

X-Ray Diffraction and X-Ray Fluorescence of Rutile and Associated Structures

Experiment #2

Characterization of Materials (96.445/545)

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Data Acquired Sept.29, 2009 and Sept 30, 2009

Written Oct. 1, 2009

Objective

The purpose of this lab is to identify metal oxide compounds, and to determine their crystal structure (mixture) and lattice parameters, in particular, to determine the lattice constants of rutile structures.

Experimental Equipment

The experimental equipment used for this lab included:

- Powdered metal oxide samples Number 8 and Number 9
- The inXitu BTX system of hardware and software
- The X Powder software on the laboratory computer

The BTX system and X Powder software were described in detail in the last lab report.

Procedure

1. Sample Preparation

The samples were already prepared by the instructor, and labeled with a number so that their chemical composition was indeterminate from visual assessment. To be compatible with the BTX, the sample has to be dry, small enough to pass through a 150 micrometer sieve, and large enough to not stick together and to convect inside the sample holder. At least 15 micrograms are needed in the sample holder.

2. Loading the BTX specimen holder

We turned on the BTX, removed the sample holder (already cleaned), and began to load the samples into the specimen holder using the shake option. This step took the longest amount of time, and at the end of the laboratory, we were unable to load the specimen holder with the equipment provided and following the instructions provided to acquire data with sufficient signal-to-noise for post-processing. The main problem that we had was the powder kept caking into little balls and getting stuck at the top of the vile on the BTX specimen holder. This was probably due to a) humidity, b) clumping already existing in the provided specimen, and c) the ultrasound shake contributing more to caking than to loading.

3. Acquire exposures.

First we tried Number 8, but didn't get quality data. So then we did Number 9. After acquiring data for Number 9, we tried Number 8 again. In both cases, the XRF data identified Ti, so we concluded that the compounds were both TiO_2 .

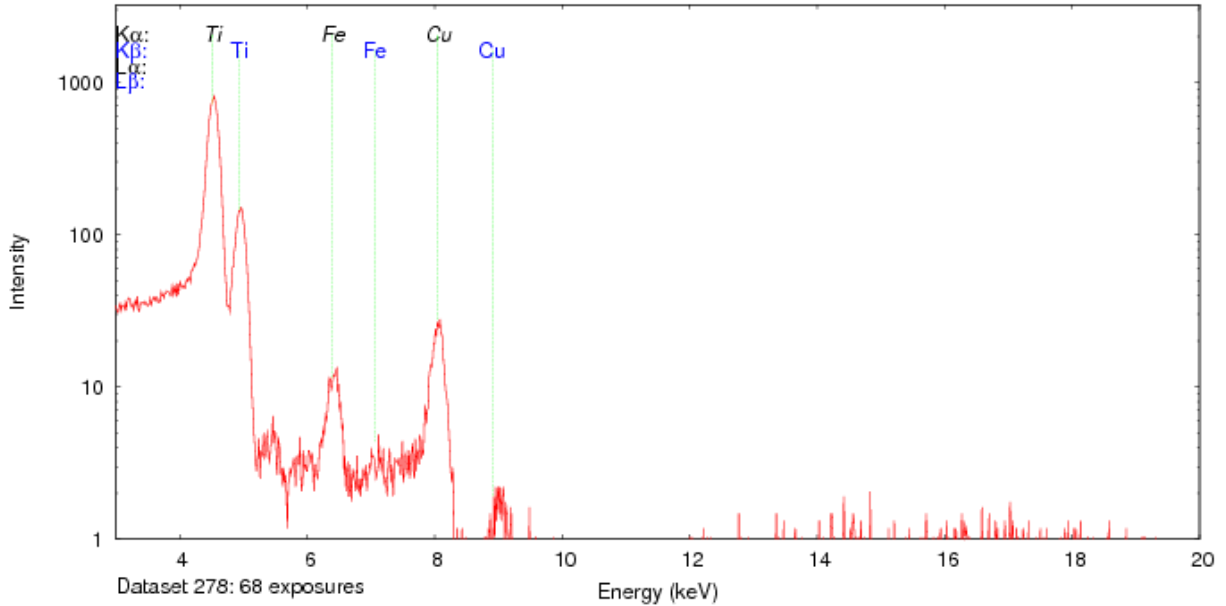
4. Save Exposures and Data

We saved the data to disk even though the data weren't good enough to post-process.

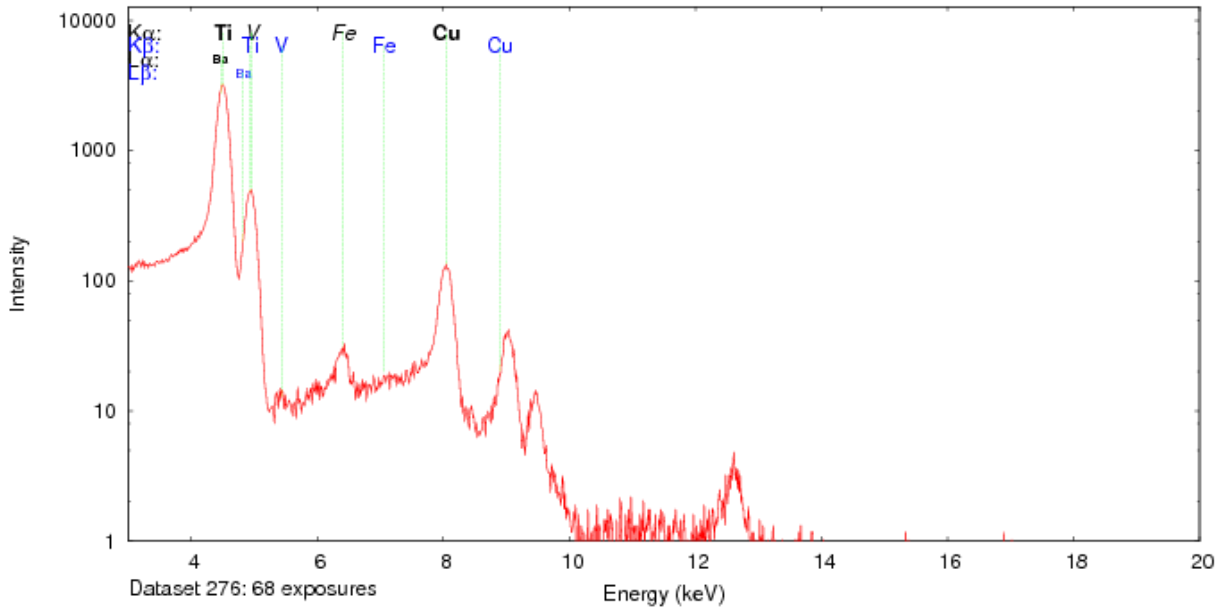
Results and Discussion

Elements identified with X-Ray fluorescence

The BTX software identified the Titanium in the compounds. We were told they were TiO_2 was the only compound being used for this lab experiment that contained Titanium.



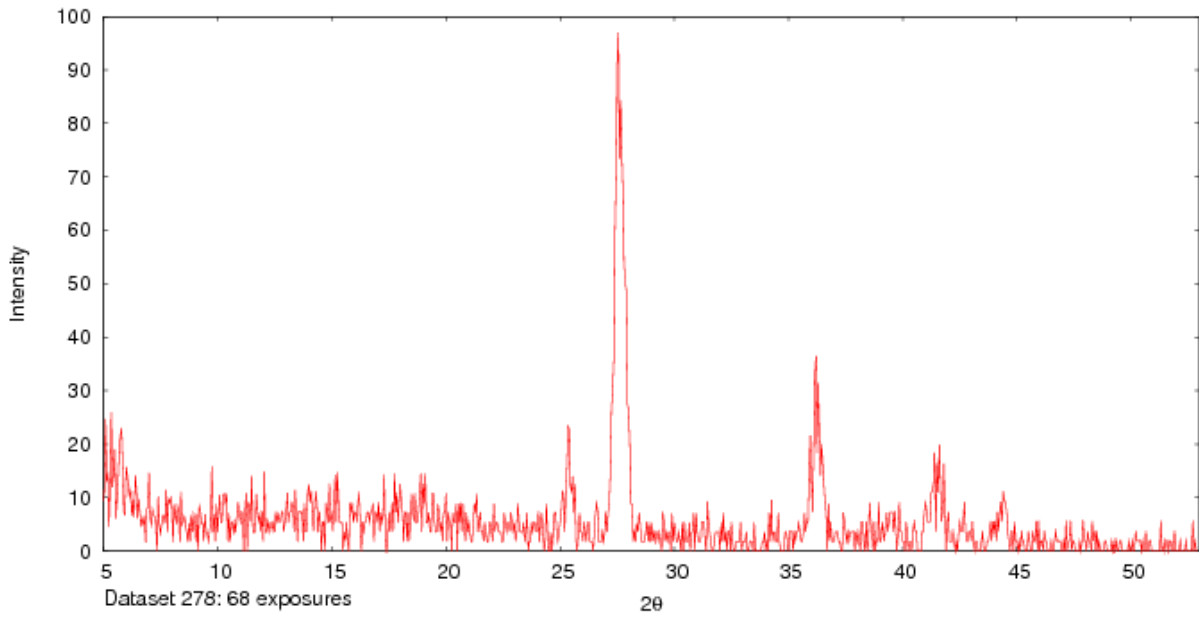
Sample Number 8 XRF Plot identifies Ti.



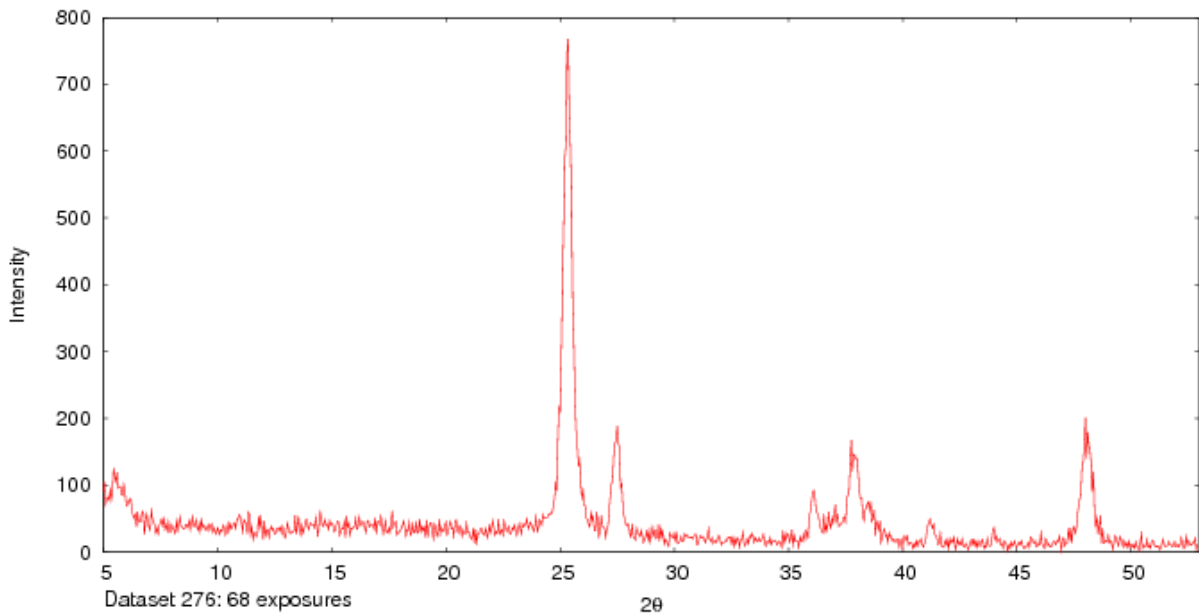
Sample Number 9 XRF Plot identifies Ti.

Data Acquired September 29, 2009

Shown in the figures below, the data acquired September 29 was too noisy to process.



Sample Number 8 XRD Plot has too much noise.



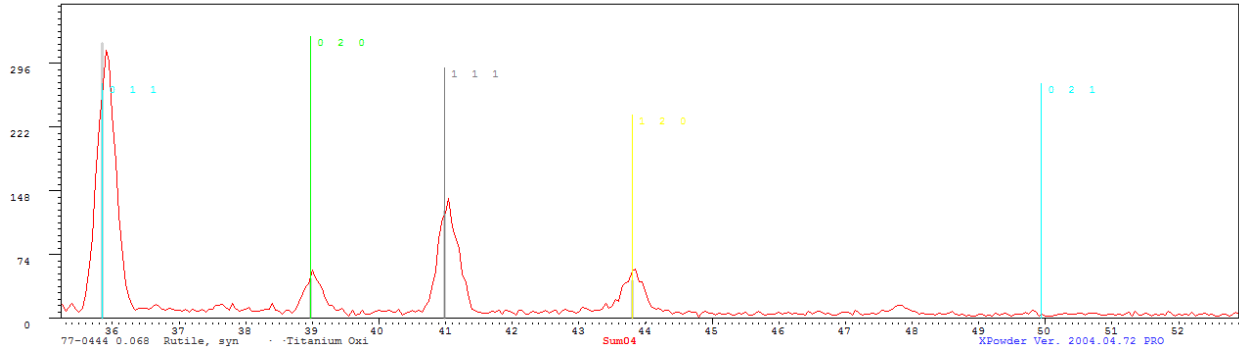
Sample Number 9 XRD Plot has too much noise.

Data Acquired September 30, 2009

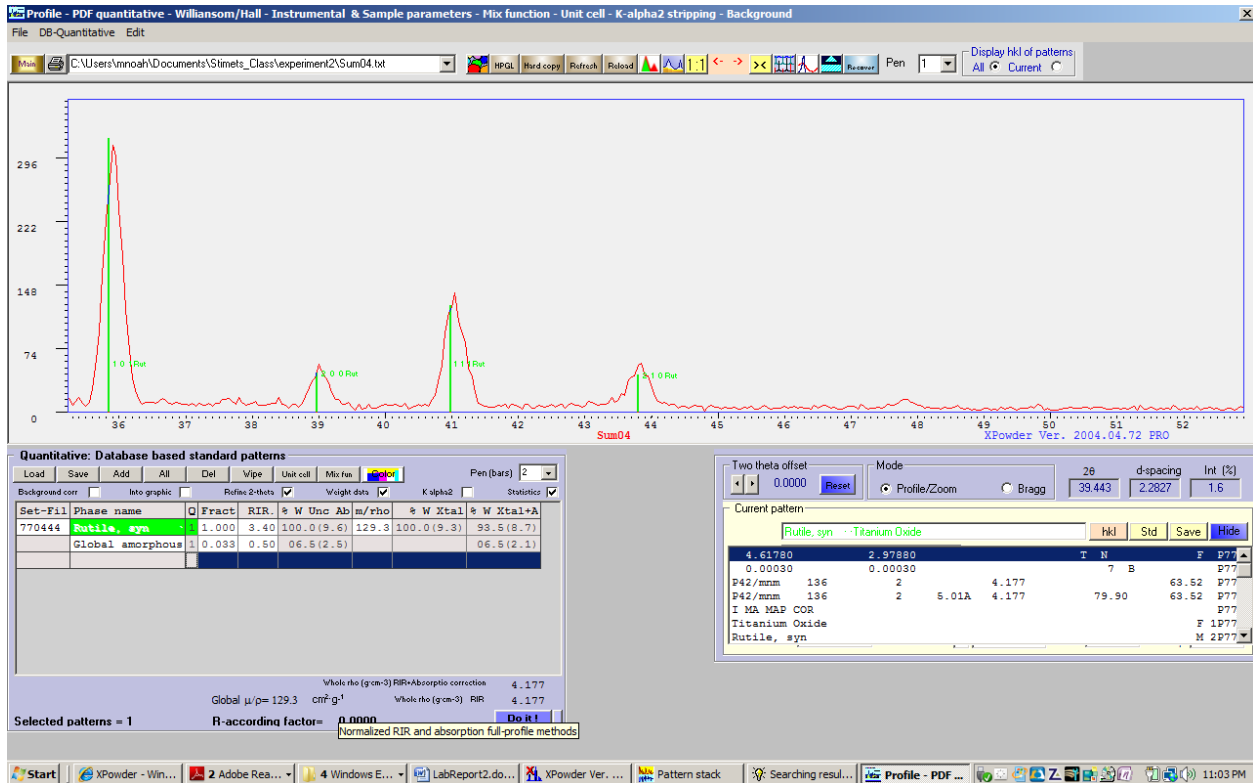
The PDF2 and AMSCD databases were described in the last lab report. Both databases identified the sample as being 100% rutile.

PDF2 Database

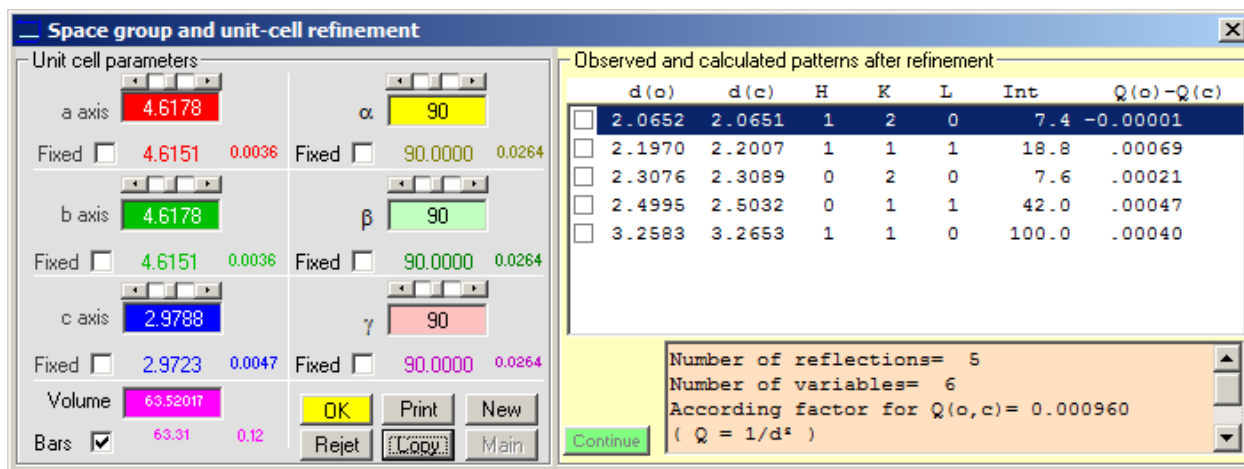
Using a supervised search in XPowder, the data acquired on September 30 (by Dr. Stimets and Hongmei Chen) showed. Using the PDF2 database, the first hit '770444 0.068 Rutile, syn Titanium Dioxide' structure was selected. The sample was determined to be 100% rutile.



PDF2 database search Bragg planes.



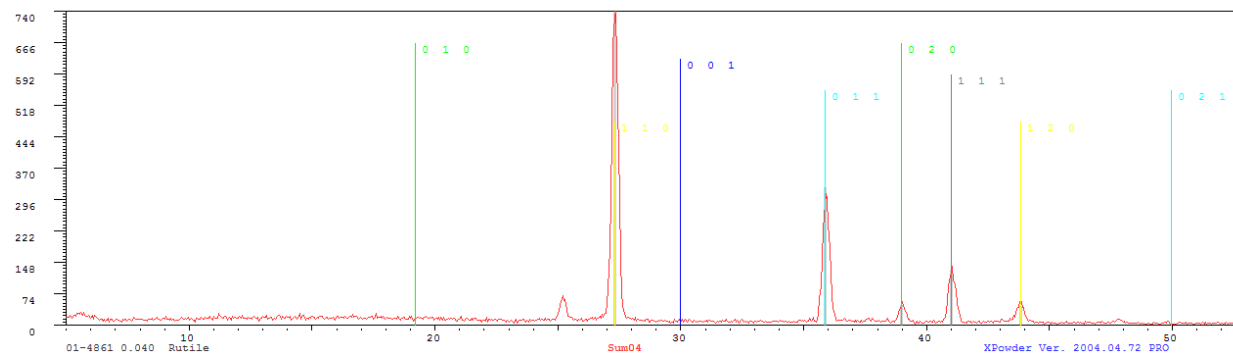
PDF2 database search quantitative analysis screen.



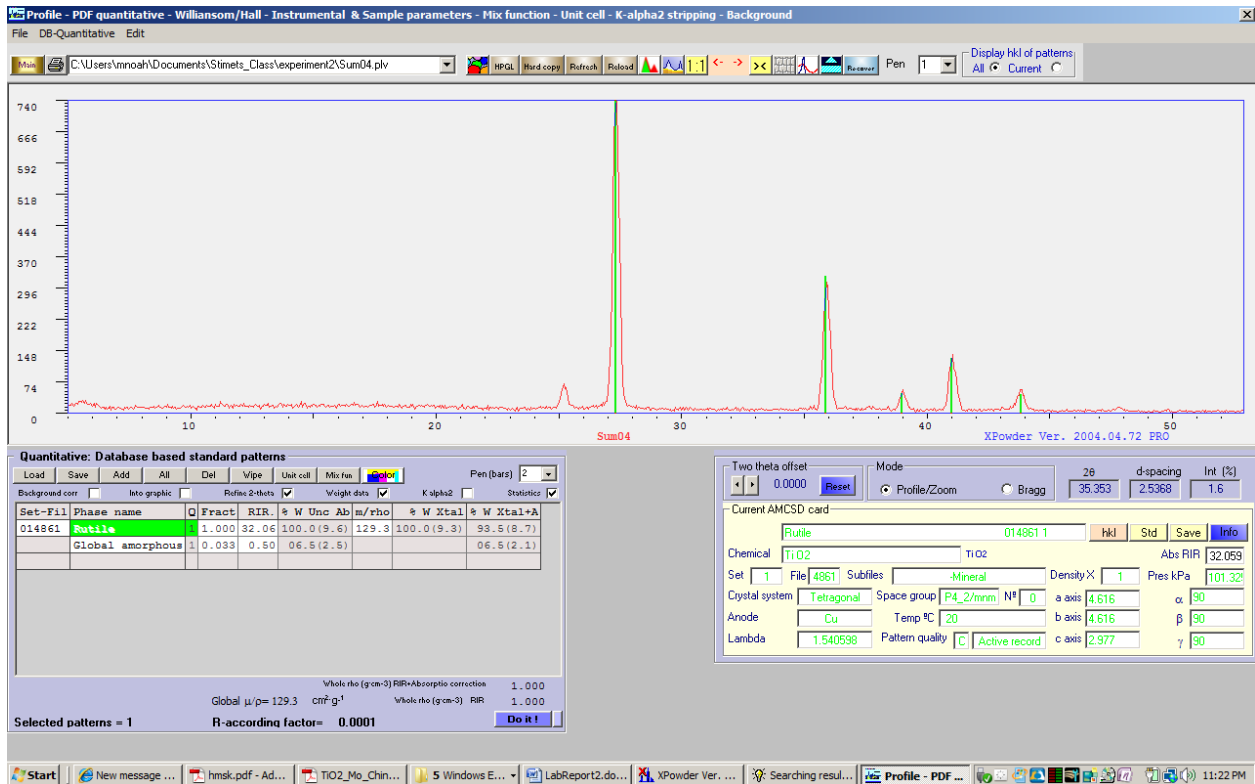
PDF2 database search space group and unit cell parameters.

AMSCD Database

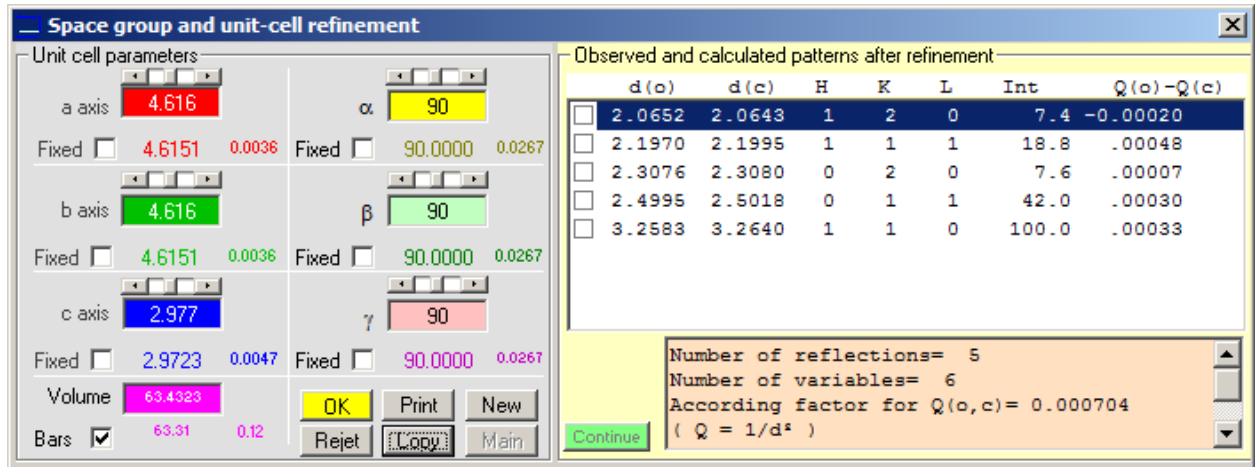
Using the AMSCD Database, the sample was determined to be 100% rutile TiO₂. The first hit record, 014861 0.040 was used to find the lattice parameters and peak intensities.



AMSCD database search Bragg planes.



AMSCD database search quantitative analysis screen.



AMSCD database search space group and unit cell parameters.

Modeling Peak Intensities

The rutile structure belongs to the P42/mmm tetragonal space group. The unit cell is defined by the lattice vectors a and c and contains two TiO₂ units with Ti ions at (0, 0, 0) and (1/2, 1/2, 1/2) and O ions at ±(u, u, 0) and ±(1/2+u, 1/2-u, 1/2) (Ma, 2007). From the lattice parameters, the plane spacing can be found from:

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

The X-Ray peak positions are given by:

$$\theta = \arcsin\left(\frac{\lambda}{2d}\right)$$

These are found automatically by X Powder and reported above. The peak intensities can be used to find the best fit value for u, hence to measure u.

The form factors involve a charge transfer parameter that is fit to the peak intensities and provides information about how the electrons in the valence are shared in the bonds:

$$f_{Ti} = \frac{(20 - 2 * C_{\text{charge-transfer}}) \sin \theta}{\lambda} \quad \text{and} \quad f_O = \frac{(12 + * C_{\text{charge-transfer}}) \sin \theta}{\lambda}$$

The Lorentz and Polarization factor, slightly different from those given in class (are given by:

$$L(\theta) = \frac{1}{\sin 2\theta \cos \theta} \quad P(\theta) = \frac{1}{2}(1 + \cos^2 \theta)$$

The Multiplicity factor is found from:

$$\text{Multiplicity} = \begin{cases} 4 & h = k \text{ or } h = 0 \text{ or } k = 0 \text{ and } l = 0 \\ 8 & h \neq k \text{ and } h \neq 0 \text{ and } k \neq 0 \text{ and } l = 0 \\ 8 & h = k \text{ or } h = 0 \text{ or } k = 0 \text{ and } l = 1 \\ 16 & h \neq k \text{ and } h \neq 0 \text{ and } k \neq 0 \text{ and } l = 1 \end{cases}$$

The Structure Factor is:

$$S(hkl) = f_{Ti} \left\{ 1 + e^{-\pi i(h+k+l)} \right\} + f_O \left\{ e^{-2\pi i(-hu+ku)} + e^{-2\pi i(-hu-ku)} + e^{-2\pi i(h(0.5+u)+k(0.5-u)+l/2)} + e^{-2\pi i(-h(0.5+u)-k(0.5-u)+l/2)} \right\}$$

A fitting function that optimizes u given measured peak intensities was written in MATLAB and the codes are attached. Without including the temperature factor, the fitting function could not fit all 5 peaks. Including the following temperature factor, with fit parameter B that characterizes the magnitude of thermal displacements, a very good fit was achieved.

$$TF(\theta) = e^{-2M(\theta)} \quad M(\theta) = \frac{B \sin^2 \theta}{\lambda^2}$$

The tables below show the modeled peak positions and intensities, and compares them to measured peak intensities found in X Powder. The third lattice parameter u was found to be 0.313493 using 5 peaks, the charge exchange was -0.0012e, and the temperature parameter was 19.8682.

Modeling Peak Intensities (fit to data) $u=0.313493$

Lambda=1.540560 Angstroms a=4.615100 c=2.972300 Angstroms u=0.313493

(h, k, l)	M	d(Ang)	T(Deg)	fTi	fO	nfTi	nfO	S(hkl)	LP(T)	Intensity
(1 1 0)	4	3.26337	27.31	3.37	1.23	2.00	0.60	7.48	8.98	2010.3
(0 1 1)	8	2.49889	35.91	4.40	1.60	2.00	-1.55	6.32	5.27	1682.5
(1 1 1)	8	2.19745	41.04	5.01	1.82	0.00	-3.40	-6.18	4.08	1246.6
(2 1 0)	8	2.06394	43.83	5.33	1.94	0.00	2.64	5.11	3.60	752.9
(2 0 0)	4	2.30755	39.00	4.77	1.73	2.00	-2.79	4.69	4.50	396.2

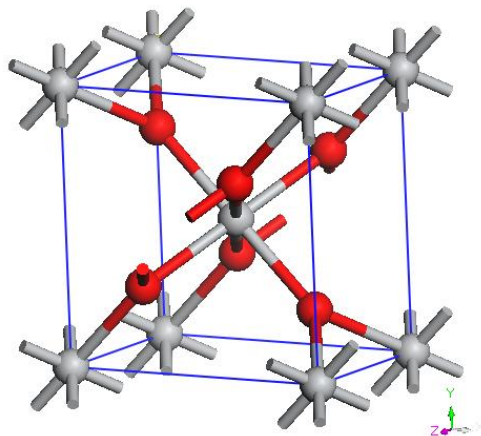
Comparing Model and Measured Peak Intensities

(h,k,l)	Modeled	Measured
(1 1 0)	100.00	100.00
(0 1 1)	43.34	43.34
(1 1 1)	20.14	20.16
(2 1 0)	9.24	9.21
(2 0 0)	7.75	7.79

CASTEP Density Functional Theory Simulation

Density functional theory (DFT) is a quasi-quantum mechanical approach to solving computationally intensive many-body problems such as the electronic structure of large molecules and condensed phases. DFT can be used to determine what molecules and what bulk structures can exist. The ground state energy and 3D electron density within such materials are computed. The equilibrium structure is the set atomic positions that minimize both the internal energy and the forces on individual atoms. From the equilibrium structure, the bond lengths and angles between atoms in crystals and molecules can be determined. Additional questions DFT can answer include determining the density of states and bandstructure, and how much energy is needed to ionize or break a bond. Ground state equilibrium structures can be determined subjected to external fields and pressures.

For this lab, CASTEP (Segall, 2002) was run to generate the equilibrium structure of rutile TiO₂. The PBE GGA Functional was used. The lattice parameters were determined to be a=4.594 Angstroms and c=2.959 Angstroms.



TiO₂ structure modeled by CASTEP.

Castep found the lattice parameters: a=4.594 Angstrom and c=2.959 The charge of each O atom was -0.65e and the charge on each Ti atom was +1.29e. The table below provides the fractional coordinates of the relaxed structure (equilibrium structure).

```

XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
x  Element      Atom      Fractional coordinates of atoms  x
x                Number          u          v          w          x
x-----x-----x-----x-----x-----x-----x-----x-----x
x  O             1           0.304800   0.304800   0.000000   x
x  O             2          -0.304800  -0.304800   0.000000   x
x  O             3           0.195200   0.804800   0.500000   x
x  O             4           0.804800   0.195200   0.500000   x
x  Ti            1           0.000000   0.000000   0.000000   x
x  Ti            2           0.500000   0.500000   0.500000   x
XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

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Conclusions

The BXF system was able to identify that both samples were TiO₂. The fluorescence data acquired September 29 were too noisy to process for crystal structure. The data acquired on September 30 were high enough quality to process to determine the crystal structure. Using X Powder, it was determined that the sample was 100% rutile structure. The rutile structure belongs to the P4₂/mmn tetragonal space group. The unit cell is defined by the lattice vectors a and c and contains two TiO₂ units with Ti ions at (0, 0, 0) and (1/2, 1/2, 1/2) and O ions at ±(u, u, 0) and ±(1/2+u, 1/2-u, 1/2) (Ma, 2007). The lattice constants are in close agreement with values found in the literature (table below). A software package was written to determine u based on three of the peak intensity values. The value extracted is

in close agreement with values found in the literature. Finally, CASTEP, a density functional theory model was used to find the equilibrium structure of rutile TiO₂. The values found are also in close agreement to the experimental values. This suggests that the rutile structure of TiO₂ is very well understood.

Lattice Parameters

	a (Angstrom)	c (Angstrom)	Ratio a/c	u
PDF2 database match	4.6151	2.9723	1.552703	0.313493
AMSCD database match	4.6151	2.9723	1.552703	0.313493
Values in Literature (Mo and Ching, 1995)	4.5936	2.9587	1.552574	0.3043
CASTEP Density Functional Theory Simulation	4.594	2.959	1.552552	0.3048

References

Ma H.L., J.Y. Yang, Y. Dai, Y.B. Zhang, B. Lu, G.H. Ma, "Raman study of phase transformation of TiO₂ rutile single crystal irradiated by infrared femtosecond laser," *Applied Surface Science* 253, 2007

Mo, Shang-Di and W. Y. Ching, "Electronic and Optical properties of three phases of titanium dioxide: rutile, anatase, and brookite," *PRB*, 51, 19, 1995

Segall, M. D., P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, M. C. Payne, "First-principles simulation: ideas illustrations and the CASTEP code," *Phys.: Cond. Matt.* 14(11) pp.2717-2743 (2002)

Warren, Mya, *Electronic and Structural Effects on the Electrochemistry of Polypyrrole*, Thesis, 2001

Matlab Code

```
function fitPeaks
options = optimset('TolX',0.1);
start = [0.31,0.7,20.0];
LC=[4.6178,2.9788]
LC=[4.6151,2.9723]
h = 0;
Peaks=[3789.0; 1642.0; 764.0; 349.0; 295.0];
v = fminsearch('ftnPeakIntensity',start,options,LC,Peaks,h)
v = [0.31,0.7];
err=ftnPeakIntensity(v,LC,Peaks,h)
```

```

function err = ftnPeakIntensity(vals,LC,Peaks,handle)

u = vals(1);
charge = vals(2);
BBB = vals(3);
InData = [[1 1 0]; [0 1 1]; [1 1 1]; [2 1 0]; [2 0 0]];
a = LC(1);
c = LC(2);
Lambda = 1.54056;
fprintf(1,'Lambda=%f Angstroms a=%f c=%f Angstroms
u=%f\n',Lambda,a,c,u);
fprintf(1,'(h,k,l) M d(Ang) T(Deg) fTi fO nfTi nfO S(hkl)
LP(T) Intensity\n');
model_peaks=zeros(5);

for i = 1:5
h=InData(i,1);
k=InData(i,2);
l=InData(i,3);

if (h==k || h==0 | k==0)
    Multiplicity = 4;
else
    Multiplicity = 8;
end
if (l ~= 0)
    Multiplicity = Multiplicity*2;
end
img = sqrt(-1);
d = 1.0/sqrt( (h^2)/(a^2) + (k^2)/(a^2) + (l^2)/(c^2) );
Theta = asin(Lambda/(2*d));
%fTi = 18*sin(Theta)/Lambda;fO = 10*sin(Theta)/Lambda;
fTi = (22-2*charge)*sin(Theta)/Lambda;fO =
(8+charge)*sin(Theta)/Lambda;
LL = 1.0/(sin(Theta)*sin(2*Theta));
PP = (1.0 + (cos(Theta))^2)/2;
LP = LL*PP;
MMM = BBB*sin(Theta)*sin(Theta)/(Lambda*Lambda);
TF=exp(-2.0*MMM);

nfTi = 1 + (exp(-img*pi*(h+k+l)));
nfO = 0;
nfO = nfO + (exp(-img*2*pi*( h*u + k*u )));
nfO = nfO + (exp(-img*2*pi*( (1-u)*h + (1-u)*k )));
nfO = nfO + (exp(-img*2*pi*( h*(0.5+u) + k*(0.5-u) + l/2)));
nfO = nfO + (exp(-img*2*pi*( h*(0.5-u) + k*(0.5+u) - l/2)));
%nfO =sqrt( nfO*conj( nfO));
%nfTi=sqrt(nfTi*conj(nfTi));

S = nfTi*fTi + nfO*fO;

```

```

%S = sqrt(S*conj(S));
fprintf(1, '(%d %d %d) %d %.5f', h, k, l, Multiplicity, d);
fprintf(1, ' %5.2f', 360.0*Theta/pi);
fprintf(1, ' %5.2f %5.2f %5.2f %5.2f', fTi, fO, nfTi, nfO);
fprintf(1, ' %7.2f', S);
fprintf(1, ' %5.2f', LP);
fprintf(1, ' %9.1f\n', S*S*Multiplicity*LP);
model_peaks(i) = S*S*Multiplicity*LP*TF;
end

%maxval=max(model_peaks);
%model_peaks = model_peaks*100.0/maxval;
model_peaks = model_peaks*100.0/model_peaks(1);
measured_peaks = Peaks*100.0/Peaks(1);
vector=zeros(5);
for i=1:5
fprintf(1, '(%d %d %d) %5.2f %5.2f\n', InData(i,1), InData(i,2),
InData(i,3), model_peaks(i), measured_peaks(i));
vector(i)=measured_peaks(i)-model_peaks(i);
end

v=vector(1:5);
err= norm(v);

```