaflection

b) Calculate the lattice constant, a.

c) Calculate the density of this element which has an atomic weight of 66.6 g/